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NAMF Management Seminars I & II

"Driving Toward the Future"

No papers available for these seminars.

ISO 9000 FROM A PLANT MANAGER'S VIEW

JOHNNY NORTON C.E.F.
AMP, INCORPORATED, GASTONIA, N.C.

Today more than ever American businesses must stay competitive in an ever increasing global market. Our national competitiveness demands us to put an increasing emphasis on:

Quality Products, Quality in Service, and Quality Documentation

We must measure quality to continue to assure our foreign business associates we have a quality system in place.

We must have a documented quality systems in place and document what we do, do what we documented and again document what we did. We also must provide evidence to support corrective actions in all areas of noncompliance.

The ISO 9000 Quality Assurance standard is being adopted by American businesses to ensure that all products and services provided to their customers are of consistent quality.

Document what we do? That is a good place to start. Make everyone in your plant aware of what ISO 9000 is and why you are striving so hard to achieve certification. Let the people know that as management you are committed to following through and continuing to use the procedures documented to run the business. Educate everyone in the plant on the requirements of ISO 9000 and how they compare with your documented manufacturing plans and quality specifications. Make sure that your trainer is certified to train in this area and that all training is documented and kept up to date. Do you have a quality policy? Does everyone know it? Make sure that they do. In order to maintain consistency throughout the plant make sure all in-house procedures are written down and everyone knows where they are and that they are kept current.

Does everyone know what they are supposed to do? Does everyone in the plant have a written job description? Is it linked to the quality policy of the plant or corporation? Is your organizational chart up to date or do you even have one? These are a few of the questions that the auditor begins with during the opening meeting with the plant manager's staff before going out onto the production floor.

Once out on the floor the auditor may begin at the receiving end of the plant to make sure that everything that comes into the plant is labeled correctly and is put in its proper place and stored correctly. The auditor may just ask the person "How do you know that you are doing the right thing? What quality specifications are you going by, and are they up to date and how do you know if they are up to date? Are you trained to do your job? Who trained you? Just wait till the auditor gets back to you, the manager, then you must show that all training is documented and is up to date. Heaven forbid the auditor finds anything suspicious.

He starts to dig deeper to make sure that all procedures are documented, up to date, and followed correctly. The auditor continues to move through the plant from one work center to another asking the same questions to different employees to guarantee consistency. If any gages are used to check quality performance, those gages must be calibrated and identified that they are calibrated by placing a sticker on them showing when they must be calibrated again. The big question in most managers mind is just what other tools must be calibrated. I have heard one manager say that "if it moves calibrate it." Well you know that may be one way of looking at it but who can afford that method? The auditor may refer you to paragraph 4.11 of ANSI/ASQC Q91 and 4.10 of ANSI/ASQC Q92. After looking for calibration stickers and dates, the auditor may start looking for non-conforming material and how you separate it from conforming material. Do you have a corrective action plan to prevent recurrences? Have they been implemented and recorded? Did you make sure the necessary procedural changes have been implemented and recorded properly as a result of the corrective action? The auditor continues to track the product from the work center back to the shipping department. The auditor continues to ask what procedures are used to handle, store, pack, and deliver the product and yes the question maybe asked again, are those procedures documented?

After the auditor is satisfied that he has all the information he needs an assessment is made as to how many hold points you have and how many observations you have. If you have a hold point you must be audited again on those points. However, if you have no hold points and you pass you must by all means celebrate!

I must leave you with these words of encouragement. If you have quality systems in place and document what you do, do what you document, and again document what you did you may just stand a good chance in getting certified. Good luck in your journey to excellence in becoming ISO 9000 Certified.

THE LONG TERM BENEFITS OF ISO 9000 CERTIFICATION

by
Joseph DeCarlo

The following will outline the long term benefits associated with gaining ISO 9000 Quality Management System (QMS) Certification based on a survey of Quality and Senior Managers who have brought their companies through the ISO 9000 registration process.

Recently, an Independent Market Research Organization was commissioned to carry out a study as to the reasons why manufacturing or service organizations' obtain ISO 9000 Quality Management certification, what impact, internally and externally, this has on their business and the future of ISO 9000 in a global marketplace.

The study was commissioned by Lloyds Register Quality Assurance, Ltd (LRQA). Lloyds is an International Certification body which assesses Quality Management Systems to the ISO 9000 standard.

The study is based on interviews with 400 Quality Managers and Senior Managers from a cross section of industries and company sizes.

To begin, let's start with the external benefits associated with certification as they largely comprise the initial reasons for seeking approval. External Market Pressure was the driving force behind the majority of decisions to obtain certification. The three (3) most important factors were:

- **ISO 9000's primary advantage lies with it's ability to open doors to European and Global markets which were previously closed.**

  89% of managers stated that the standard had enabled them to improve business by bidding for tenders from which they were otherwise excluded.

- **Expanding or Maintaining Marketshare**

  78% of the managers interviewed cited the ability to expand or maintain marketshare by holding certification as a major benefit.

- **Use as a valuable Marketing Tool**

  Cited by 69% of the managers as the 3rd most important benefit.

Small Businesses (those with up to 25 employees) were most strongly influenced by the external market pressures to obtain certification as well. 88% of those interviewed cited the main reason they sought ISO 9000 certification was to be able to stay in business by bidding for tenders.

Small Businesses also felt the most benefit from certification internally. The findings were:

- **83%** said ISO 9000 certification had improved management control of their activities.

- **70%** cited an improvement in Customer Service.

- **48%** stated that they found a marked increase in their Marketshare.

For all businesses the study found that the internal benefits of ISO 9000, such as better management control, reduced waste, increased efficiency and productivity were much greater than anticipated.

With regard to the reduction of operating costs, the long term benefits show that of the companies registered less than one (1) year over 1/3 (35%) had already cited a reduction in operating costs. While over 60% of the managers with firms registered for more than 5 years cited a definite reduction in operating costs.

Although better management control was not cited as a reason for certification, 86% of the managers stated that this was the standards primary achievement.

- **73%** said a Quality Management System had enabled them to deliver better service to customers and ensured a consistency of systems company-wide.

- **Over 2/3 (69%)** of these managers surveyed reported productivity gains and increased efficiency.

- **67% (2/3)** of the managers said that independent approval to ISO 9000 is essential in maintaining the integrity of their Quality Mgmt. Systems.

- **42%** stated that certification has reduced the need for customer audits.

In the **majority** of cases **(89%)** the benefits associated with the certification met or exceeded the expectation of those interviewed. Disappointments with certification were relatively low. For example, **only 3%** of those surveyed said it increased their overall paperwork, and **just 6%** cited the cost of certification as a disappointment.

Finally, Total Quality Management (TQM) programs were seen as complimentary to the ISO 9000 effort. **97%** of the managers said they were developing a TQM program in conjunction with their ISO 9000 program.

In conclusion, the benefits of ISO 9000 QMS certification -

- **Increase Market Share**
- **Use as a Marketing Tool**
- **Ability to bid for otherwise excluded tenders**
- **Competitive Advantage**
- **Increased Productivity and Efficiency**
- **Marked reduction in Operating Costs**

are greater the longer an organization has held a certification. From an Internal and External viewpoint, the full benefit of an ISO 9000 Quality Management System increase as the years pass on. Thus certification must be viewed as a long term business investment.

THE ISO-9000 REGISTRATION PROCESS FROM THE REGISTRAR'S PERSPECTIVE

By David Wolfe
Underwriters Laboratories Inc.

THE ISO-9000 REGISTRATION PROCESS FROM THE REGISTRAR'S PERSPECTIVE

by David Wolfe
Underwriters Laboratories Inc.

Many of you may be in the early stages of investigating ISO-9000 and understanding its relevance to your organizations, and to the marketplace. This paper is intended to detail the basic steps and thought processes that a company might take to begin the ISO-9000 registration process. It will also explore the areas of the standard where companies are typically weak, and will explore the logical organization of the standard.

REGISTRATION PROCESS

1. *Make a decision and get management commitment.*

   If customer driven, this might be easier than if internally driven. Emphasize that this is an objective way to demonstrate commitment to customers, and a means to get into specific markets. Also this drives consistency and feedback loops throughout the business process. After the initial effort to set up the system, the effort will typically be paid back in less than 2 years.

2. *Get a copy of the standard, read it, and review and discuss with key personnel.*

   The standard is available from ANSI, ASQC, and UL, to name a few. You can either purchase the single standard, or the compendium. The compendium contains the 9001, 9002, and 9003 standards as well as associated guideline procedures and draft procedures.

3. *Contact a registrar and get an information kit.*

   The kit typically contains a preliminary information form to provide information about your company and a Quality System Checklist to enable your company to critique its quality system and procedures, assess compliance, and determine readiness for a registration audit. The kit usually also contains general registration information and provides answers to commonly asked questions.

   To start the process, send in the appropriate forms and arrange some tentative dates for the services that you have requested. In addition, your Quality Manual needs to be forwarded to the registrar to enable the assessment team to prepare in advance for the visit.

4. *Arrange for a pre-audit meeting from a registrar, or engage someone knowledgeable in ISO-9000 interpretation.*

   This visit is typically a round table discussion that serves to enhance a company's

understanding of the ISO-9000 standards and explain the mechanics of the registration process. During the visit, an auditor can review the company's Quality documentation, discuss assessment schedules, and assist in determining the company's readiness for an ISO-9000 evaluation. In addition, if desired, the link between ISO-9000 and the European community may be discussed as well as the registrar's accreditations and memoranda of understanding between the primary registrar and other registration bodies. This is an excellent chance to ask questions, to discuss time frames, to help create enthusiasm on the part of management, and to help you assess your readiness.

5. *Develop and document the Quality System.*

ISO defines a Quality System as the...

organizational structure,
assignment of responsibilities,
procedures,
processes,
and resources,

put in place for the purpose of implementing quality management.

An effective Quality System will...

- identify what the customer expects to receive.
- ensure that the raw materials are of good and consistent quality.
- control the operation for consistency of product.
- have procedures in place to properly handle defective raw materials and products.
- have adequate documentation so that it is possible to trace the cause of a problem if one is detected.

Each of the 20 ISO clauses must be addressed completely in the Quality System. If a clause does not apply, this fact must be stated in the documentation. Simply omitting a nonapplicable clause is not acceptable.

Approach as a project. Assign responsibilities to appropriate people to complete various sections. Develop milestones.

6. *Do an internal review of the documentation as well as submitting it to your registrar for feedback.*

A good manual review will verify that each clause has been addressed or referenced in the Quality Manual. The documentation system must then be tied together. This is most commonly done through a tiered layout of procedures as illustrated by the following:

Quality Policy Manual
Departmental Procedures Manuals
Work Instructions Manuals
Detailed Instructions Manuals
(forms, tags, labels)

The author of each document in the system should be the person who uses it to do a job. Otherwise, have people actually working in an area review the documentation for the area and fill in the missing information as well as remove the extraneous information.

7. *Implement procedures and gather objective evidence of a functioning system.*

   Conduct several internal audits to see that all involved are doing what they said they would do and that they are keeping accurate records. Pay particular attention to verifying that feedback loops are operating as designed.

8. *Get a benchmark on where you are before the actual registration audit.*

   A preliminary audit or evaluation is an informal or mock audit intended to assist a company in preparing for registration. This evaluation will point out strengths and weaknesses in your Quality System. Unlike the actual registration assessment, the scope of a Preliminary is limited and covers only a small sample of your Quality System. A written report is provided, enabling the company to establish a time frame for the actual assessment based on work yet needed to comply with the requirements. The assessor will also typically provide "on the spot" explanations of findings as they are discovered. In addition, a preliminary evaluation gives a company first-hand experience in undergoing an ISO-9000 evaluation before the actual registration assessment takes place. Unlike the actual registration assessment, a preliminary assessment does not need to assess the entire system; the scope of a Preliminary can be limited to cover only portions of your Quality System.

9. *Correct any system deficiencies.*

10. *Submit your system to a third party audit for registration.*

    The registration assessment is the formal audit performed at the facility to be evaluated. The number of days this takes and the number of auditors required are dependent on the scope of the assessment and the size of the facility. The assessment consists of an opening meeting, the actual audit, a closing meeting, and the follow-up. If the system is found to be compliant, your firm would be recommended for registration.

Summary of Steps to Obtain and Maintain Registration

- Submit to ISO assessment by accredited registration organization.
- Assessment team makes recommendation.
- Notes, discrepancies, and recommendations reviewed in a multi-step process.
- All discrepancies resolved.
- Management review of report and concurrence or reversal of recommendation.
- Client officially notified of official management approval.
- Twice-per-year assessments to insure continued compliance.

ISO-9000 Standard Review

Management Responsibility (4.1)

Quality System (4.2)

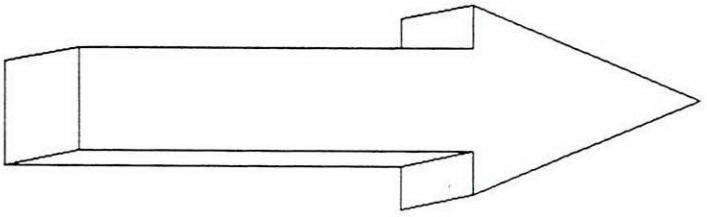
Specifics	Company-wide
Contract Review (4.3)	Document Control (4.5)
Design Control (4.4)	Product Identification and Traceability (4.8)
Purchasing (4.6)	Inspection and Test Status (4.12)
Purchaser Supplied Product (4.7)	Control of Nonconforming Material (4.13)
Process Control (4.9)	Corrective Action (4.14)
Inspection and Testing (4.10)	Quality Records (4.16)
Inspection, Measuring, and Test Equipment (4.11)	Internal Quality Audits (4.17)
Handling, Storage, Packaging and Delivery (4.15)	Training (4.18)
Servicing (4.19)	
Statistical Techniques (4.20)	

Specifics

Company-wide

4.3
4.4
4.6
4.7
4.9
4.10
4.11
4.15
4.19
4.20

Provides Performance Indicator Results



4.13
4.14
4.16
4.17

Corrective Action (4.14)

Management Review (4.1)

Paper Not Available In Time For Publication

International Organization for Standardization Initiative to Create International Environmental Management Standards

James Connaughton and Christopher Bell, Sidley & Austin, Washington, DC

The International Organization for Standardization (ISO) is leading an effort to develop global standards that will direct companies in how to systematically manage, measure and improve environmental compliance and performance. Industrial, governmental and other parties are engaged in a rapidly changing process of reaching international consensus on environmental standards in the following areas: Environmental management systems; environmental auditing; environmental performance evaluation; environmental labeling; life cycle analysis; and environmental aspects of product standards. Companies that operate in the U.S. will encounter significant challenges as they try to conform with the ISO standards. U.S. companies that manufacture or sell products abroad may find their trade severely restricted if they fail to conform to the standards. If the standards become domestic standards, even U.S. companies that have no foreign operations or sales will be affected.

For copies of this paper please contact:

Jim Connaughton
Sidley & Austin
1722 Eye Street NW
Washington, DC 20006

Paper Not Available—AESF Course Materials Only

An Overview of AESF's New ISO 9000 Course for Platers & Finishers

Bev Sewell, Twickenham Plating Group, Brentford, Middlesex, England

The American Electroplaters and Surface Finishers Society has just produced a training course and guide on the implementation of a quality management system for plating and finishing companies. The relevance of the ISO 9000 standards will be clearer when the concept of quality management systems is understood. The main theme of the new course, therefore, is the quality system, its purpose and function, the company activities that must be included in the system, and how they must be described as policies, procedures and instructions. Some of the activities will be new to many companies and finishing shops.

The requirement of ISO 9002, which the quality management system must satisfy, are dealt with in Part 2. Part 2 explains some of the more obtuse clauses of the standard and some of the features that have particular relevance to finishing activities.

Implementation of the quality system is covered in Part 3. A proposed schedule of actions takes the student from initial motivation and decision to commit, through the stages of system construction and implementation to trial assessment. This part of the course will be of particular relevance to company chief executives.

Documentation is covered in Part 4. Vital to obtaining third-party approval to an ISO 9000 standard, documentation must be carefully prepared and structured. The quality manual, procedures, quality plans, instructions, forms and records are covered in this session, with finishing companies in mind. A hierarchial documentation structure is suggested.

The course is intended for all levels of management. It is recommended that company principals and chief executives take the course in order to be able to direct their management toward implementation of a quality system and eventual registration to an ISO 9000 standard.

For details on this AESF educational course please contact:

AESF Headquarters
Educational Services Dept.
12644 Research Parkway
Orlando, FL 32826-3298
407/281-6441
FAX: 407/281-6446

Documentation and ISO-9000

H.S. Trop
AT&T Bell Laboratories
9999 Hamilton Blvd.
Breinigsville, PA 18031

ABSTRACT

The proper organization and control of documentation is a fundamental key of the ISO-9000 standard. This paper will describe the differences between controlled documents and quality records, the requirements for both, options for distribution and control, and examples of these documents. Common pitfalls and how to avoid them will be discussed.

The proper organization and control of documentation is a fundamental key of the ISO-9000 standard. In late 1992, the Lightwave Strategic Business Unit within AT&T began its journey towards ISO registration. During an initial pre-assessment audit, close to 300 violations of the ISO standards were uncovered, with 32% being in documentation (Figure 1). The non-compliances found ranged from minor problems (~80%) to major gaps or total lack of control within specific organizations. A major effort was undertaken to bring the organization under compliance in this area. As a result of that effort, several useful guidelines for insuring good document control have been identified. These guidelines can be applied for small and large size organizations.

Documentation can take many forms: it could be a piece part drawing, a work instruction, a list of requirements for a product, a record of training, or a record of some activity, such as plating thicknesses for a specific lot of parts. The first three examples are considered *controlled documents;* the latter two are examples of *quality records.* Quality records will be discussed following controlled documents.

Features of Controlled Documents

A controlled document is any document that contains information that is required for some person to satisfactorily complete a task. Examples of controlled documents are engineering drawings, shop instructions, general procedures, manufacturing layouts, etc. Controlled documents all should have the following attributes:

1. Title
2. Process Owner
3. Document Number
4. Issue Number
5. Date
6. Distribution List
7. Page Numbering
8. Revision Record
9. Approvals

Figures 2 through 5 show different examples of controlled documents, in a variety of document formats. Figure 2 is an example of an electronically maintained document. Figure 3 and 4 are local issue controlled documents, in a format that is standardized within the local organization or Quality Document Center (QDC). QDC's will be discussed later. Figure 5 shows an example of an engineering drawing, maintained through a distributed computer network. Each, in their own way, contain these nine elements.

1. Title The title of the document is provided by the process owner, and should be a unique description of the task or item. Either the title or the document number should appear on all pages of the document, to aid in identification.

2. Process Owner The process owner attests to the authenticity, completeness, and correctness of the document. The process owner has an understanding of the process, has the authority/ability to create or change the process with appropriate approvals and is responsible and accountable for the process.

3. Document Number The document number should be a unique identifier. Typically, high level quality documents will describe numbering schemes and their significance. It is possible, however, to have a system as simple as starting with the number 1, and sequencing to 2, 3, etc. Many systems incorporate all or part of the date the document was generated as part of the numbering scheme.

4. Issue Number This serves to identify changes to a document. The initial issue would be 1, subsequent changes would be recorded by increasing issue numbers.

5. Date The date the document becomes effective.

6. Distribution List The distribution list will have the name of each individual or area to receive a controlled copy of the document and the number of copies each will receive. This makes it easier to provide copies of the document where needed, and also helps to recall documents when they are no longer needed or have been up-issued.

7. Page Numbering Each page should be numbered and should state the number of pages in the entire document. This can be done using the format, "Page Y of X". This makes it easy to determine if pages are missing from a document, or if the instructions are in the correct sequence.

8. Revision Record If a document is changed, the reason for reissue and a description of the change(s) should be provided. This can be done by referencing a change request document (Figure 3) or by including space in a cover sheet for this purpose (Figure 2 and 4). Within Figure 5, the changes made for each revision are documented along with the dates the revisions were made. Figure 3 makes use of a reference to another document, in this case Change Request 94Si0001. Anyone wishing to determine what changes were made and the reasons for these changes would be able to find this information filed within the Change Request. In some circumstances, this approach may be preferred over being limited to a few brief words, especially if the changes are complex.

9. Approvals The document must be approved by the process owner. In many cases, additional approvals may be required; for example, Environmental Health & Safety, specific management approvals, etc. Depending upon the document control system, approvals can be done electronically (Figures 2 and 5) or with a signature on the document itself (Figures 3 & 4).

In addition to these common features, controlled documents will also contain information describing an activity or design, and certain guidelines can prove helpful.

1. *Keep it simple and to the point:* Avoid the temptation to over specify. If it isn't critical or important to the task or design, it may not need to be included. This includes superfluous dimensions on drawings, as well as excessive verbiage in shop instructions.

2. Watch those dimensions!: In shop instructions especially, there is a tendency to call out specific conditions when a range would be adequate. Unless the temperature of a plating bath has to be 50°C, use a range, for example, 45 to 55 °C, or 50 ± 5°C.

3. Reference other documents when necessary: You can simplify and shorten specific documents by calling out other documents within the body of the document. Figure 6 shows a controlled document that provides information on chemical content of a plating bath, as required by company and government regulations. Within the text, a reference to the instruction for the actual makeup and maintenance of the bath is provided (Figure 7). In addition, one should describe the location of quality records generated by the instruction within the document (Figure 8). The instruction calls out the Temperature Controller Process Log as the location for the quality records for that operation.

4. Include corrective actions within the document: An important part of ISO-9000 is the identification and correction of problems. For example, in the case of metal finishing, there are often specific corrective actions that can be taken should a bath not plate properly. A brief description of problems and their resolution can be very helpful. As shown in Figure 9, this information need not be excessively detailed to be effective.

5. The document should describe what you do, not what you want to do: In a classic example, an inspection document required that personnel were required to have corrected 20/20 vision to perform the inspection. No records were available to verify if the personnel had corrected 20/20 vision, or if they had ever been checked. An effective approach to making sure that the document describes what actually takes place is to have the people performing the task review the documents for accuracy. Some companies and organizations will have the shop people generate the initial draft version of a new shop document, thus incorporating their understanding of the task into the document.

Maintaining Control of "Controlled Documents"

Once the documents are in place, one needs to be able to keep track of the documents and insure that only the current version of each document is available. This can be done in a number of ways. For a large organization, electronic filing and retrieval may be an option. Using a distributed computer network and a custom software database, one can store documents electronically and generate paper copies as required using a variety of printers. In such a system, only the most current version is readily accessible by anyone except the process/document owner. Printed copies are date stamped (Figure 10) with the printing date. Within our organization, such documents are only valid on the date printed. Drawbacks to this system are the high initial set up cost, ongoing overhead for maintenance, and the handling of photographs and other "non-text" output.

For many organizations, an fully electronic system is too costly to set up or may not be justified due to the number of people needing access to the information. Controlling paper copies is generally performed by a Quality Document Center (QDC). The manager of the QDC is responsible for making sure that all areas administered by the QDC are using up to date documents. The QDC uses the distribution list on each document to track and issue copies to the necessary individuals/areas. The QDC will maintain a "master list" of documents within its control. The QDC maintains a copy of the controlled document and distributes authorized copies to other QDC's, engineers and to the "point-of-use". Within the QDC, mechanisms for identifying current controlled documents, through means of a QDC mark or stamp, should be established. (An example of such a mark is shown in Figure 3. A red stamped copy distinguishes this document as being official and authoritative, and identifies the issuing entity.) The QDC disposes of obsolete documents, and may maintain a collection of obsolete documents as quality records.

Quality Records

Quality Records are generated as the result of performing the activities described by controlled documents. These records can take the form of training records (Figure 11), experimental data (Figure 12), process control checks on equipment (Figure 13), requests for work (figure 14), incoming inspection documents,

etc. These documents can be hand written (with ink) or printouts and can exist in a number of formats. Some general guidelines for quality records are:

1. Dated and Signed Quality records should be signed and dated by the person performing the activity. This can be in the form of a name and date on a computer printout. In many instances, a set of initials is sufficient.

2. Reference Controlled Document Quality Records should reference the operation under which they are generated, especially in cases where the significance of the information may not be intuitively obvious to a casual viewer. When standard forms are used for data collection, this can be easily accommodated (Figure 12). In other cases, such as purchase orders, the nature of the record is obvious.

3. Filing Most organizations have specific time periods under which quality records must be maintained. For example, if a product is under warranty for five years, the quality records will probably be maintained for at least that period, if not longer. Quality records should be stored in a manner that facilitates retrieval.

4. Completely Filled Out One of the most typical problems associated with quality records is missing data. Often, shop personnel fail to fill in all the blanks. In many cases, the blanks are for data that may be optional or not applicable to a certain situation; in such cases N/A or a dash should be placed in the blank(s).

LIST OF FIGURES

1. Pareto Chart of Non-Compliances from an initial pre-assessment audit of a large (~3000 person) organization. Roughly 32% of all non-compliances were in area of document control.

2. Cover sheet from an electronically stored controlled document. This example contains the required elements of a controlled document. This particular example describes the operations and procedures of a local Quality Document Center (QDC).

3. Controlled document describing a particular operation in a manufacturing operation. This document is maintained by a local QDC, but still contains the same basic elements as in Figure 2.

4. Controlled document from another local QDC within the author's organization. This document varies in format from Figures 2 &3, yet contains the essential elements of a controlled document.

5. Engineering drawing of a ceramic package is another example of a controlled drawing. This drawing is maintained in a computer network. Note that changes and the dates associated with those changes are displayed on the drawing.

6. "Right to Know" document (93PLT023) with reference to bath makeup instructions (another controlled document) within text of document.

7. Front page of Wood's Nickel Strike process instruction (93PLT013). Note that ranges are used rather than a specific value. In addition, this instruction references another instruction, 93PLT004, for another operation (nickel content analysis).

8. Document (93PLT007) describing temperature controller process checks. The location of quality records generated through the use of this instruction is described.

9. Page 2 of Wood's Nickel Strike instruction. Note that potential problems and corrective actions are described within the document.

10. Cover page for controlled document 93GEP0844, Issue 3. This is an example of a computer stored document. When printed, the date it was printed appears in the upper left hand corner. This date is used to determine the "useful life" of the document.

11. Example of a form used for keeping a record of training on operations within a facility. This form covers activities within a prototype plating facility.

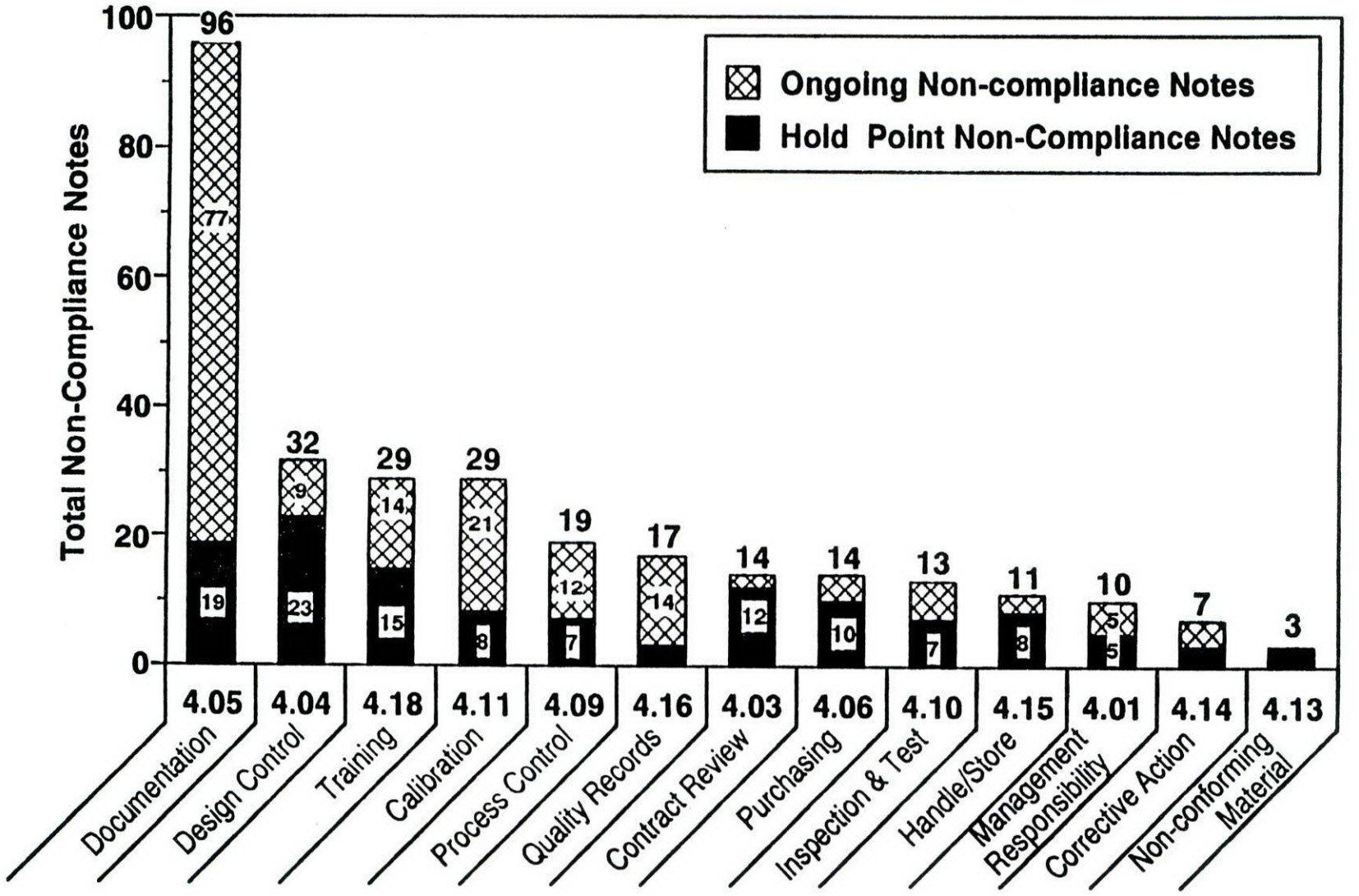
12. Quality record of experimental data. This data was generated during performance of operation. This form references the controlled document (93LIN017) controlling the operation.

13. XRF Memory Calibration Check log. Note that all entries are dated and initialed.

14. Job Request Form. When completed, form will be filed with supporting information as quality record.

LW-SBU ISO 9001 Pre-Assessment

Non-Compliance Notes per ISO 9001 Element



STA30174KK001

FIGURE 1

GENERAL PROCEDURE

QDC PROCEDURES FOR ORGANIZATION BL011148J

GEP NUMBER:	93RD0844
ISSUE:	03
SBU/IBU:	LW
REASON FOR ISSUE:	CHANGE DEPT FROM 53333J TO BL011148J
ASSOCIATED WITH:	05.02, 05.03
ORIGINATOR:	Trop, Harvey S.
GRAPHICS PAGES:	0
GRAPHICS OPTION:	

REQUIRED APPROVALS

NONE

SPECIFIED APPROVALS

(Trop, Harvey S. OR Kershner, Richard C. OR Brady, Angelique X.)

NOTIFICATIONS

(All Approvers) AND
(Trop, Harvey S.) AND (Hoffman, Mel J.)

FIGURE 2

AT&T - PROPRIETARY
Use Pursuant to Company Instructions
WARNING: COMPUTER GENERATED DOC.
CHANGES MUST be MADE in DATA FILE.
OFFICIAL DOCUMENT

Controlled Document
(WHEN STAMPED IN RED)
LW12

OSA RECEIVING OPERATION		
DOCUMENT NUM: 93PAC004	ISSUE NUM: 03	ISSUE DATE: 18 January 1994
ENGINEER: R. C. Kershner	LAST CHG. REQ.: 94Si0001	PAGE 1 OF 1

PURPOSE: To verify that the received parts match the shipping ticket, and are properly handled and stored for future use.

1) OSAs are received in 2" waffle packs.

2) Waffle packs may only be opened in an ESD Class 0 approved area.

3) Mark receiving paper with discrepancies. If data is missing, call immediately to Murray Hill for clarification of data. Request new copy of written data.

4) Place received OSAs into appropriate area of parts storage dry box.

Distribution: BL0111480 QDC(LW12)
533260000 QDC(LW05)
PI Notebook in Room 2G-229

Authorized Supervisor: _____ Date 1/18/94.

AT&T PROPRIETARY - Use Pursuant to Company Instructions

FIGURE 3

Sheet 1 of 4 LI-091 ISSUE 1

ISSUED: FEB. 22,1994

TITLE:RF DIE TEST

Associated with: Lithium Niobate Modulator Die

Reason for Issue: Initial Release

DISTRIBUTION: BL011148E QDC, BL011148J QDC, POINT OF USE

Approvals: R.S. Moyer MTS BL011148J

R S Moyer 2/22/94

AT&T Proprietary-- Use pursuant to Company Instructions

FIGURE 4

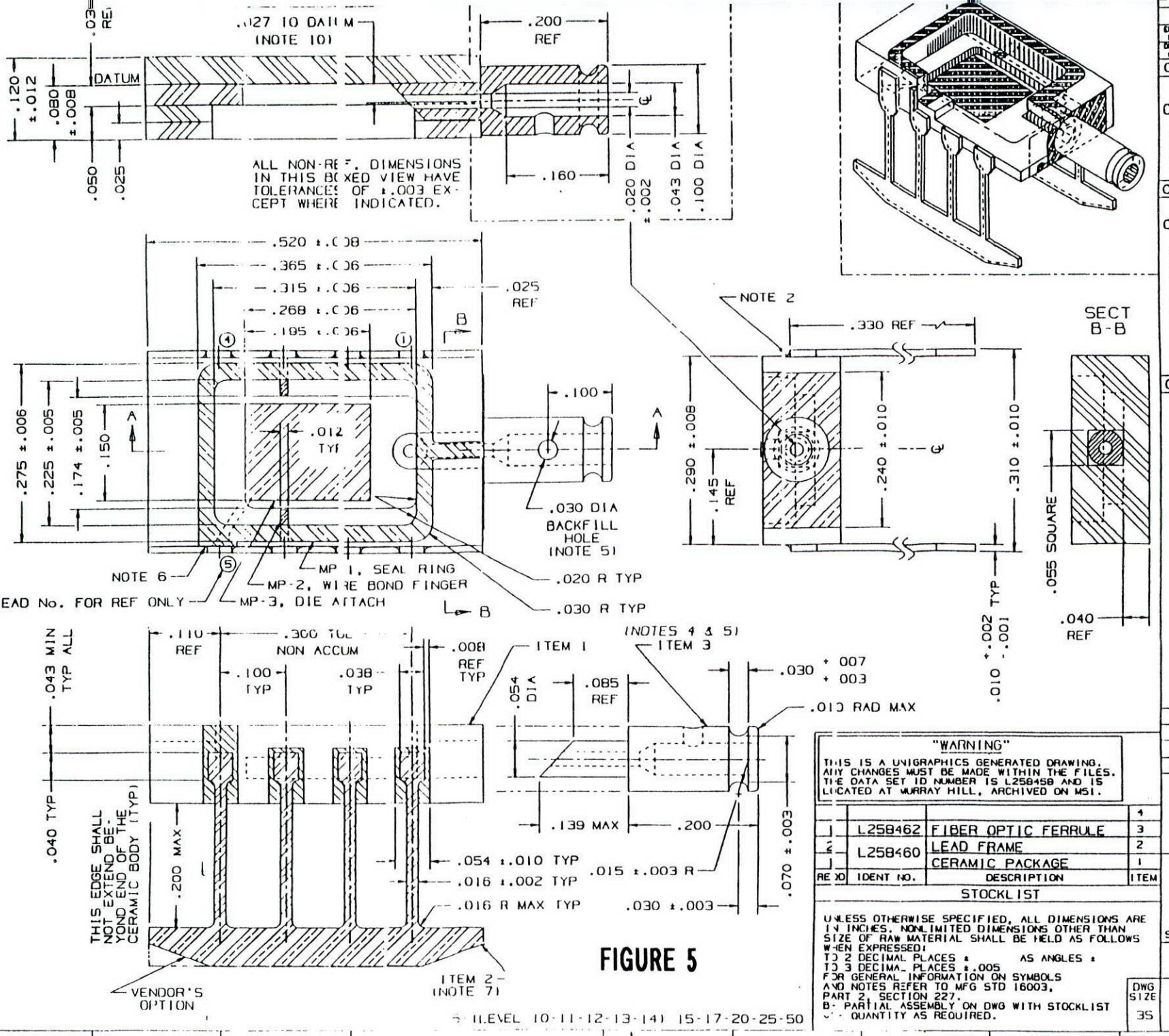


FIGURE 5

			4
	L258462	FIBER OPTIC FERRULE	3
	L258460	LEAD FRAME	2
		CERAMIC PACKAGE	1
REV	IDENT NO.	DESCRIPTION	ITEM

STOCKLIST

"WARNING"
THIS IS A UNIGRAPHICS GENERATED DRAWING. ANY CHANGES MUST BE MADE WITHIN THE FILES. THE DATA SET ID NUMBER IS L258458 AND IS LOCATED AT MURRAY HILL, ARCHIVED ON MSI.

UNLESS OTHERWISE SPECIFIED, ALL DIMENSIONS ARE IN INCHES. NONLIMITED DIMENSIONS OTHER THAN SIZE OF RAW MATERIAL SHALL BE HELD AS FOLLOWS WHEN EXPRESSED:
TO 2 DECIMAL PLACES ± AS ANGLES ±
TO 3 DECIMAL PLACES ±.005
FOR GENERAL INFORMATION ON SYMBOLS AND NOTES REFER TO MFG STD 16003, PART 2, SECTION 227.
B- PARTIAL ASSEMBLY ON DWG WITH STOCKLIST
C- QUANTITY AS REQUIRED.

DWG SIZE 3S

ENGR W.O. GERMAN
DRAWN C. DUNAENKO
06-23-88 ISSUE 1

CHANGED:
CAVITY DIM
WAS .220 ±.006
NOW .268 ±.006

06-29-88 ISS 2

CHANGED:
FERRULE DIM
WAS .036 DIA
NOW .054 DIA

PKG LAYER THK
WAS .035
NOW .025

WAS .052
NOW .050

07-12-88 ISS 3

USED ON | DRAWING

AT&T - PROPRIETARY USE PURSUANT TO COMPANY INSTRUCTIONS

8 LEAD DIP W/ FERRULE ASSEMBLED

SCALE: 10/1

L258458

FINISHING TECHNOLOGIES GROUP
POD 7 PLATING LABORATORY PROCEDURES

Chemical Composition of Wood's Nickel Strike Bath		
DOCUMENT NUM: 93PLT023	ISSUE NUM: 02	ISSUE DATE: 20 August 1993
Process Owner: C.A. Mattoe	LAST CHG. REQ.: N/A	PAGE 1 OF 1

The following information is provided to meet the requirements of TSCA and OSHA regulations concerning labeling of chemicals in use in a laboratory environment. The values shown are approximate; this information is not intended to be used as a work instruction. For bath makeup and maintenance, please follow the instructions described in the following document, 93PLT013.

ACID SOLUTION pH < 2.0

Wood's NICKEL STRIKE BATH

Solution Constituents:

Nickel Chloride (Ni content)	216 g/L (52.5 g/L)	$NiCl_2x6H_2O$
Hydrochloric Acid	100 mL/L	HCl

AVOID CONTACT WITH SKIN

USE PERSONAL PROTECTIVE EQUIPMENT

IN CASE OF SPILL, CONTACT SAFETY IMMEDIATELY

x2600

Distribution:
53333J000 QDC
533260000 QDC
Pod 7 Plating Lab

Authorized Supervisor: _____ Date 8/20/93.

AT&T PROPRIETARY - Use Pursuant to Company Instructions

FIGURE 6

FINISHING TECHNOLOGIES GROUP
POD 7 PLATING LABORATORY PROCEDURES

WOODS NICKEL STRIKE MAKEUP / MAINTENANCE / OPERATION / SUPPLY INFO.		
DOCUMENT NUM: 93PLT0013	ISSUE NUM: 02	ISSUE DATE: 20 August 1993
Process Owner: C.A. MATTOE	LAST CHG. REQ.: N/A	PAGE 1 OF 3

WOODS NICKEL STRIKE

SOLUTION MAKEUP:	NOMINAL	RANGE
NICKEL CHLORIDE	240 G/L	200 TO 280 G/L
HYDROCHLORIC ACID (CC 901181248)	125 ML/L	100 TO 150 ML/L
NICKEL CONTENT	59.3 G/L	54.3 TO 64.3 G/L

SOLUTION MAINTENANCE:

RECORD ALL DATA IN NICKEL STRIKE LOG BOOK

ANALYZE FOR NICKEL CONTENT ONCE A MONTH USING X.R.F. (93PLT004) OR UPON MAKEUP OF BATH.

	NOMINAL	RANGE
pH.	0.75	0.4 TO 0.95

AT&T PROPRIETARY - Use Pursuant to Company Instructions

FIGURE 7

FINISHING TECHNOLOGIES GROUP
POD 7 PLATING LABORATORY PROCEDURES

Temperature Controller Process Check		
DOCUMENT NUM: 93PLT007	ISSUE NUM: 01	ISSUE DATE: 20 August 1993
Process Owner: C.A. Mattoe	LAST CHG. REQ.: N/A	PAGE 1 OF 1

Purpose: Insure that devices in the Pod 7 plating lab that are used to control temperature are operating accurately.

Scope: This process check applies to all temperature controllers located on the Reynoldstech plating tools, as well as the drying oven located within the Pod 7 plating lab, and the oven located in the fiber plating area.

Procedure: At periodic intervals, described below, the set point temperature of a given temperature controlling device will be checked using a certified thermometer (see 93PLT0006) and the following information recorded in the Temperature Controller Process Check Log (located in the plating lab):

Date: Date test made
Initials: Initials of person performing test.
Equip. ID: Unique indentifier for controller
Set Pt.: Temperature set point for controller
Therm. #: Thermometer number (see 93PLT0006)
Therm. Reading: Temperature as recorded by thermometer
Comments: Field for additional information, corrective action, etc.

Frequency: The frequency of the temperature controller process checks shall be as follows:

Reynoldstech (Fuji) Controllers: every three months

Fountain Plater Temp. Controllers: every three months

Plating Lab Drying Oven: every month

Fiber Plating Oven: verify before daily use; otherwise monthly

Corrective Action: In the event that the temperature observed using the thermometer varies by more than 3°C from the controller set point value, record the result, then repeat the measurement to confirm. Record the results of the second test in the Temperature Controller Process Check Log, and if still outside the 3°C range, the apparatus should be shut down until repairs can be made. In the case of the Fuji Electric Controllers used in the Reynoldstech plating tools, an instruction manual is stored in 2G-223, for use in resetting the controllers. For the ovens, corrective action may require servicing by the manufacturer. After repair, re-test the units and record the result, before using.

Distribution:
Copy 1 53333J000 QDC
Copy 2 533260000 QDC
Copy 3 Pod 7 Plating Lab

Authorized Supervisor: _____ Date 8/20/93

AT&T PROPRIETARY - Use Pursuant to Company Instructions

FIGURE 8

WOODS NICKEL STRIKE MAKEUP / MAINTENANCE / OPERATION / SUPPLY INFO.		
DOCUMENT NUM: 93PLT0013	ISSUE NUM: 02	ISSUE DATE: 20 August 1993
Process Owner: C.A. MATTOE	LAST CHG. REQ.: N/A	PAGE 2 OF 3

PROBLEM	CORRECTIVE ACTIONS:
LOW NICKEL CONTENT	CHECK ANODES, CLEAN OR REPLACE IF NECESSARY ADD NICKEL SALTS TO BRING BACK TO NOMINAL
pH OUT OF RANGE	CHECK ANODES, CLEAN OR REPLACE IF NECESSARY. ADD HYDROCHLORIC ACID TILL pH NOMINAL
HIGH NICKEL CONTENT	CHECK BATH MAKEUP AND CALCULATIONS. DILUTE IF POSSIBLE USE ENGINEERING JUDGMENT

AFTER TAKING CORRECTIVE ACTION, RE ANALYZE SOLUTION, RECORD DATA IN LOG, AND REPEAT AS NECESSARY UNTIL BATH IS IN PROPER RANGE.

OPERATION:

10 TO 60 AMPS PER SQUARE FOOT (20 A.S.F. RECOMMENDED)

OPERATE AT ROOM TEMPERATURE

FIGURE 9

AT&T PROPRIETARY - Use Pursuant to Company Instructions

GENERAL PROCEDURE

QDC PROCEDURES FOR ORGANIZATION BL011148J

GEP NUMBER:	93RD0844
ISSUE:	03
SBU/IBU:	LW
REASON FOR ISSUE:	CHANGE DEPT FROM 53333J TO BL011148J
ASSOCIATED WITH:	05.02, 05.03
ORIGINATOR:	Trop, Harvey S.
GRAPHICS PAGES:	0
GRAPHICS OPTION:	

REQUIRED APPROVALS

NONE

SPECIFIED APPROVALS

(Trop, Harvey S. OR Kershner, Richard C. OR Brady, Angelique X.)

NOTIFICATIONS

(All Approvers) AND
(Trop, Harvey S.) AND (Hoffman, Mel J.)

FIGURE 10

AT&T - PROPRIETARY
Use Pursuant to Company Instructions
WARNING: COMPUTER GENERATED DOC.
CHANGES MUST be MADE in DATA FILE.
OFFICIAL DOCUMENT

POD 7 PLATING LAB
TRAINING RECORD

Who Was Trained? _____

What Process (include applicable document/issue numbers)?

_____

_____

Date Training Completed: _____

Who Did Training? _____

Comments: _____

_____

_____

FIGURE 11

MODULATOR FIBER ATTACHMENT FORM

(SEE PI93LIN017)

DATE: 10/25/93 OPERATOR ID: CGS

CRYSTAL #: C030-004-05 DESIGN: ☐ 1.3 ☒ 1.5

PACKAGE #: 69-0001 LENGTH: ☐ 2 cm ☐ 3 cm ☒ 4 cm ☐ ____

FIBER IN: ☒ STD # 73 ☐ PMF # ____

FIBER OUT: ☒ STD # 73 ☐ PMF # ____ ☐ PEP # ____

EPOXY TYPE: PROPRIETARY INFO EXP. DATE: 12/93

1st SIDE: ☐ ☒ ☐ OUT

LASER: (☐ 1.3 ☐ 1.5) IDL: 49.9 BFM: 0.65 TEMP: 15.3

POWER OUT: ROTARY: 250 FIBER ARRAY: 260

Z-AXIS READING: 2810 POWER: MIN 0.24 µW @ ~~-1.25~~ 4.08 V

MAX 3.78 µW @ -1.25 V

2nd SIDE: ☐ IN ☒ OUT

Z-AXIS READING: 2695 POWER: MIN 0.206 µW @ -3.76 V

MAX 119 µW @ -.81 V

FINAL POWER OUT: ROTARY: 241

FIBER ATTACHMENT SUMMARY:

INTENSITY EXT RATIO (dB): 27.6

INSERTION LOSS (dB): 3.07

COMMENTS:

FIGURE 12

11/12

XRF MEMORY CALIBRATION CHECK

MEMORY No. 1 APPLICATION: Au/Ni/Kovar (4mil)

Nominal Value(s) for Standard: 22 Au (µin)

Standard No. (OPTIONAL): 1

DATE	TOTAL # READINGS	MEAN	STD.DEV.	MIN	MAX	RANGE	INITIALS
9/8/92	10	21	1	20	22	2	HST
9/15/92	11	21	1	20	22	2	HST
9/21/92	11	20	0	20	21	1	HST
9/30/92	11	21	0	20	21	1	HST
1/6/93	11	21	1	20	22	2	HST
3/2/93	11	21	1	20	22	2	HST
3/10/93	11	21	1	21	21	2	CAM
3/23/93	11	21	1	20	22	2	CAM
4/7/93	11	21	0	20	21	2	CAM
4/13/93	11	21	0	21	22	1	HST
7/8/93	11	21	0	20	21	1	CAM
8/11/93	11	22	1	20	23	3	CAM
11/17/93	11	22	1	20	23	3	CAM
1/10/94	11	22	1	20	23	3	CAM

This file exists in LOTUS format on a PC in 2G-204 in directory:

C:\123data\XRFfiles\ mem1 Au1

Control charts can be run using this file format using HARVARD GRAPHICS. See LOTUS file listed above for details...

FIGURE 13

Effective 8/16/93 C.A. Mattoe

STC POD 7 PLATING JOB REQUEST FORM - ISSUE 3.0

NAME_____ DEPT._____

ROOM_____ PHONE_____ WPN _____

DATE JOB SUBMITTED _____ JOB COMPLETE REQUEST DATE♦ _____

♦DATE YOU'D LIKE TO HAVE PARTS BACK (ASAP = WHEN WE GET AROUND TO IT)

IS THIS PART USED IN AN M- OR FULL CODE DEVICE? Y N
if YES, ATTACH VALID SI/PI OR MIDS DOCUMENT NUMBERS.

PARTS DESCRIPTION: COMCODE:_____

SUBSTRATE - CU _____ NI _____ ST. STEEL TYPE _____

WCU _____ KOVAR _____ MO _____

BRASS _____ INVAR _____ Fe/Ni _____

Cu ALLOY _____ OTHER _____

NUMBER OF PARTS: _____ SURFACE AREA / PART: _____

♦ ATTACH APPLICABLE DRAWINGS TO SHEET ♦

SERVICE (S) REQUIRED:
List Requested Services (i. e. electroless Ni with Au) below, along with thickness ranges required and any additional information or instructions.

Is this the first time we've plated this part? _____ Yes _____ No

DATE JOB STARTED _____ COMMITMENT DATE _____

DATE JOB COMPLETED _____ MET REQUEST? Y N
MET COMMIT? Y N

LAB BOOK REFERENCE: _____

SPECIAL NOTES (ATTACH ALONG WITH PROCESS DATA):

PLATING LOT ID _____

FIGURE 14

Effective 8/16/93 C.A. Mattoe

STC POD 7 PLATING JOB REQUEST FORM - ISSUE 3.0

NAME_____ DEPT._____

ROOM_____ PHONE_____ WPN _____

DATE JOB SUBMITTED _____ JOB COMPLETE REQUEST DATE♦ _____

♦DATE YOU'D LIKE TO HAVE PARTS BACK (ASAP = WHEN WE GET AROUND TO IT)

IS THIS PART USED IN AN M- OR FULL CODE DEVICE? Y N
if YES, ATTACH VALID SI/PI OR MIDS DOCUMENT NUMBERS.

PARTS DESCRIPTION: COMCODE:_____

SUBSTRATE - CU _____ NI _____ ST. STEEL TYPE _____

WCU _____ KOVAR _____ MO _____

BRASS _____ INVAR _____ Fe/Ni _____

Cu ALLOY _____ OTHER _____

NUMBER OF PARTS: _____ SURFACE AREA / PART: _____

♦ ATTACH APPLICABLE DRAWINGS TO SHEET ♦

SERVICE (S) REQUIRED:
List Requested Services (i. e. electroless Ni with Au) below, along with thickness ranges required and any additional information or instructions.

Is this the first time we've plated this part? ____ Yes ____ No

DATE JOB STARTED _____ COMMITMENT DATE _____

DATE JOB COMPLETED _____ MET REQUEST? Y N
MET COMMIT? Y N

LAB BOOK REFERENCE: _____

SPECIAL NOTES (ATTACH ALONG WITH PROCESS DATA) :

PLATING LOT ID _____

FIGURE 14

Paper Not Available In Time For Publication

Environmental Management Systems Standards are Following the Quality Lead in International Standards

Gary C. Roper, C.Q.A., H-R Industries, Inc., Richardson, TX

The International Organization for Standards has convened a technical committee (TC207) to write ISO (Greek for *equal)* standards for the environmental field. The idea is to put everyone on an equal playing field in the environmental arena as the ISO 9000 Standards are doing in the quality arena. TC207 has been asked to harmonize its results with the ISO 9000 Standards. If customer concerns about environmental compliance continue to increase, the environmental standards will be important to industry and could result in environmental registration to maintain quality registration.

For copies of this paper please contact:

Gary C. Roper, C.Q.A.
V.P. Process Engineering
H-R Industries, Inc.
1302 East Collins Blvd.
Richardson, TX 75081
214/301-6624
FAX: 214/699-3704

Paper Not Available In Time For Publication

Quality: Smoke and Mirrors or Reality in Your Plating Shop?

Dr. Paul Piplani, CEF, and Ron Lee, SW United Industries, Tulsa, OK

Quality conformance to stipulated purchase order requirements, in most plating jobshops, still happens to be an end-of-the-line inspection by the quality manager, who too often still rejects or accepts by temperament and company politics rather than facts. Who really dictates plating quality in your shop? The plater, the QA manager or the bean counter? Major manufacturing giants (such as Xerox, Harley Davidson, Chrysler) have recognized that production employees must understand customer requirements. Jobshop production employees must also incorporate on-going process improvement and process ownership in order to survive and grow. Substantive quality practices go beyond manipulating results to satisfy those in the plating shop. This paper will review how the 20 key quality elements of ISO 9002 restrict or promote quality in this type of environment.

For copies of this paper please contact:

Dr. Paul Piplani, CEF
SW United Industries
422 S. St. Louis
Tulsa, OK 74120
918/587-4161
FAX: 918/582-6158

THIN GOLD CONTACT FINISHES FOR ELECTRONIC CONNECTORS: A PERSPECTIVE

Morton Antler

Contact Consultants, Inc.
821 Strawberry Hill Rd. East
Columbus, Ohio 43213

ABSTRACT

The traditional finish for the contacts of separable electronic connectors is 0.75-1.25 μm of Co- or Ni-containing cyanide hard gold (HG) on nickel underplate. This finish combines corrosion resistance with durability, and a low contact resistance is maintained in most high reliability applications. However, alternate finishes have been developed that are less expensive, or provide better performance where unusually severe requirements are imposed on the connection. These systems involve a flash gold deposit in combination with one or more underlayers to enhance key properties like the thermal stability of contact resistance at elevated temperature or sliding friction and wear. This paper reviews some of these systems from the application point of view including gold flash on: palladium and its alloys, SnNi, ruthenium, nickel, NiP, and clad noble metals.

INTRODUCTION

An electric contact is required to have a stable and generally low contact resistance for the intended life of the component of which it is a part. It may be subjected to thermal, mechanical, chemical, and other stresses; thus, the contact should be corrosion resistant, be low wearing, etc. to whatever extent is required for its particular application (1).

The finish is the most important characteristic in determining whether the contact will be satisfactory. Many of today's practices in the selection of finishes originated in the requirements of separable connectors that are used to interconnect components, printed circuit boards, and assemblies employed in telephone equipments and computers. But now there are many new applications having different contact requirements. There is a growing need for connectors used in medical devices, connectors for batteries in commercial service, for wireless personal communications equipments, in automobile electronics, and for other products that did not exist or were unimportant only a few years ago.

Acceptable contact performance is not being achieved in many cases. This is due often to an inadequate acquaintance by the user, the connector designer, and the plater with the basic principles of contact behavior despite an extensive literature on the subject (2). There may be a lack of understanding of the properties that the finish must have. The result is poor performance or sometimes over-engineered products that are too costly. Of course, the contact finish is not the only element that controls performance. The design of the connector, how well it is manufactured, and the quality of all of the materials from which it is made are other determinants of behavior.

Thick Hard Gold is a plating from cyanide solutions containing from 0.1-0.5% cobalt or nickel with a thickness of about one μm. It has been a savior to the contact industry. Thick Hard Gold combines a small contact resistance, corrosion resistance, and unique durability (3). Although satisfactory in most cases, it does have some deficiencies such as a low thermal limit, about 125°C, due to diffusion-caused instabilities in its contact resistance. Because of the high cost of gold, there has always been an interest in lowering its usage, and selective plating technologies and, in some cases, base metals have been adopted.

THE GOLD FLASH

The most interesting developments that have reduced the commitment to thick gold involve the application of gold flash on non-noble or semi-noble underplates or substrates. A flash is defined here as a surface layer of from 0.05-0.2 μm thickness. The technical advantages of a gold flash are many, depending on its underplate and substrate.

On hard underlying materials that are prone to adhesive wear, especially palladium and clad noble metals, the gold flash serves as a thin metallic film lubricant (4). Its effectiveness can be still further enhanced with a supplementary organic contact lubricant. The gold flash has been found to persist on the surface of PdNi for a surprisingly long time and to increase its durability by a factor of 10 or more (5).

Underplatings and substrates that are subject to frictional polymerization, like palladium, PdNi, ruthenium, and rhodium, will not degrade by that mechanism so long as the gold flash is present.

A system involving a gold flash on a porous underplate or a clad metal will be less porous, hence less subject to environmental degradation in aggressive environments.

Some platings have a low thermal stability limit due to diffusion to the surface of base alloying elements which then oxidize to insulating films, as with Pd20Ni whose thermal limit is below 100°C (6). In these cases, a gold flash can raise the temperature-use range.

Gold flashed base metals and underplates usually have a lower contact resistance; the natural oxides on these base metals that cause contact resistance to rise are unable to form. In the case of SnNi, galvanic corrosion does not occur with the gold flash due to the passivity of the SnNi. However, a gold flash on pure nickel is satisfactory only in benign atmospheres since attack of the nickel through pores in the gold can be troublesome.

Should fretting occur, the gold will mitigate oxide formation (fretting corrosion) for some time, depending on the frequency, amplitude, and load.

Finally, a gold flash on base metal substrates has long been used to preserve their solderability.

This review does not discuss processes for the platings and other materials on which the gold is used. It seems that when there was a need, creative researchers have been able to devise satisfactory underplating technologies. An example is the development of palladium finishes. In 1960 the known palladium plating processes were slow, difficult to control, and sometimes gave reticulated deposits. We now have superior and versatile chemistries for depositing palladium and some of its alloys. There are a growing number of job shops and captive facilities that plate these metals.

TIN NICKEL

The first of the gold flashed systems involved equiatomic SnNi underplate. This practice originated about 1960 with the application of SnNi as an etch resist in subtractive processes for making printed circuit boards (7). Because SnNi is difficult to solder, it became usual to coat the entire circuit with a gold flash. Bare SnNi is extraordinarily inert; but its surface oxide is an insulator and, together with the low deformability (high hardness) of the deposit, cause its contact resistance to be unacceptably high (8). A gold flash reduces this resistance, and it was then desirable to extend the gold flashed SnNi to the edge contacts of the board. For corrosion to not occur at pores in the gold flash, the SnNi must be non-porous which is achieved at a thickness of about 5 μm.

The demise of the gold flashed SnNi system was due in part to its mechanical limitations. SnNi is very brittle. On sliding,

cracks tend to appear in the finish which destroys its inertness. Adding a nickel subplate to the gold flashed SnNi was not a satisfactory solution to this problem. Gold flashed SnNi can only be used on rigid substrates with relatively low pressure contacts to preclude this cracking.

PALLADIUM

The next gold flashed system that was developed was palladium on a nickel subplate (9-14). The rationale was the use of a semi-precious metal that is significantly cheaper than gold at equivalent deposit thickness. Despite the higher expense of palladium plating salts and limitations in stripping technologies, the net expense of gold flashed palladium usually is still less than that of gold. Palladium without the gold flash is susceptible to attack by some chlorine-containing air pollutants above 60% relative humidity. The gold flashed PdNi system is said to be more durable than one based on pure palladium, although definitive tribological studies that compare them have not been reported. Hard Gold is preferred to pure gold for the flash. Hard Gold flashed Pd20Ni is thermally equivalent to Hard Gold (6).

The gold flashed palladium silver system has not been a commercial success perhaps due to deficiencies in the plating processes. Hard Gold flashed PdNiCo and Hard Gold flashed PdCo finishes have been devised, but there is little reported information on their contact properties.

The literature on the gold flashed palladium and PdNi systems is large, and the reader is referred to it for further information. At present, they are the only promising replacements for thick Hard Gold, and there is a growing acceptance of them by the contact industry (15).

RUTHENIUM

Gold flashed ruthenium was the next finish to be proposed (16). Uncoated ruthenium is comparable in many ways to palladium and cheaper than it at the same thickness. Bare ruthenium tarnishes, forms frictional polymers, and wears poorly when mated to itself. However, with a gold flash, its wear is markedly reduced, being equivalent to or better than Hard Gold. The current lack of interest in ruthenium-based systems is probably attributable to the rapid development of the competing gold flashed palladium systems and to the larger world supplies of palladium.

It is also worth noting that an early study of sliding wear indicated the effectiveness of a gold flash in improving the durability of rhodium (17).

NICKEL PHOSPHORUS

Another recently developed plating system involves gold flash on an electrolytic NiP deposit having a phosphorus content of between 3-8% (18). At a 5 μm thickness, the deposit is smooth and bright. The bare NiP layer had a low contact resistance even after aging at elevated relative humidity and temperature (19), and with the gold flash contact resistance stability was further improved so that the composite finish survived aging in a mixed gas laboratory test (MGT) which simulates a non-air conditioned business office environment (Battelle Class II, 20 days (20)). The test vehicle was a commercial connector that was periodically cycled to assess wear resistance during the MGT. Contact resistance behavior was comparable to that of contacts having a gold flashed palladium finish. The gold flashed NiP plating did not have a nickel subplate, unlike gold flashed palladium. While the paucity of the data make it difficult to draw conclusions about this new finish, clearly, the authors' claim that it performs similarly to gold flashed palladium suggests that it may be useful for other products.

A different process (21, 22) for obtaining electrolytic NiP produces a grey coating having a fine acicular morphology. Coupons with these deposits gave a stable contact resistance, especially with a Hard Gold flash, in an elevated humidity and in simulated industrial environmental tests. It is believed that the sharp asperities of the surface facilitated the rupture of any films that may have formed during the probing determinations of contact resistance. The Hard Gold flash also enhanced the wear resistance of the NiP in a laboratory study (23).

The possible advantage of gold flashed electrolytic and electroless NiP finishes was also pointed out in European work (24).

NICKEL

In some cases gold flash on a nickel underplate has proven to be a satisfactory finish. Large numbers of contacts having only from 0.1-0.2 μm gold are in service. Some suppliers have found that these finishes can be enhanced by a supplementary thin layer of microcrystalline wax or a chromating treatment to upgrade contact durability or to provide some corrosion protection. These thin gold coatings are inadequate for most high reliability separable connectors, especially those having exposed contacts that are used in aggressive atmospheres. But in sealed components, and when wearout is not an issue (as when mating occurs only once during product assembly), a gold flash may be adequate.

It is not often realized that only a few surface asperities need to be metallic for contact resistance to be low, say, less than 50 milliohms. This resistance is satisfactory for many applic-

ations with signal levels of current. With high current circuits, the possibility of resistive heating requires that contact resistance be much less. Thus, most of the contact surface can be covered with insulating material such as nickel oxide provided that there are a few conductive (gold coated) high spots and that the contact is not disturbed which could separate these conductive regions.

CLAD METAL

Clad contact metals are generally more formable than their electroplated counterpart. This facilitates the fabrication of contact structures since the clad material, usually made as an inlay with the noble metal selectively located in the substrate, can be blanked and formed to the required contact configuration. Thick Hard Gold plated substrates cannot be formed without cracking of the noble layer. Thick Hard Gold, on the other hand, is much less prone to severe adhesive wear than a high carat clad gold. Guidelines based on wear have been written for the use of plated Hard Gold and clad noble metal contact finishes which, among other things, discourages the design of connection systems in which both contacts in a pair are made of clad metal (25,26). A cladding can be utilized, however, if it is located only on one contact member, with the other being Hard Gold. A further guideline is that the Hard Gold be on the contact having the larger area involved in making the connection. An example is a backplane contact pin, the "larger" member, joined to a connector having contacts in the form of curved springs with a localized, "smaller," mating area.

The restrictions concerning the use of clad metals can be eliminated if the clad metal is flashed with gold, preferably Hard Gold (27). Hard Gold flash is more formable than thick Hard Gold. Furthermore, the gold flash reduces the porosity of the inlaid metal.

CONCLUDING REMARKS

This review has brought together salient facts on a number of thin gold contact finishes that have been developed over the past 35 years. Most of them were conceived for cost reduction because of the expense of the traditional thick Hard Gold platings which they would replace. There has been significant work also in non-gold contact materials, outside of the scope of this review, which also has helped to relieve the cost pressures of thick Hard Gold.

The pace of exploration of thin gold plated finishes has slowed markedly. There now appear to be sufficient options in this class of materials to satisfy current needs. It is desirable to

have more information of the engineering properties, especially corrosion behavior, thermal properties, and fabrication characteristics of these finishes to demonstrate their utility in new applications. Further process development of the more promising systems will obviously occur in response to new product requirements.

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METALLIZATION OF POLYPYRROLE FILMS PART I: ELECTRODEPOSITION OF NICKEL

Maria Hepel and Richard Stephenson

Department of Chemistry, State University of New York at Potsdam, Potsdam, New York 13676

ABSTRACT

Electrodeposition of nickel on a variety of substrates including conductive polymer films with different compositions have been studied. The enhancement of the nickel electrodeposition rate was observed for composite polypyrrole films with cation-exchange properties in comparison to undoped polypyrrole films with anion-exchange properties and the bare gold electrode. An explanation of this effect is presented. An Electrochemical Quartz Crystal Microbalance (EQCM) with 10 MHz AT-cut piezoelectrodes was used in this study. Use of the EQCM technique allowed for simultaneous monitoring of voltamperometric and resonance frequency vs. potential or time characteristics. By the control of frequency readings, the thickness of the electropolymerized polypyrrole film substrate and also the amount of the electrodeposited nickel was exactly monitored.

The nucleation density has been determined from Scanning Electron Microscope (SEM) experiments and has been correlated with the current-time and frequency time transients. The effect of potential, type of anions and different additives on the nucleation and growth of nickel has also been investigated.

INTRODUCTION

Recent advances in science and technology of conductive organic polymers indicate a variety of potential applications of these materials, including microcircuit transistor devices, electrochromic devices, capacitors, batteries, controllable ion gates, ion exchangers, sensors, drug release systems and electrocatalysts. A number of investigations have focused on the insertion of metal as catalysts (e.g. Pt or Pd) [1-6] and quantum size semiconductor (CdS) particles [7] into conductive polymer films. Some applications require reinforcement of usually somewhat brittle conductive polymers while others utilize very smooth thin films of these materials. In most cases, a strong adherence of electrodeposited film to the substrate is necessary. For various electronic applications, good ohmic or rectifying contacts would be needed between the conductive polymer structures and metallic leads. Deposited metal on polymer will facilitate electrical contact with other circuit components or can form a protective topcoat layer. Another useful application of metal deposition on polymer is in the fabrication of composite materials eg. metal-polymer-metal multi-layers.

Among the variety of methods used in polymer metallization, the electrodeposition from aqueous solutions is the most promising.

The electrodeposition of various metals on polypyrrole carried out in typical industrial plating baths was examined by cyclic voltammetry by Tan et al. [8]. The electrodeposition of palladium, platinum, lead, and ruthenium on polypyrrole film was reported by Pletcher et al. [9]. As in virtually any technological application of conductive polymers, the polymer morphology is an important factor. We have undertaken systematic studies of electropolymerization of conductive organic polymers with various formulations and subsequent electrodeposition of metals on

these materials with special emphasis paid to the morphological developments and possible procedures for nanostructure engineering.

In this work, we report on electrodeposition of nickel on polypyrrole (PPy) and composite PPY(PSS) coated Au electrodes evaporated onto a piezoelectric quartz crystal. We used composite polypyrrole films with permanently incorporated bulky anions e.g. poly(styrenesulfonate) (PSS) during pyrrole electropolymerization process. In addition to simultaneously recorded current, we were able to follow changes in the electrode mass by measuring the oscillation frequency of these piezoelectrodes. Several factors influencing the micromorphology of nickel deposits such as composition of the substrate electrode, deposition potential, effect of anions and different organic additives have been investigated. The effect of the polypyrrole film on the kinetics of nucleation and growth of nickel nuclei will be described.

EXPERIMENTAL

An Electrochemical Quartz Crystal Microbalance (EQCM) with 10 MHz AT-cut quartz oscillators was used in this study. The EQCM is a hybrid technique allowing for simultaneous monitoring of voltamperometric and resonance frequency vs. potential or time characterics. The EQCM technique is based on the piezoelectric effect. The resonant frequency of the quartz crystal lattice vibrations in a thin quartz crystal wafer is measured as a function of the mass attached to the crystal interfaces. For thin rigid films, the interfacial mass changes are related to the changes in oscillation frequency of the EQCM through the Sauerbrey equation:

$$\Delta f = - \frac{2\Delta m n f_o^2}{A\sqrt{\mu_q d_q}} \qquad (1)$$

In this formula, the change in the resonant oscillation frequency (Δf) is equal to minus the change in the interfacial mass (Δm) per unit area (A) times a constant. Thus, the frequency decreases as the mass increases. The constant is evaluated with knowledge of the oscillation frequency of the fundamental mode of the EQCM (f_o), the overtone number (n), the density of quartz (d_q = 2.648 g/cm^3) and the shear modulus of quartz (μ_q = 2.947 x 10^{11} g cm^{-1}s^{-2}).

The EQCM is well suited to the measurements of mass transport that can accompany redox processes occurring in thin rigid films on electrodes [10-18]. The excellent sensitivity and large dynamic range of this device permit characterization of mass transport (both ions and solvent) in films.

A Model EQCN-700 Electrochemical Quartz Crystal Nanobalance (ELCHEMA, Potsdam, NY) was used to monitor frequency variation (mass changes) of piezoelectrodes. The active surface area of the working Au electrode was 0.25 cm^2. The oscillator crystals were sealed to the side opening in a glass vessel of 30 mL capacity. The working electrode was polarized using a Pt-wire counter electrode and its potential measured *vs.* saturated calomel electrode (SCE). A Model PS-605 Precision Potentiostat/Galvanostat (ELCHEMA) was used in the measurements. The program waveform was generated and measurements performed by VOLTSCAN real-time data acquisition system with 16-bit precision. The software trigger utility of the VOLTSCAN was used to control precisely the amount of deposited metal. This feature appeared to be extremely useful for measurements of nucleation density and nuclei size which could have been done for the given amount (mass) of deposit and irrespective of the deposition rate. The software trigger allowed to stop electrolysis after a given preset mass of the metal has been deposited. Scanning Electron Microscope Model ISI SX-40A

was employed to obtain surface images of metal deposits.

The electropolymerization of pyrrole was carried out on gold piezoelectrode from aqueous electrolyte solutions containing organic dopant, e.g. poly(styrene-sulfonate) (PSS), 20-70 mM pyrrole, and supporting electrolyte, by potential step to E = +600 mV vs. SCE. Films with thicknesses below 1 μm were typically grown. All chemicals were of analytical grade purity and were used without further purification except for pyrrole which was purified by distillation. Solutions were prepared using Millipore Milli-Q deionized water. They were deoxygenated by bubbling with purified nitrogen. All experiments were performed at room temperature, 22°C.

RESULTS AND DISCUSSION

Deposition of Nickel on PPy and PPy(PSS) Modified Gold Piezoelectrodes

In electrodeposition of metals, surface properties of a subtrate play a key role in initial stages of the deposition process, including metal ion discharge, surface diffusion, and formation of nuclei. In our experiments, nickel was being deposited on polypyrrole coated gold electrodes. Reduction current on these electrodes has two components, one due to reduction of polypyrrole with concomitant release of anions as counterions according to reaction (1):

$$(PPy^{+}A^{-}) + e^{-} \rightarrow PPy^{o} + A^{-} \qquad (1)$$

and when negative enough potential for nickel reduction is applied, the reaction (2) occurs:

$$Ni(L)_x^{+2} + 2e \rightleftharpoons Ni^{o} + xL \qquad (2)$$

The following reactions are occuring during the electrodeposition of nickel on composite PPy(PSS) films. Reduction of PPy(PSS) polymer occurs with concomitant incorporation of nickel cations or other cations as counterions to balance the negative charge on permanently incorporated dopant molecules PSS^{-}, according to reaction (3):

$$(PPy^{+}\cdot PSS^{-}) + e^{-} + 0.5\ Ni^{+2} \rightleftharpoons (PPy\cdot PSS^{-}\cdot Ni_{0.5}^{2+}) \qquad (3)$$

and when negative enough potential for nickel reduction is applied the reaction (4) corresponding to the reduction of nickel ions present inside the polymer matrix without ligands occurs:

$$(PPy\cdot PSS^{-}\cdot Ni_{0.5}^{2+}) + e^{-} + M^{+} \rightleftharpoons (PPy\cdot PSS^{-}\cdot M^{+}) + 0.5\ Ni^{0} \qquad (4)$$

where M^{+} is the cation of the supporting electrolyte.
In addition, electrodeposition of nickel ions present in the solution in the form of hydrated complexes or other complexes according to the reaction (2) also occurs.

Properties of some polypyrrole films were modified by incorporation of large immobile poly(styrenesulfonate) anions (PSS), rendering the ion dynamics of these films predominantly cationic [10,19]. In this way, the effect of the type of ion conductivity of the two substrate materials (with virtually identical chemical nature) on nickel deposition process could have been examined. First experiments were performed using linear potential scan voltammetry and microelectro-gravimetry. The results obtained in 1 g/L Ni(II) for Au/PPy(PSS) and Au/PPy piezoelectrodes are presented in Figures 1 and 2, respectively. The current-potential curves indicate that the nickel electrodeposition process is enhanced on PPy(PSS) films in comparison to unmodified PPy and bare Au electrodes. The resonant frequency change vs. potential characteristics confirm this conclusion.

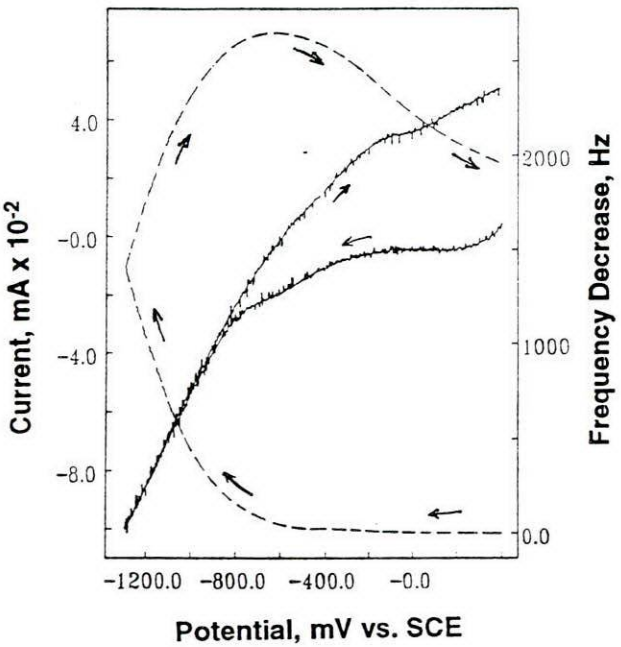


Figure 1. Linear potential scan voltammetric and microelectrogravimetric characteristics: current (solid line) and resonance frequency (dashed line) *vs.* potential, obtained at a PPy(PSS) modified gold EQCM electrode in 1 g/L Ni(II) solution. Scan rate: 50 mV/s.

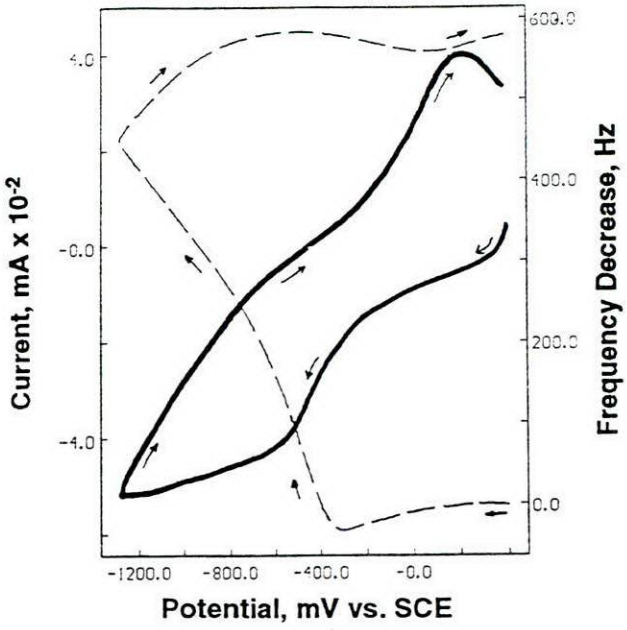


Figure 2. Linear potential scan voltammetric and microelectrogravimetric characteristics: current (solid line) and resonance frequency (dashed line) *vs.* potential, obtained at a PPy modified gold EQCM electrode in 1 g/L Ni(II) solution. Scan rate: 50 mV/s.

The amount of electrodeposited nickel during the negative going potential scan was about 590 ng on PPy substrate and 2650 ng on PPy(PSS) composite film. Significant enhancement of the amount of nickel electrodeposited on PPy(PSS) composite films with cation-exchange properties in comparison with PPy films with anion-exchange properties was observed for linear potential scan experiments. This enhancement effect was also confirmed by potentiostatic electrodeposition of nickel performed at E = -1300mV. In Figure 3, the resonant frequency change vs. potential was compared for Au/PPy(PSS), Au/PPy and bare Au electrode. It is apparent that the PPy overcoat on Au, in general, accelerates the deposition of nickel. When the potential of the electrode was stepped from E = +400 mV to E = -1300 mV and held at this potential for 1 minute, significantly larger amount of electrodeposited nickel was observed on PPy(PSS) substrate than on PPy film. Under the same conditions, much less nickel was deposited on the gold electrode. Hydrogen evolution is inhibited to a greater extent on conductive polymer film than on metallic electrode, resulting in a higher current efficiency for the nickel deposition. It is interesting that the organic conductive film would enhance the deposition process so strongly. Basically, one might expect an effect just opposite since the electrical conductance of Au is much higher than that of PPy(PSS) or PPy. In the latter case, and especially at more cathodic potentials, there must develop an ohmic potential drop decreasing the effective deposition potential at the PPy/solution interface. Therefore, an explanation of the increased rate of nickel

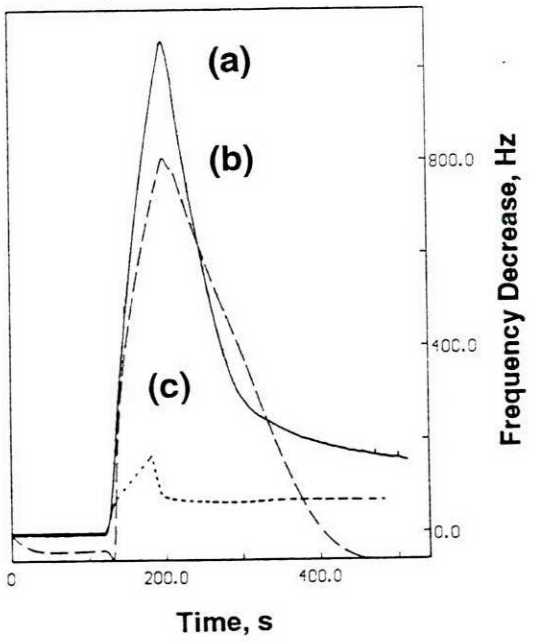


Figure 3. Mass change *vs.* time transients, obtained in potential step experiments, for Ni deposition and stripping at (a) Au/PPy(PSS) electrode (solid line), (b) Au/PPy electrode (dashed line), and (c) bare Au electrode (dotted line), in 1 g/L Ni(II) solution. Conditions: E_{cond} = +400 mV, E_{dep} = -1300 mV, E_{strip} = +400 mV; t_{dep} = 60 s, t_{strip} = 300 s.

deposition on PPy in comparison to that on bare Au electrode has to be found in specific interaction between nickel and pyrrole units of the polymer. Such an interaction may involve PPy-mediated electron transfer in Ni(II) reduction process and/or complexation of Ni(II) ions at the nitrogen site followed by its reduction through an injection of bipolarons to the polypyrrole carbon chain. The complexation of copper with polypyrrole has been reported by Inoue et al. [20]. Using the X-ray photoelectron spectroscopy, they have found that copper atoms are coordinated to pyrrole nitrogen in alkaline solutions. The PPy-mediated electron transfer has been postulated by Dong et al. [21]

Further enhancement of nickel deposition rate on PPy(PSS) films in comparison to unmodified PPy, also requires an explanation. It is rather unlikely that the incorporated PSS could affect the Ni-PPy interaction due to the highly localized nature of complexation. To rationalize the observed increase in nickel deposition rate on PPy(PSS) modified substrate, we can take into account accumulation of nickel(II) cations into the polymer film. The PSS modified PPy attracts cations during polypyrrole reduction. The ingress of Ni(II) ions into PPy(PSS) film may result in considerable increase of Ni(II) concentration in the film which may even exceed its solution concentration. The hydration shell of Ni(II) ions may also be substantially depleted in the film effectively increasing the nickel reduction rate. In this situation, the formation of Ni^0 nuclei may be expected not only on the polymer surface but also inside the polymer matrix.

The morphology of a typical PPy film is depicted on the SEM microgram presented in Figure 4a. The thickness of the film is 0.5 μm. In solutions without any additives, cracks are observed in nickel deposits, as illustrated in SEM microgramms, Figures 4b and 4c, for 10 μg of nickel deposited at a constant potential E = -1200 mV vs. SCE from 1 g/L Ni(II) on Au/PPy and Au/PPy(PSS), respectively. It is evident that the surface of nickel is smoother when deposited on Au/PPy(PSS) in comparison to that on Au/PPy, however, due to the surface cracking, the quality of the deposit is poor when no organic additives are added to the plating bath. The quality of Ni films can be substantially improved by carrying the electrodeposition process in the presence of leveling and brightening additives.

Effect of Deposition Potential

Deposition potential affects not only the metal ion discharge rate but also the effective surface supersaturation with adatoms thus

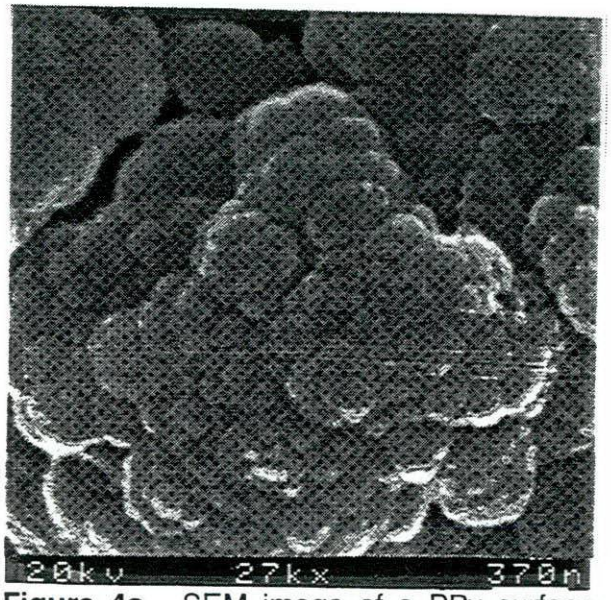


Figure 4a. SEM image of a PPy surface prior to Ni deposition. PPy film was electropolymerized at constant potential E = +600 mV on a gold EQCM electrode from 50 mM pyrrole solution. Film thickness: 0.5 μm; scale marker: 370 nm.

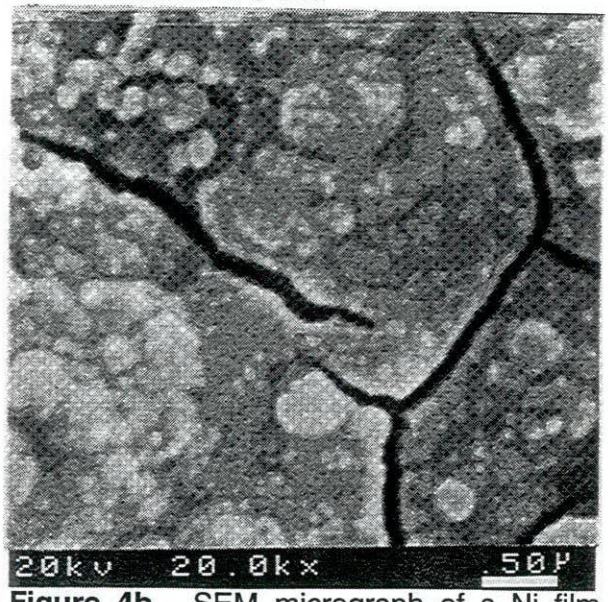


Figure 4b. SEM micrograph of a Ni film electrodeposited on a Au/PPy EQCM electrode from 1 g/L Ni(II) solution, at E = -1200 mV. Deposit mass: m_{Ni} = 10 μg; scale marker: 0.5 μm.

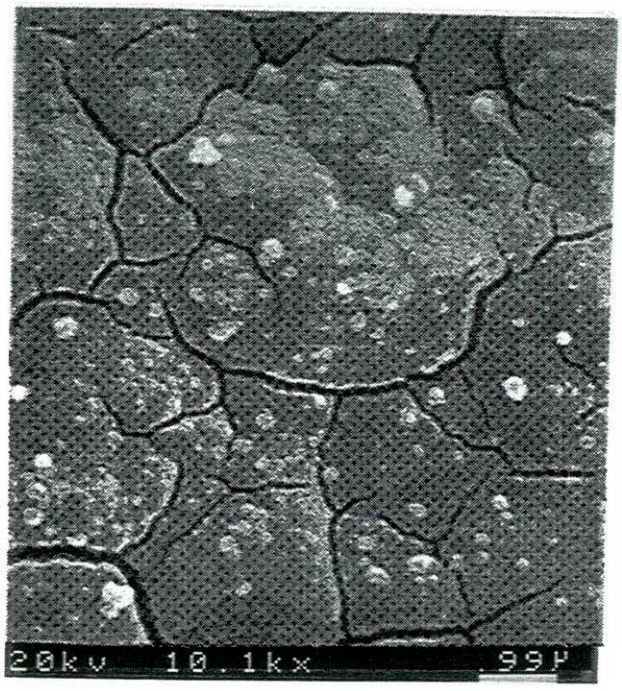


Figure 4c. SEM micrograph of a Ni film electrodeposited on a Au/PPy(PSS) EQCM electrode from 1 g/L Ni(II) solution, at E = -1200 mV. Deposit mass: m_{Ni} = 10 μg; scale marker: 0.99 μm.

controlling the rate of nucleation. Series of experiments with nickel deposition on Au/PPy and Au/PPy(PPS) electrodes were performed under potentiostatic control with a potential step from E = 400 mV vs. SCE to E = -500, -1100 and -1300 mV. The current-time and frequency-time transients obtained in these experiments are presented in Figure 5. The increase of the deposition current in later stages of the process indicates a secondary nucleation on nickel coated electrode. Typical i=f(t) transients in the absence of secondary nucleation and growth should consist of a current rise due to the primary nucleation and growth, followed by a peak associated with nuclei overlapping, and a steady-state current reflecting continuous growth of a smooth film [22]. Any increase in the post-peak

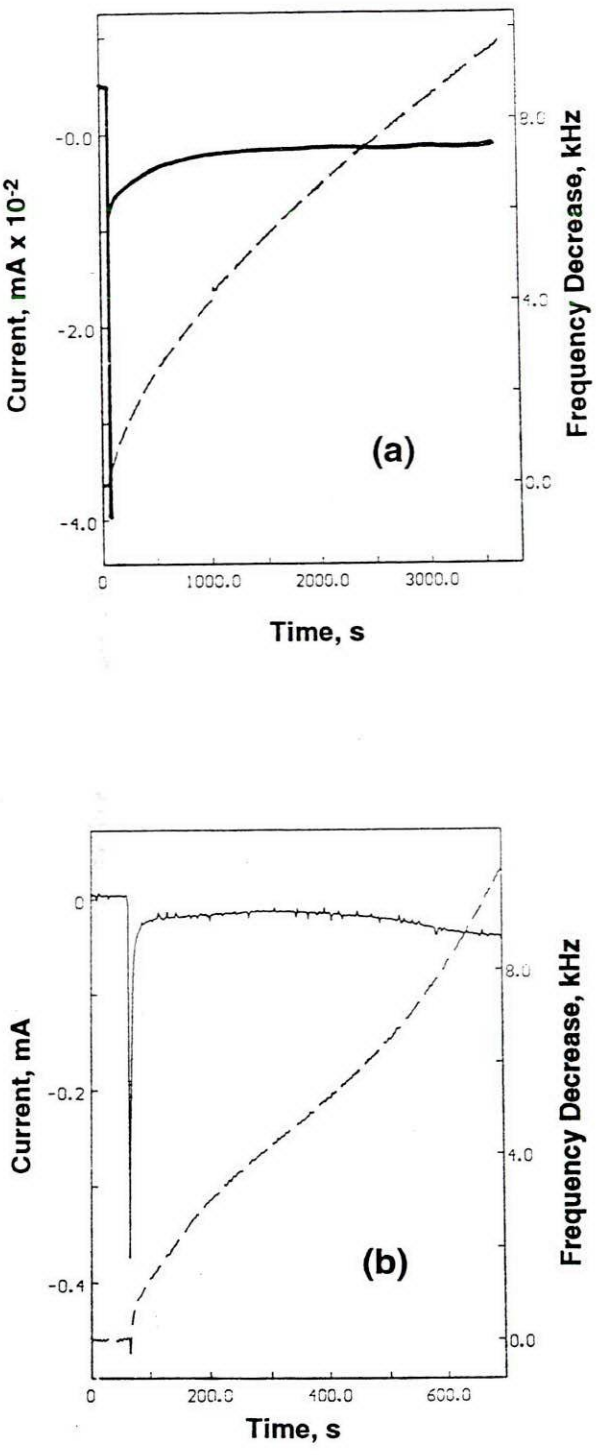


Figure 5. Current (solid line) and resonance frequency (dashed line) *vs.* time transients, obtained in potential step experiments, for Ni deposition at Au/PPy(PSS) electrode (a,b) and Au/PPy electrode (c,d), in 1 g/L Ni(II) solution. Deposition potential: (a,c) -500 mV; (b,d) -1300 mV *vs.* SCE. Other conditions: E_{cond} = +400 mV, t_{cond} = 60 s.

region indicates the formation of secondary nucleation centers. The inspection of SEM micrographs confirms the presence of nuclei growing on a thin, cracked primary film of nickel. The comparison of SEM micrographs for different deposition potentials reveals that smoother nickel deposits were obtained at higher cathodic overvoltages (Figures 6 and 7). In Figure 6, the morphology of 10 μg deposits of nickel on Au/PPy(PSS) piezoelectrodes are presented. They were obtained at E = -500 and -1300 mV vs. SCE (Figures 6a and b, respectively). The surface cracking is observed in the entire deposition potential range investigated. Similar situation was observed in nickel deposition on Au/PPy electrodes, even for Ni films twice as thick.

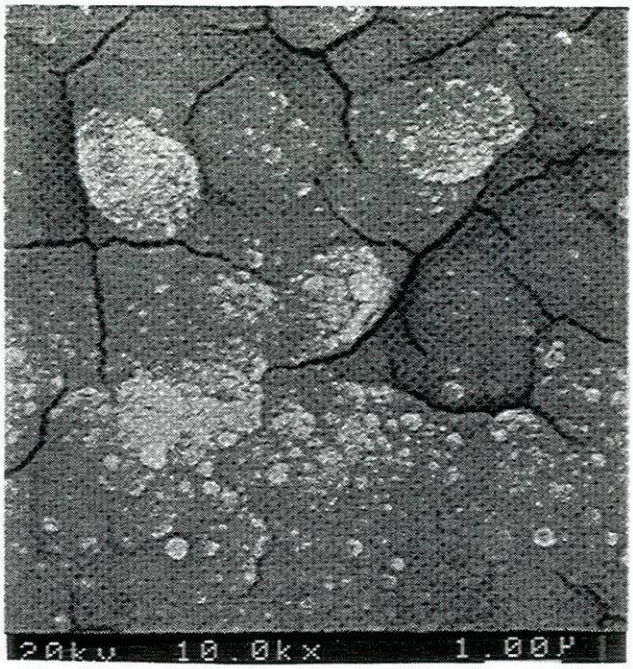


Figure 6a. SEM micrograph of a Ni film electrodeposited on a Au/PPy(PSS) EQCM electrode from 1 g/L Ni(II) solution, at E = -500 mV. Deposit mass: m_{Ni} = 10 μg; scale marker: 1 μm.

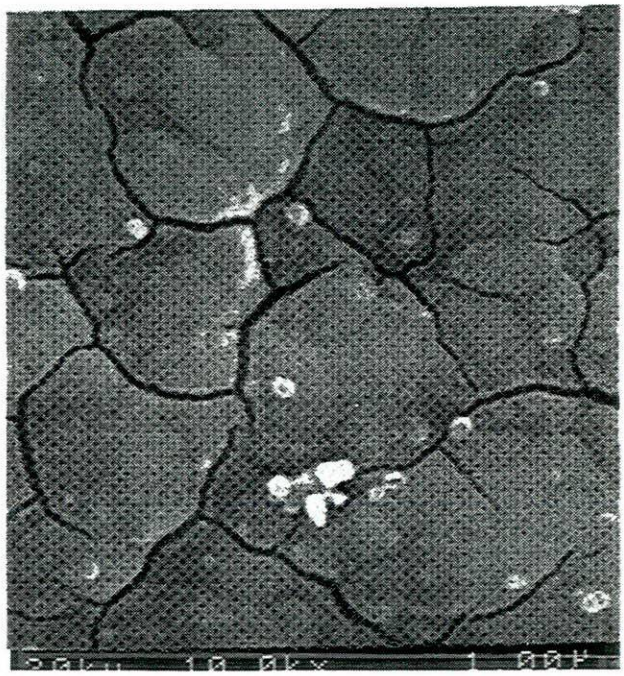


Figure 6b. SEM micrograph of a Ni film electrodeposited on a Au/PPy(PSS) EQCM electrode from 1 g/L Ni(II) solution, at E = -1300 mV. Deposit mass: m_{Ni} = 10 μg; scale marker: 1 μm.

The SEM micrograms presented in Figures 7a and b illustrate this for 20 μg Ni^0 films deposited at E = -500 and -1300 mV, respectively. It is seen that with increasing cathodic overvoltage, the mean crack width increases and the mean plate size (or the average distance between cracks) increases as well. For example, from surface images shown in Figure 7, one can estimate that the mean crack width increases from 0.1 μm to 0.25 μm, for the deposition potential decreasing from -500 to -1300 mV. At the same time, the mean plate size increases approximately twice.

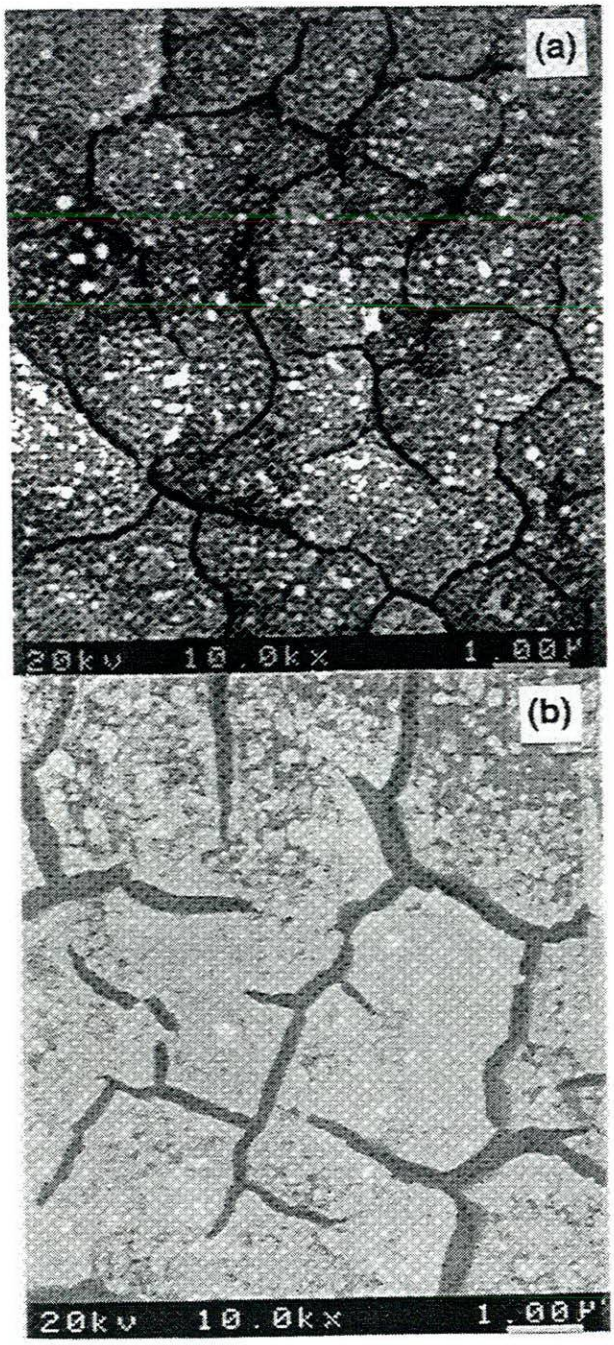


Figure 7. SEM micrographs of Ni films electrodeposited on a Au/PPy EQCM electrode from 1 g/L Ni(II) solution, at E_{dep}: (a) -500 mV; (b) -1300 mV. Deposit mass: m_{Ni} = 10 μg; scale marker: 1 μm.

Results of microelectrogravimetric measurements in potential step experiments concerning the effect of electrode composition and the deposition potential are summarized in Table 1. It is evident that the mass increase (frequency decrease) accompanying the nickel deposition is faster for Au/PPy(PSS) substrates than for Au/PPy as already pointed out in the previous section. With increasing overpotential, the enhancement of nickel deposition on Au/PPy(PSS) piezoelectrodes becomes even more pronounced, for instance, at E = -1300 mV the deposition of 9,700 ng of nickel takes 3,000 s on Au/PPy and only 600 s on Au/PPy(PSS). An enhancement by a factor of 5 is then observed for nickel electrodeposition on Au/PPy(PSS) electrode in comparison with Au/PPy electrode.

TABLE 1

Effect of the Deposition Potential on EQCM Frequency Change due to the Deposition of Nickel on PPy and PPy(PSS) Substrates

Solution: 1.0 g/L Ni(II)

PPY/PPS⁻ Film

Frequency Decrease (Hz)	Deposition Potential (mV)	Deposition Time (sec)
2,600	-500	600
6,200	-800	600
9,000	-1300	600

PPy Film

Frequency Decrease (Hz)	Deposition Potential (mV)	Deposition Time (sec)
8,000	-500	3000
8,500	-800	3000
9,500	-1300	3000

Effect of Additives on Morphology of Nickel Deposits

Effects of various additives known to influence morphology of metal deposits were examined for higher nickel concentrations using both the PPy and PPy(PSS) coated piezoelectrodes. The additives examined were: boric acid, 1,5-naphthalene disulfonic acid, and thiourea. Typical potential step chronoamperometric and micro-electrogravimetric characteristics recorded are presented in Figure 8 for solution containing 0.85 M $NiSO_4$ + 0.15 M $NiCl_2$ + 0.36 M H_3BO_3.

The morphology of nickel deposited on PPy and PPy(PSS) substrates in the presence and absence of additives has been examined using Scanning Electron Microscopy. The deposition of nickel was carried out under potentiostatic control at E = -1100 mV vs. SCE. The time of electrolysis was controlled by VOLTSCAN data acquisition system with software trigger configured to stop the electrolysis after 10 μg of Ni had been deposited. In this way, we could compare the nucleation density and the size of nuclei for different samples with the same mass deposited and irrespective of the differences in the deposition rate. The SEM micrograms of nickel deposits obtained on PPy(PSS) coated electrodes in the absence of additives and in the presence of 1,5-naphthalene disulfonic acid and thiourea are presented in Figures 9 and 10 at lower and higher magnification, respectively. Surface images shown in Figure 9 were used to determine the nucleation density and those presented in Figure 10, for measurements of the size of nuclei. The shape of nuclei is almost perfectly spherical in case of both additives. The surface of Ni spheres formed on PPy(PSS) substrate in the presence of 1,5-naphthalene disulfonic acid shows more crystalline texture while in the case of thiourea, the surface of Ni spheres is ideally smooth. Also, the primary nickel film is smooth and does not show any cracks. The results of the analysis of SEM images of Ni nuclei formed on Au/PPy(PSS) piezoelectrodes are collected in Table 2.

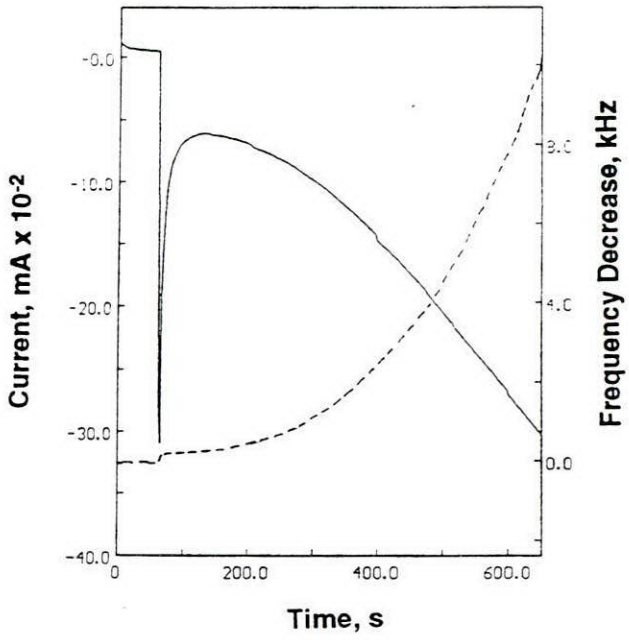
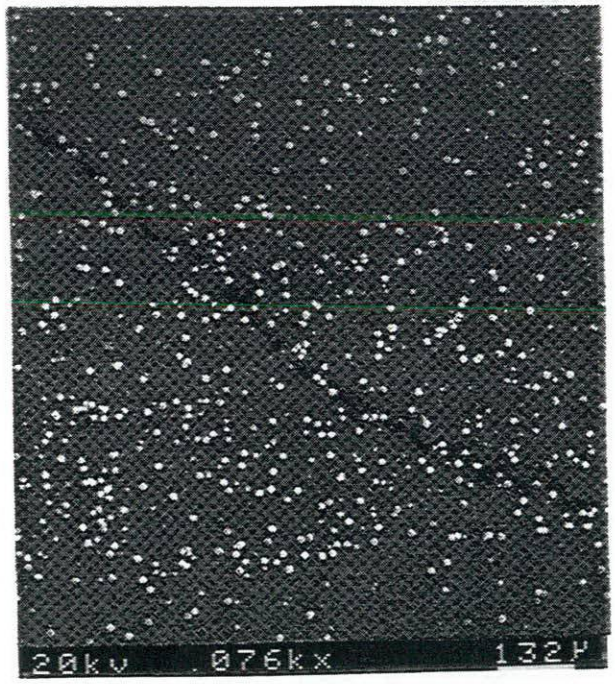
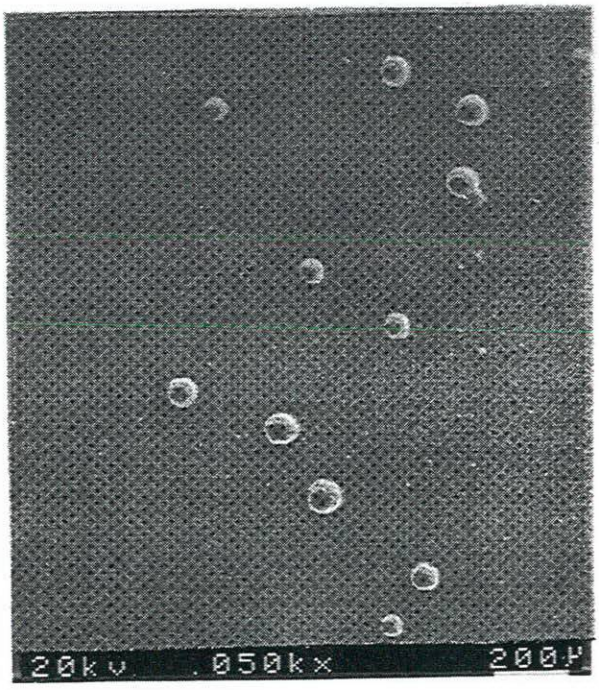


Figure 8. Current (solid line) and resonance frequency (dashed line) *vs.* time transients, obtained during potentiostatic deposition of Ni at a Au/PPy electrode, from 0.85 M $NiSO_4$ + 0.15 M $NiCl_2$ + 36 g/L H_3BO_3 solution. Conditions: E_{cond} = +400 mV, E_{dep} = -1100 mV; t_{cond} = 60 s, t_{dep} = 650 s.

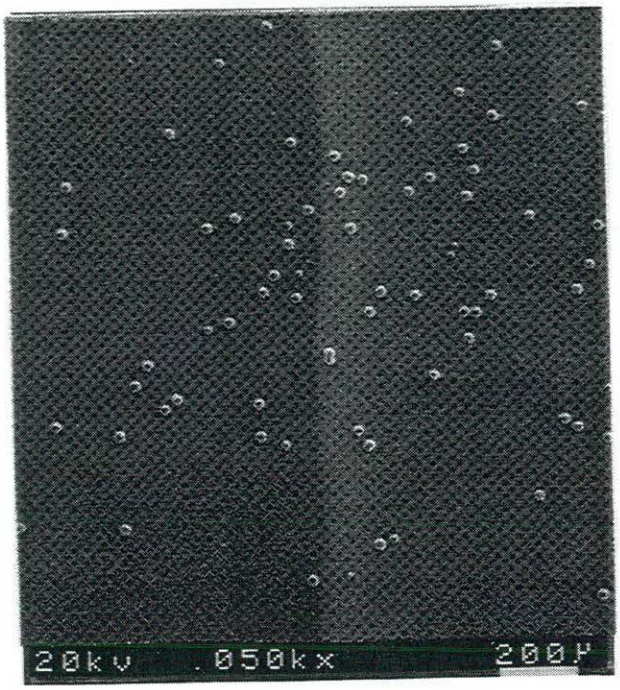
Very high secondary nucleation density (29,500 nuclei per cm^2, Figure 9a) observed in the case of deposition from 1 M $NiSO_4$ without any additives can be substantially reduced by adding 1,5-naphthalene disulfonic acid to the plating bath (Figure 9b). Further reduction of the secondary nucleation density is achieved by using thiourea as the nucleation suppressant (Figure 9c). In the latter case, only 450 secondary nuclei per cm^2 are being formed under the experimental conditions employed. The increase in size of



(a)

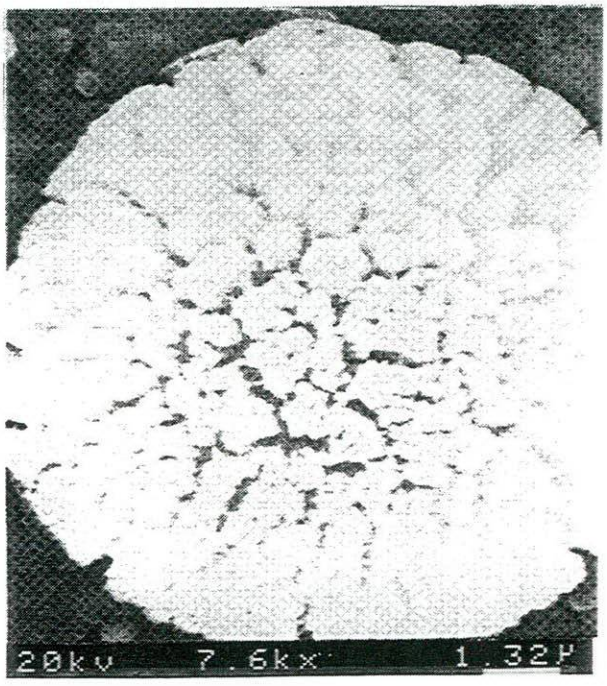


(c)

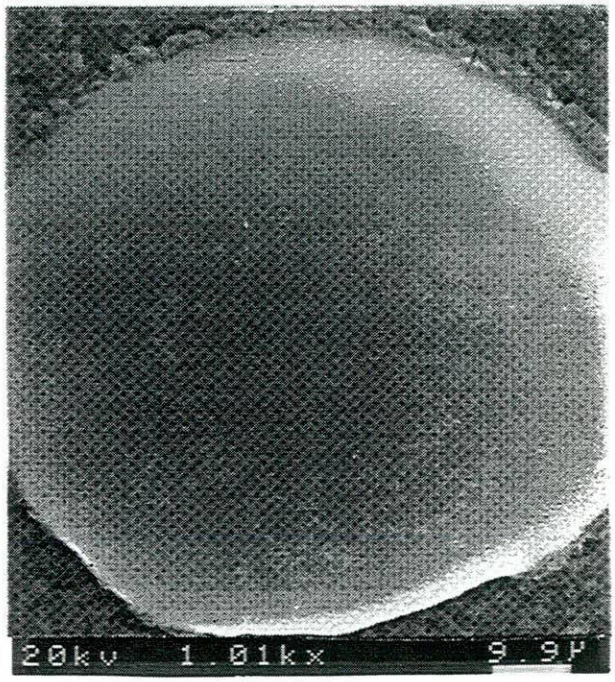


(b)

Figure 9. SEM micrographs of Ni films with secondary nuclei, electrodeposited on Au/PPy(PSS) EQCM electrode at E = -1300 mV, from (a) 1 M $NiSO_4$ solution without any additives; (b) 0.85 M $NiSO_4$ + 0.15 M $NiCl_2$ + 0.1 mM 1,5-naphthalene disulfonic acid solution; (c) 0.85 M $NiSO_4$ + 0.15 M $NiCl_2$ + 30 g/L H_3BO_3 + 1 mM thiourea solution. Deposit mass: m_{Ni} = 10 µg; scale marker: (a) 132 µm; (b,c) 200 µm.



(a)



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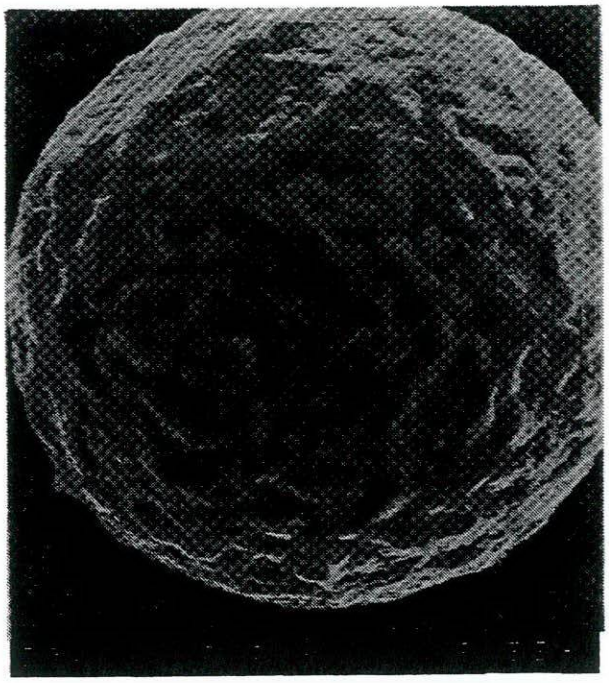

(b)

Figure 10. SEM micrographs of Ni films with secondary nuclei, electrodeposited on Au/PPy(PSS) EQCM electrode at E = -1300 mV, from (a) 1 M $NiSO_4$ solution without any additives; (b) 0.85 M $NiSO_4$ + 0.15 M $NiCl_2$ + 0.1 mM 1,5-naphthalene disulfonic acid solution; (c) 0.85 M $NiSO_4$ + 0.15 M $NiCl_2$ + 30 g/L H_3BO_3 + 1 mM thiourea solution. Deposit mass: m_{Ni} = 10 µg; scale marker: (a) 1.32 µm; (b) 3.33 µm; (c) 9.9 µm.

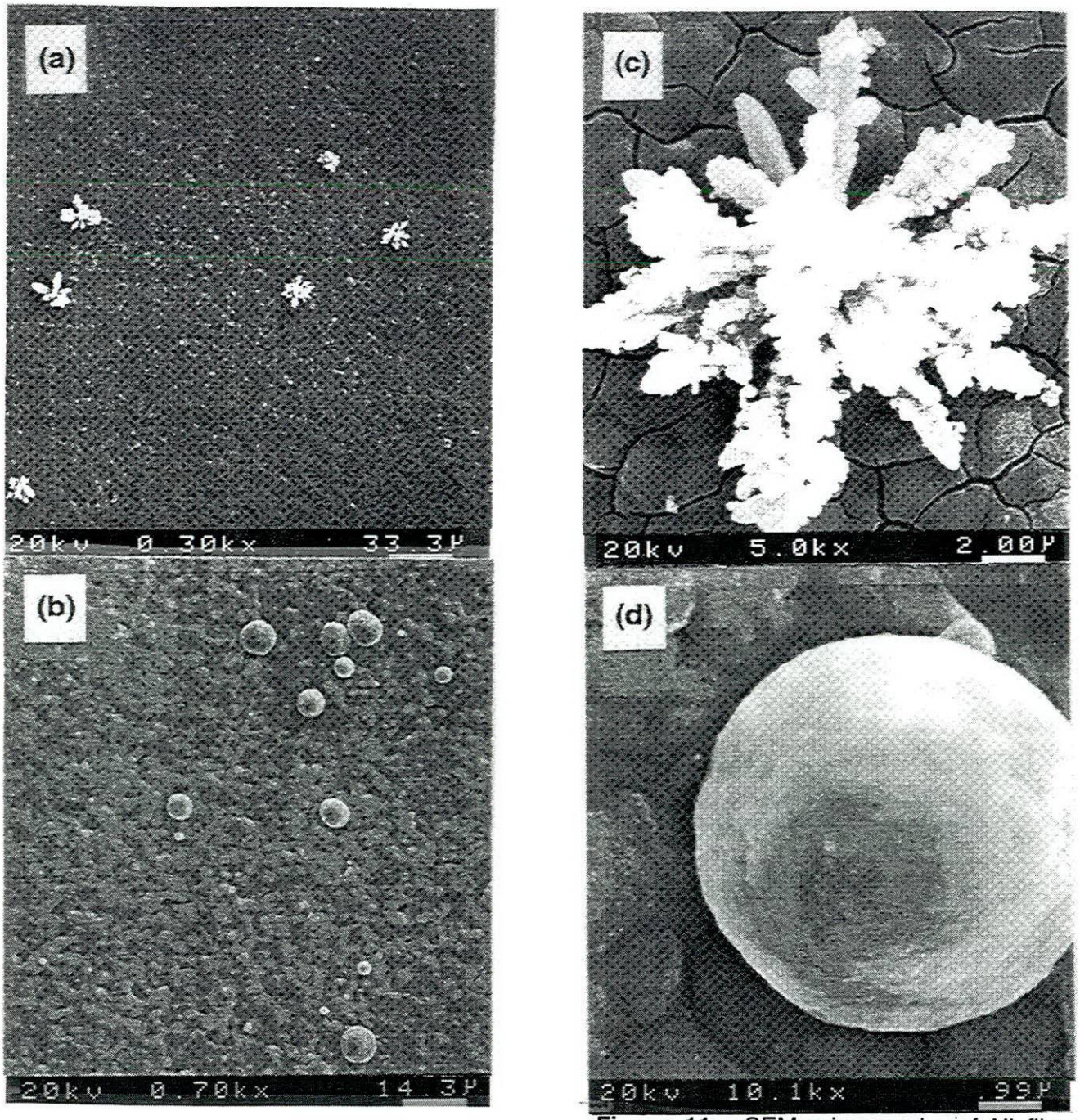

Figure 11. SEM micrographs of Ni films electrodeposited on Au/PPy(PSS) EQCM electrode at E_{dep} = -1300 mV, from 1 g/L Ni(II) solution containing: (a,c) 25 mg/L, and (b,d) 30 g/L, of H_3BO_3, at E = -1300 mV. Deposit mass: m_{Ni} = 10 µg; scale marker: (a) 33.3 µm; (b) 14.3 µm; (c,d) 1 µm.

TABLE 2

Effect of Additives on Secondary Nucleation of Ni Deposited on Au/PPy Piezoelectrodes

E_{dep} = -1100 mV vs.SCE; m_{Ni} = 10μg

Solution Composition	Nucleation density (cm^{-2})	Nucleus diameter (μm)
1 M $NiCl_2$		(1-2)
1 M $NiSO_4$	29,500	12.0
0.85 M $NiSO_4$ 0.15 M $NiCl_2$ 0.1 mM Naphthalene disulfonic acid	2,560	27.8
0.85 M $NiSO_4$ 0.15 M $NiCl_2$ 1 mM thiourea	450	88.4

typical secondary nuclei with decreasing nucleation density is due in part to the experimental condition limiting the amount of nickel deposited to 10 μg. Similar effect of the decreasing secondary nucleation density has been observed for solutions containing 5 x 10^{-3}M coumarin.

The addition of boric acid to the plating bath increases smoothness of Ni deposit, as illustrated in Figure 11 for Ni^0 electrodeposition on Au/PPy(PSS) piezoelectrodes from 1 g/L Ni(II) solutions containing 0.025 g/L (Figures 11a and c) and 30 g/L (Figures 11 b and d) of boric acid. With low concentrations of boric acid, 0.025 g/L, highly dendritic secondary Ni^0 deposits are obtained and the primary Ni^0 film is cracked. With high concentrations of boric acid (30 g/L), the secondary Ni^0 nuclei are smooth, almost perfectly spherical, and no dendritic features are observed. The primary Ni^0 film is also smooth.

Effect of Anions

Anions play an important role in determining the electrodeposit morphology in metal plating. In this work, two different anions, Cl^- and SO_4^{2-}, have been investigated. Effect of these two anions on the surface structure of Ni electrodeposits is presented in Figures 12a and b. Nickel films obtained in the presence of 1.0 M SO_4^{2-} anions are smoother, and generally of better quality, than those deposited from solutions containing 2.0 M Cl^- anions which are of microdendritic type. The effect of chloride ions may be rationalized by taking into account high adsorbability of these anions on a metal surface. A smooth metal deposit can only be obtained when the surface diffusion of metal adatoms can provide sufficient amount of building material (metal adatoms) to the defective sites (kinks, traps, corners, etc.) on the metal surface. The strong adsorbability of chloride anions may hinder the free surface diffusion of metal adatoms thus effectively stimulating the nucleation and growth of dendritic branches. This should explain such a dramatic difference in the morphology of nickel deposits obtained from 1.0 M $NiSO_4$ and 1.0 M $NiCl_2$ solutions.

In the case of nickel deposition from $NiCl_2$ solution without any additives, the deposit morphology is of microdendritic type and no smooth primary film is observed (Figure12a). Some larger secondary "nuclei" are also observed but they differ considerably in size, are irregular and dendritic.

CONCLUSIONS

Metallization of conductive polymer films based on polypyrrole can be achieved by using plating baths similar to those employed in standard metal electroplating. Enhancement of the nickel electrodeposition on conductive

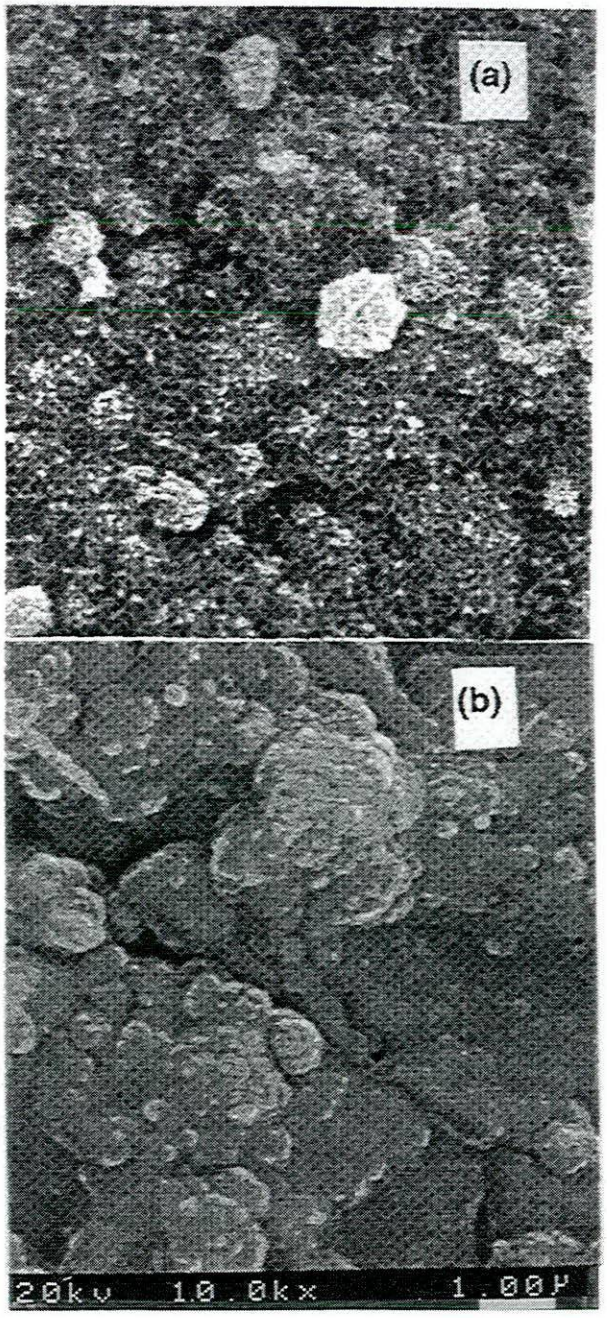

Figure 12. SEM micrographs of Ni films electrodeposited on Au/PPy EQCM electrode, at E_{dep} = -1300 mV, from: (a) 1 M $NiCl_2$, and (b) 1M $NiSO_4$ solution, without any additives. Deposit mass: m_{Ni} = 10 μg; scale marker: 1 μm.

polymer in comparison to bare gold electrodes was found. Despite the organic nature of the PPy and PPy(PSS) substrates, smooth nickel films can be deposited using the same surface active agents used as additives in nickel plating on metallic substrates, *viz.* naphthalene disulfonic acid, thiourea, coumarin, and boric acid. Further enhancement of the nickel electrodeposition rate was achieved on the composite PPy(PSS) films with cation dynamics in comparison to PPy films with dominating anion dynamics. The type of ion dynamics (ionic conductance) is important because the rate of deposition of Ni^0 increases when the polymer film is made with predominantly cationic dynamics by incorporation of large immobile anions, e.g. PSS. This is due to the fact that such films exhibit extended conductivity region toward more cathodic potentials. Also, in this case, the metal cations can readily enter the polymer film. Nickel nuclei are formed not only on the electrode surface but also inside the polymer matrix. Formation of nickel nuclei near the film surface may increase the adherence of metal overlayer to the polymer.

ACKNOWLEDGEMENTS

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SPOT PLATING ON UNMASKED SUBSTRATE WITH AN IMPINGING JET

C. Karakus and D.-T. Chin
Department of Chemical Engineering
Clarkson University
Potsdam, NY 13699-5705

ABSTRACT

This paper describes a study using an impinging jet to localize electrodeposit on an unmasked substrate. Copper and nickel platings on a maskless cathode were carried in a laboratory setup, and local deposit thickness was measured as a function of radial position from the point of jet impingement. The effect of various scale-up parameters, such as plating current density, nozzle diameter, nozzle height, and jet velocity, on metal thickness distribution were examined.

INTRODUCTION

The impinging jet has been recognized as an important fluid flow system because of its high heat and mass transfer rates [1-8]. The combination of a high mass transfer rate and its special flow characteristics makes the impinging jet suitable for localized spot plating on an unmasked cathode. The contact area or desired region of electronic and machine parts is often electroplated with a metal to increase the conductivity and corrosion resistance. In the electronic industry, sliding contacts and electric connectors are locally plated with gold. Among the spot plating methods, impinging jet stands out owing to its extremely high rate of electroplating. High speed spot plating without using insulating masks or photo-resists can provide substantial saving in production cost.

The purpose of this work is to study the metal thickness distribution of an electrodeposit on an unmasked cathode obtained by jet plating with an unsubmerged impinging jet. Copper plating from an acidic copper sulfate bath and nickel plating from a Watt's nickel bath and a nickel sulfamate bath were studied experimentally. The metal thickness distribution was examined as a function of current density, electrolyte composition, mass transfer, and nozzle height. A dimensional analysis was used to identify the scale-up parameters which influence the metal thickness distribution on the cathode surface.

EXPERIMENTAL

Jet Plating Cell

The schematic representation of a jet electroplating cell is shown in Figure 1. The cell was made of a Plexiglass pipe of 20 cm in height by 15 cm in diameter and with a wall thickness of 0.635 cm. The upper section of the cell was a cathode assembly, and the bottom part was a nozzle assembly. The cathode assembly consisted of a threaded Plexiglas cylinder of 2.54 cm in diameter and 10 cm in length, a Plexiglas nut, a Plexiglas cathode holder, and a brass cathode substrate. The replaceable brass cathode substrate had a dimension of 10 cm in diameter and 1 mm in thickness; it was held onto the cathode holder by a circular Plexiglas ring having a dimension of 14 cm outside diameter and 10 cm inside diameter. A steel spring and a copper rod of 0.5 cm in diameter and 10 cm long were used as the electric contact to the brass cathode substrate. The entire cathode assembly was inserted into the plating cell through a threaded cell cover as shown in Figure 1. The nozzle assembly consisted of a Plexiglas nozzle, a Plexiglas nozzle chamber, a soluble anode and an anode connector. The Plexiglas nozzle had an exit diameter of 0.635 cm, and was mounted on the top of the nozzle chamber. The nozzle chamber was conical in shape with a base diameter of 5 cm, a top diameter of 2 cm, and a height of 4 cm. A spring-shaped copper or

nickel wire of 10 cm in length inserted to the nozzle chamber through a sealed tube connector was used as the soluble anode. The plating solution was forced through the nozzle, flowed upward through an air space in the form of an unsubmerged circular jet, and impinged on the brass cathode substrate. The nozzle height (or the distance between the nozzle exit and cathode surface) was adjusted by rotating the threaded Plexiglas cylinder of the cathode assembly up and down through the cell cover and by tightening the Plexiglas nut on the cell cover. A micrometer depth gage was used to measure the nozzle height prior to the plating operation.

The solution flow system consisted of a PVC solution tank, a pump, rotameters, polypropylene tubes, control valves, and the jet plating cell. The solution tank was 6.5 liters in volume, and the pump was a magnetic-drive centrifugal pump (Cole-Parmer K7083-10) having a polyethylene body and an epoxy coated impeller. Four rotameters (Gilmont F-1500) made of a tapered glass tube and a glass float were used to measure the rate of solution flow. The plating solution was pumped from the solution tank through the rotameters to the jet plating cell, and returned to the solution tank. A bypass PVC valve and a set of Nylon needle valves on the upstream of the rotameters were used to control the solution flow rate.

Copper Plating Bath

ACS certified reagent grade chemicals were used to prepare the acidic copper sulfate bath. Three bath concentrations were used:

i) 0.75 M copper sulfate and 0.75 M sulfuric acid;
ii) 0.1 M copper sulfate and 0.1 M sulfuric acid;
iii) 0.05 M copper sulfate and 0.5 M sulfuric acid.

Nickel Plating Bath

A Watt's nickel bath and a nickel sulfamate bath were used in the present study. Their chemical compositions were:

Watt's nickel bath: 1.25 M nickel sulfate, 0.19 M nickel chloride, and 0.61 M boric acid;
Nickel sulfamate bath: 1.8 M nickel sulfamate and 0.49 M boric acid.

Experimental Procedures

The plating operation was carried out by directing a jet of plating solution at an unmasked brass cathode substrate and by applying a constant electric current to the jet plating cell through a galvanostatic circuit. The electrodeposition of copper or nickel took place selectively on a localized area around the point of jet impingement on the brass substrate. After passing 60 coulombs, the current was switched off, and the cathode substrate was removed from the plating cell and rinsed with water. The local thickness of electrodeposit was then measured with a coulometric thickness gage (UPA Technology M100) as a function of the radial position from the point of jet impingement. The experiment was carried out for copper and nickel platings at a room temperature of 23°C. The effect of applied geometric average current density (based on the nozzle exit area), nozzle height, jet velocity, and bath concentrations on the metal thickness distribution was examined.

RESULTS AND DISCUSSION

For jet plating with a constant cathode current efficiency, a dimensional analysis reveals that the ratio of local thickness of a metal deposit, $\delta(r)$, to the deposit thickness at the stagnation point, δ_o (i.e., at the center of deposit with $r = 0$), is a function of the following dimensionless variables:

$$\frac{\delta(r)}{\delta_o} = f\left[\frac{r}{d}, \langle i_n^* \rangle, \frac{H}{d}, N, J\right] \quad (1)$$

with

$$\langle i_n^* \rangle = \frac{\langle i_n \rangle}{i_{lim,o}} \quad (2)$$

$$N = \frac{nFdi_{lim,o}}{\kappa RT} \quad (3)$$

$$J = \frac{nFdi_o}{\kappa RT} \quad (4)$$

where r is the radial position from the center of deposit; d is the nozzle diameter; H is the distance between the nozzle exit and cathode substrate; n and i_o are the number of electrons transferred and the exchange current density of the metal deposition reaction; $\langle i_n \rangle$ is applied average current density based on the area of nozzle exit; R is the universal gas constant; F is the Faraday constant; T and κ are the absolute temperature and conductivity of the electrolyte. The quantity, $i_{lim,o}$, in Equations (2) and (3) is the limiting current density at the stagnation point; its value may be calculated from the following mass transfer correlation [4]:

$$i_{lim,o} = 0.9 \frac{nFC_\infty D}{d} Sc^{1/3} Re^{1/2} \left(\frac{H}{d}\right)^{-0.09} \quad (5)$$

where C_∞ and D are the bulk concentration and diffusivity of metal ion; Sc is the Schmidt number; and Re is the nozzle Reynolds number based on the nozzle diameter and solution velocity at the nozzle exit.

Copper Plating

The cathode current efficiency for copper plating with three acidic copper sulfate baths was constant at 99% - 100% in the cathode current density range of 0.01 - 0.2 A/cm^2; this condition made the metal thickness distribution of copper deposit equal to the current distribution at the cathode substrate. Copper plating was used to examine the effect of various process parameters, including the dimensionless applied current density, $\langle i_n^* \rangle$, dimensionless nozzle height, H/d, dimensionless limiting current density, N, and dimensionless exchange current density, J, on the metal distribution in jet plating.

Effect of Applied Current Density

The effect of dimensionless geometric average current density on the thickness distribution of copper deposit was examined for the range of $\langle i_n^* \rangle$ from 0.25 to 4.0. Dendritic free deposits were obtained from the 0.1 M copper sulfate + 0.1 M sulfuric acid and the 0.05 M copper sulfate + 0.5 M sulfuric acid baths at $\langle i_n^* \rangle$ less than 4, and from the 0.75 M copper sulfate + 0.75 M sulfuric acid bath at $\langle i_n^* \rangle$ less than 2.5. The copper deposit became more localized with increasing applied geometric average current density. Figure 2 shows the typical metal distribution data in the form of δ/δ_o versus r/d for copper deposits obtained from the 0.75 M copper sulfate + 0.75 M sulfuric acid bath with three dimensionless applied geometric average current densities at a common H/d = 1 and N = 205. The metal distribution curve with a $\langle i_n^* \rangle$ = 2 was more localized than those at $\langle i_n^* \rangle$ = 0.5 and 0.25.

Effect of Nozzle Height

The effect of dimensionless nozzle height on the metal thickness distribution of copper deposit was examined for the range of H/d from 0.25 to 4. For a given plating bath at fixed dimensionless applied and limiting current densities, the copper deposit tended to become more localized with decreasing values of H/d. The metal distribution data obtained from the 0.75 M copper sulfate + 0.75 M sulfuric acid bath are given in Figure 3 for three H/d values at a common setting of $\langle i_n^* \rangle$ = 1 and N = 205. The copper thickness distribution curve with a H/d = 0.25 was more localized than those with H/d = 1 and 4.

Effect of Mass Transfer

The dimensionless limiting current density, N, may be interpreted as the ratio of ohmic resistance to mass transfer resistance in electroplating. A value of N = 0 corresponds to the circumstances where the electrodeposition reaction is limited by mass transfer of the metal ion to the cathode surface. At large values of N, ohmic resistance would become predominant. In jet plating, the value of N for a given bath may be changed by varying the solution velocities and nozzle Reynolds numbers of the impinging jet. Figure 4 shows the metal distribution of copper deposits obtained with the 0.75 M copper sulfate + 0.75 M sulfuric acid bath for three N values at $\langle i_n^* \rangle = 1$ and H/d = 1. The metal distribution curve for N = 0 in the figure was calculated from the local mass transfer correlations of an unsubmerged circular impinging jet [4]:

$$\frac{\delta(r)}{\delta_o} = 1 \qquad (for\ \frac{r}{d} < 0.8) \qquad (6)$$

$$\frac{\delta(r)}{\delta_o} = 0.64\left(\frac{H}{d}\right)^{-0.09} \frac{1}{\sqrt{r/d}}$$

$$(for\ 0.8 < \frac{r}{d} < 4) \qquad (7)$$

The results indicate that more localized copper deposits were obtained at higher values of N.

Effect of Dimensionless Exchange Current Density

The dimensionless exchange current density, J, represents the ratio of ohmic resistance to kinetic resistance of the electrodeposition reaction in electroplating; its value may be changed by varying the bulk concentrations of metal ion and supporting electrolyte. The primary current distribution prevails at large values of J, and the current distribution tends to be more uniform when J is small. The values of J for the three acidic copper sulfate baths used in the present study were: 1.57 for the 0.75 M copper sulfate + 0.75 M sulfuric acid bath; 1.31 for the 0.1 M copper sulfate + 0.1 M sulfuric acid bath; and 0.11 for the 0.05 M copper sulfate + 0.5 M sulfuric acid bath. Figure 5 shows a comparison of copper thickness distribution curves for the three copper plating baths at a common nozzle Reynolds number of 5000, a H/d of 1.0 and an $\langle i_n^* \rangle$ of 1.0. The results indicate that the copper thickness distribution obtained at J = 0.11 with the 0.05 M copper sulfate + 0.5 M sulfuric acid bath was less localized than those obtained from the other two baths at J = 1.31 and 1.57.

Nickel Plating

The cathode current efficiency for nickel plating from Watt's nickel and nickel sulfamate baths are given in Figure 6 for the cathode current density range of 0.005 - 0.1 A/cm^2. The nickel plating baths did not exhibit a constant current efficiency behavior. The current efficiency was 75% at a low cathode current density of 0.005 A/cm^2, increased with increasing current density, reached a maximum of 95 - 99% at 0.05 A/cm^2, and then decreased with a further increase in the cathode current density. This non-constant current efficiency behavior exerted an important influence on the metal distribution in nickel plating.

The nickel thickness distributions obtained from the Watt's nickel and nickel sulfamate baths are shown in Figure 7 for two dimensionless applied current densities of $\langle i_n^* \rangle$ = 0.04 and 0.2. The data were obtained in the descending region of the current efficiency curves shown in Figure 6. The difference in metal distribution between the Watt's nickel and nickel sulfamate baths was insignificant; however, for the both baths, a more localized nickel deposit was obtained at the low applied current density of $\langle i_n^* \rangle$ = 0.04 than that at $\langle i_n^* \rangle$ = 0.2. The result was opposite of that of copper plating, where the metal distribution was less localized at lower applied current densities. This was clearly due to the non-constant current efficiency behavior of nickel plating baths. In jet plating, the local cathode current density was the

highest at the stagnation point and decreased with increasing radial position from the center of deposit. Since the data shown in Figure 7 were obtained on the descending portion of the current efficiency vs. current density curves, the thickness of nickel deposit at the center was less than that expected theoretically because of a low local cathode current efficiency; whereas in the outskirts of nickel deposit where the local current density was low, the nickel deposit was thicker than that theoretically expected because of a higher current efficiency. Thus, a more localized nickel deposit was obtained at a lower applied current density in jet plating.

CONCLUSIONS

An experimental study has been made of jet plating by directing an unsubmerged circular jet of plating solution at a large unmasked cathode substrate. Copper plating from an acidic copper sulfate bath and nickel plating using a Watt's nickel and a nickel sulfamate bath were studied. A dimensional analysis was used to identify the process parameters influencing the metal thickness distributions on the cathode surface. The results indicate that for jet plating with a constant cathode current efficiency, the ratio of local deposit thickness to the thickness at the deposit center is a function of a dimensionless radius, r/d, a dimensionless applied geometric average current density, $\langle i_n^* \rangle$, a dimensionless nozzle height, H/d, a dimensionless limiting current density, N, and a dimensionless exchange current density, J. For copper plating where the cathode current efficiency was a constant of 99 - 100%, it was found that the copper thickness distribution became more localized with: i) increasing applied dimensionless geometric average current density, $\langle i_n^* \rangle$; ii) decreasing dimensionless nozzle height, H/d; iii) increasing dimensionless limiting current density, N; and iv) increasing dimensionless exchange current density, J. For nickel plating, where the local cathode current efficiency decreased with increasing local current density, the nickel deposit was more localized with decreasing applied geometric average current densities. There was no significant difference in nickel thickness distributions between the Watt's nickel and nickel sulfamate baths.

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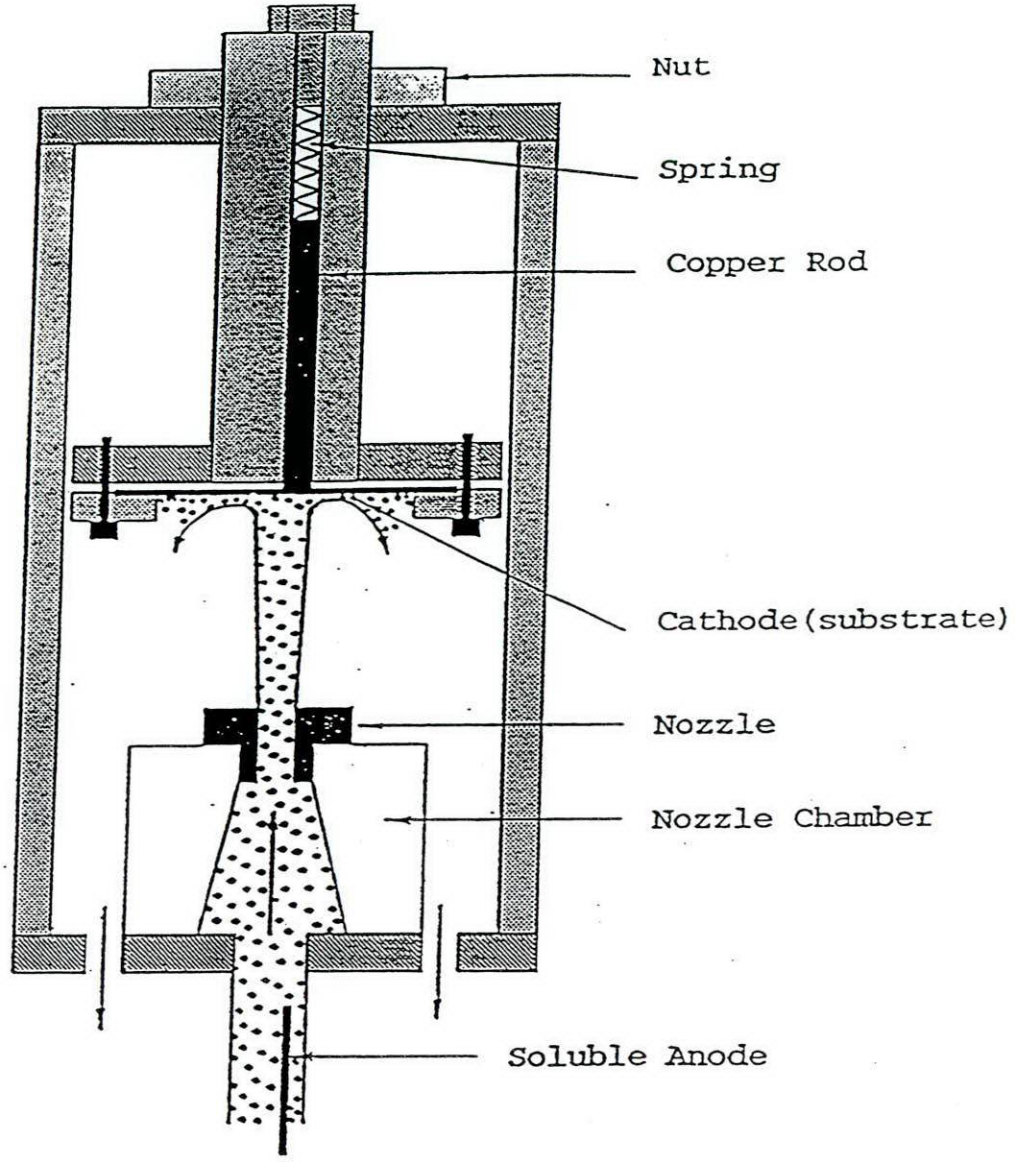

Figure 1: Schematics of a jet plating cell.

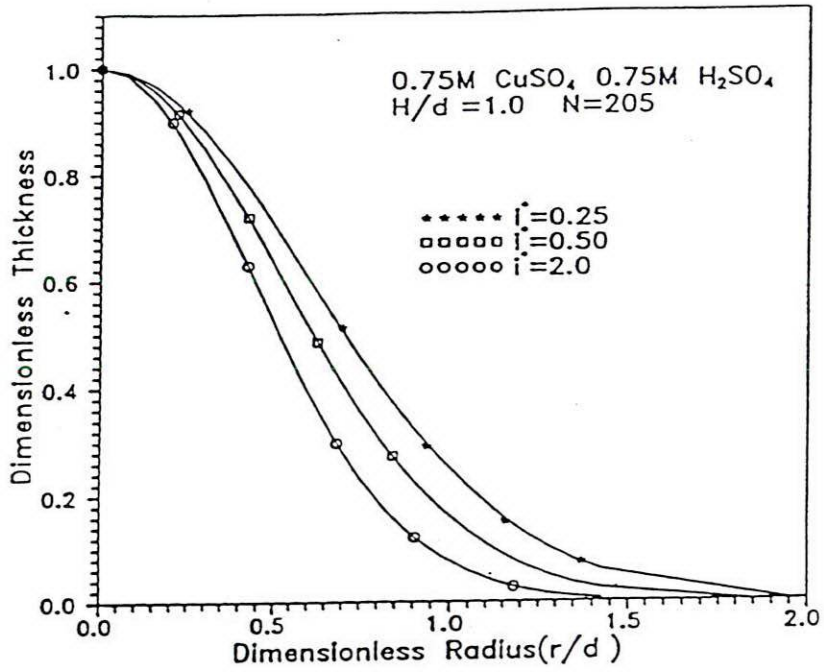

Figure 2: Dimensionless metal thickness, δ/δ_o, vs. r/d for copper plating from the 0.75 M copper sulfate + 0.75 M sulfuric acid at three dimensionless applied geometric average current densities.

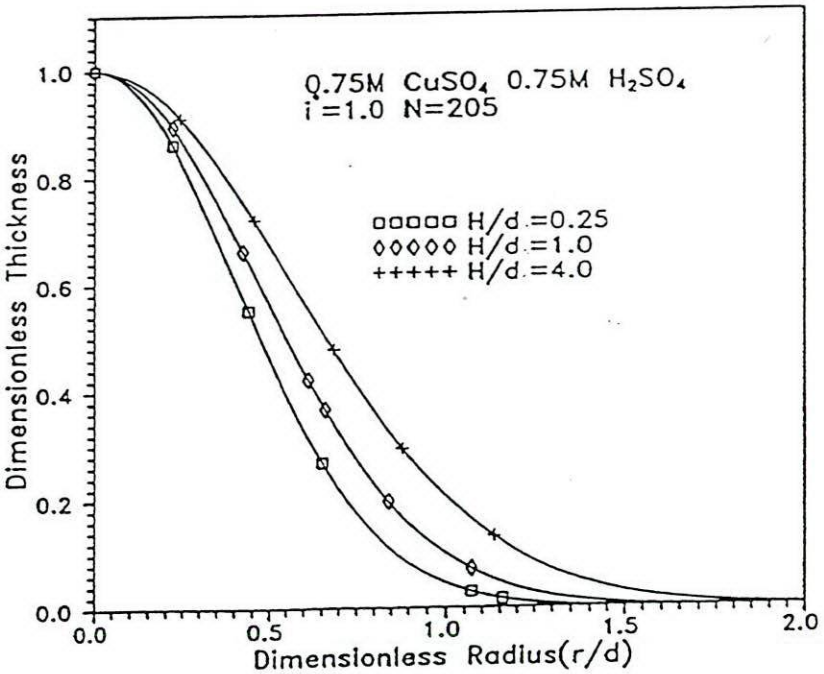

Figure 3: Effect of dimensionless nozzle height on the dimensionless metal distribution of copper deposit obtained from the 0.75 M copper sulfate + 0.75 M sulfuric acid bath.

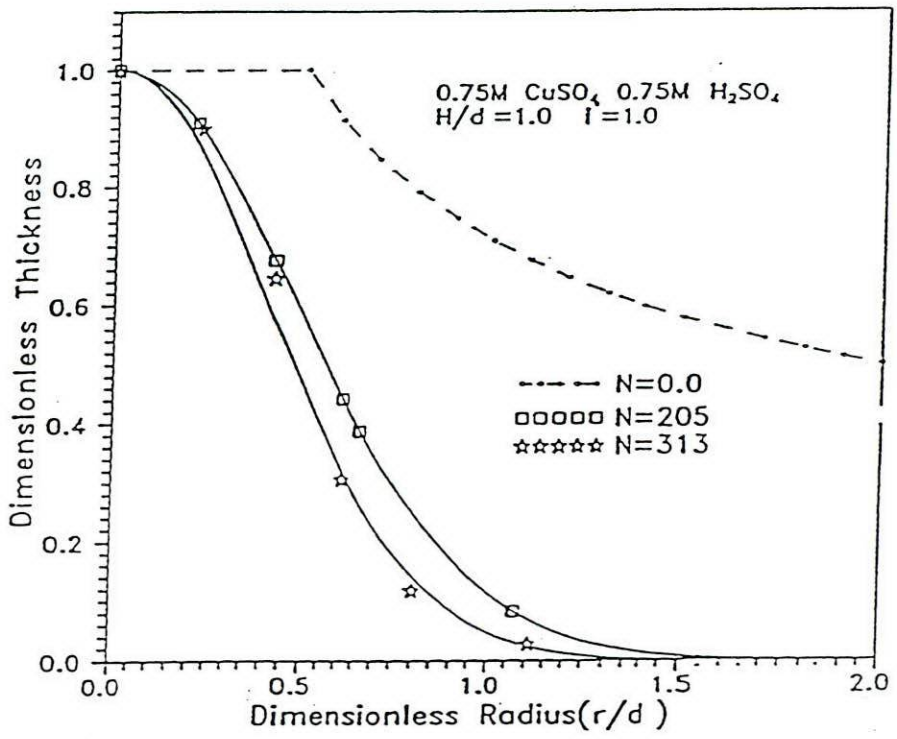

Figure 4: Effect of N on the dimensionless metal thickness distribution of copper deposit obtained from the 0.75 M copper sulfate + 0.75 M sulfuric acid bath.

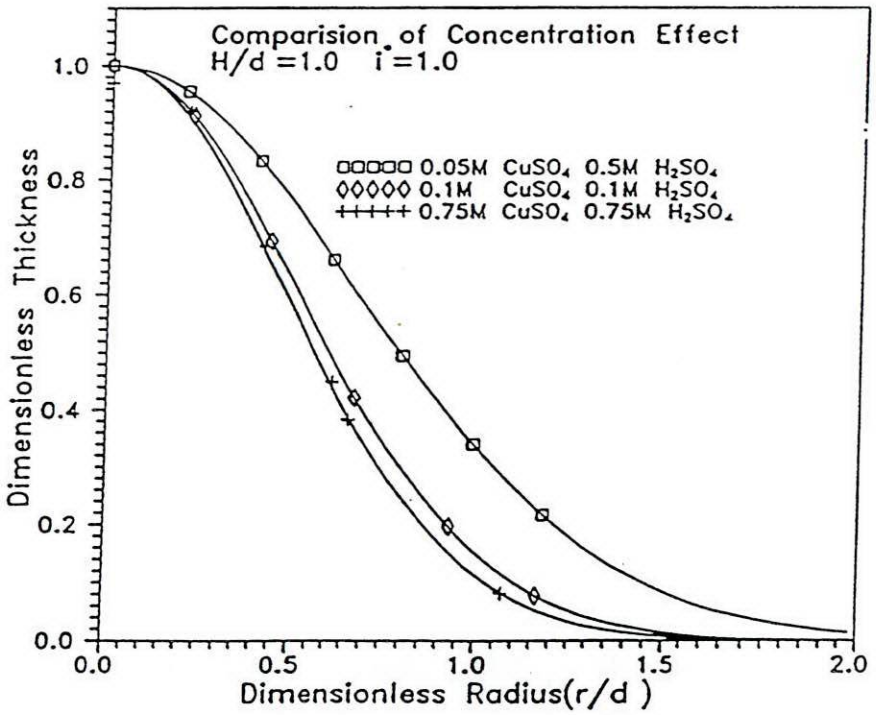

Figure 5: Dimensionless metal distributions of copper deposits obtained from three different concentrations of the acidic copper sulfate bath.

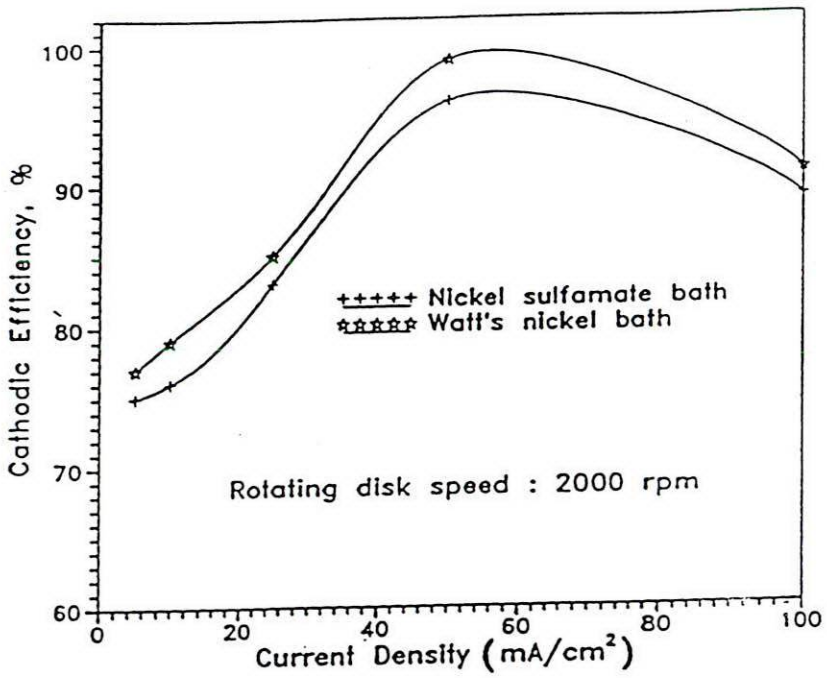

Figure 6: Cathode current efficiency vs. cathode current density for nickel deposition on a rotating disk electrode.

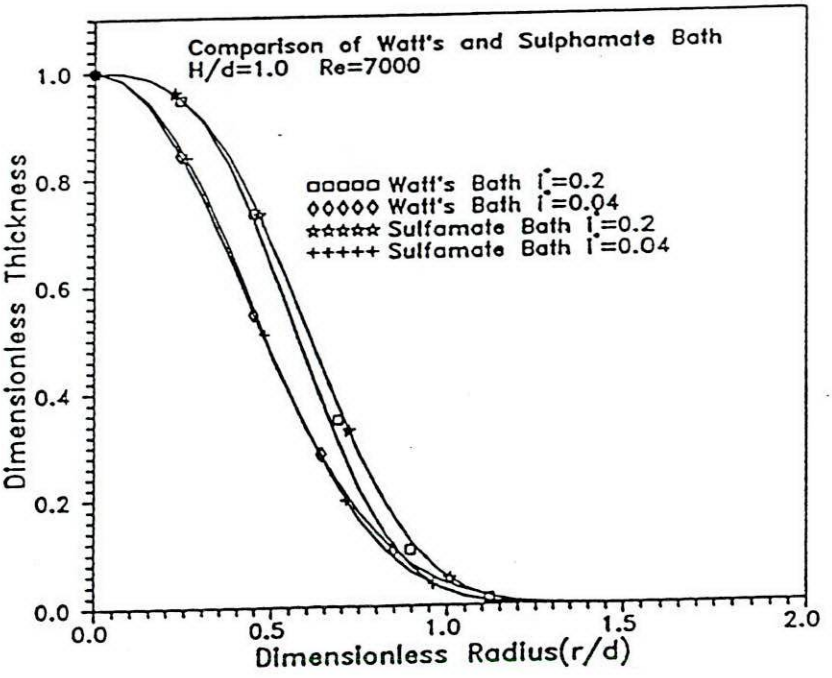

Figure 7: Dimensionless metal distributions of nickel deposits obtained from the Watt's nickel and nickel sulfamate baths at two different applied geometric average current densities.

Optimization of Throwing Power in Pulse Reversal Plating from a Silver Cyanide Solution

PETER **L**EISNER, **P**ETER **T.** **T**ANG & **G**REGERS **B**ECH-**N**IELSEN

Centre of Advanced Electroplating (CAG), The Technical University of Denmark, building 425, 2800 Lyngby, Denmark

Introduction

The aim of the investigation presented here has been to improve the throwing power in silver plating by combining periods of electrodeposition and periods of electrodissolution in a low frequency (< 2 Hz) pulse reversal plating (PR) process. A similar process has recently proved advantageous in copper plating [1,2], where it is possible to produce coatings with a "reverse" material distribution, i.e. the deposition is thickest in the low current density area.

Experimental Procedure

Silver was deposited from a cyanide solution without additives (AgCN 35 g/l; KCN 60 g/l; K_2CO_3 20 g/l). The bath was operated at room temperature under magnetic stirring. A computer controlled pulse rectifier (CAPP) was used to supply pulsed current [3].

Previous to the plating the mild steel substrate was degreased, pickled and plated with a silver strike in a pre-silver bath (AgCN 1.5 g/l; KCN 100 g/l; K_2CO_3 20 g/l) for 30 s at 0.4 A/dm^2. The function of the pre-silver plating was to prevent electroless displacement of iron in the silver bath.

In the first part of the investigation silver was deposited on both sides of simple panels (6 x 4 cm^2). The silver anodes having the same dimensions were placed facing the panel at a distance of 6.5 cm. Following the plating the thickness was measured at eleven points along a line running from the middle of an edge to the center of the panel, on both sides. The throwing power is expressed as the ratio between the mean of the lowest values on each side of the panel and the average thickness calculated from the weight of the coating.

In the second part of the investigation silver was deposited on Assaf test panels [4], which are very useful for investigating the throwing power on complicated geometries. The test panel consists of a quadratic (4 x 4 cm^2) mild steel cathode mounted at a distance of 5 mm from a plastic board. The panel was placed facing the anode at a distance of 13.5 cm. Following the plating the thickness was measured at the center of both sides of the panel. The throwing power is expressed as the back to front thickness ratio.

The Taguchi statistical method was used for experimental planning and process optimization. The application of Taguchi statistics for optimization of pulse plating processes has recently been described [5] and will not be discussed further here. The influence on the throwing power of the following four parameter was investigated: Cathodic (i_c) and anodic (i_a) current density, anodic pulse duration (T_a) and the ratio of anodic to cathodic charge (Q_a/Q_c). The cathodic pulse duration (T_c) is dependent on these four parameters. Since T_c is rather high, stationary conditions are assumed during the cathodic period and the variation of T_c is presumed to have no significant influence.

Theory

In electroplating from a silver bath, where the current efficiency is 100 %, the material distribution is proportional to the current distribution. Thus, the throwing power can be expressed by the Wagner number (Wa), which describes the current distribution during a plating proces:

$$Wa = \frac{\kappa}{L}\left(\frac{d\eta}{di}\right) \qquad (1)$$

where κ is the electrolyte conductivity (S/cm), L is the characteristic length of the process (cm), and $d\eta/di$ is the slope of the polarization curve. For small values of

Wa (Wa « 1) the current distribution is dominated by the Ohmic drop in the electrolyte and therefore uneven. Conversely, the current distribution is dominated by the activation resistance at high values of Wa (Wa » 1) and therefore more even.

A more uneven current distribution in the anodic period compared with the distribution in the cathodic period is needed in order to obtain a levelling effect during pulse reversal plating. Hence, $Wa_a < Wa_c$, which can be formulated as;

$$\left(\frac{d\eta_a}{di_a}\right) < \left(\frac{d\eta_c}{di_c}\right) \qquad (2)$$

In the Tafel-region this can be written as;

$$\frac{b_a}{i_a} < \frac{b_c}{i_c} \qquad (3)$$

where b is the Tafel-slope and subscripts a and c refer to anodic and cathodic conditons, respectively.

According to the work of Vielstich and Gerischer [6] both b_a and b_c have values close to 118 mV at room temperature. Inserting these values in eq. (3) one obtaines;

$$i_a > i_c \qquad (4)$$

Consequently, improved throwing power is predicted when eq. (4) is fulfilled and both the cathodic and the anodic reactions proceed in the Tafel-region.

If,

$$i_a = i_c \qquad (4a)$$

then the same material distribution is expected in the anodic and the cathodic periods.

Of course, the ratio between the amount of silver dissolved in the anodic period and the amount of silver deposited in the cathodic period is also an important parameter in optimization of the throwing power. This ratio can be expressed as

$$\frac{Q_a}{Q_c} = \frac{i_a T_a}{i_c T_c} \qquad (5)$$

Throwing Power on Simple Geometries

Experimental plan and results are shown in table 1. Results of direct current experiments are illustrated in figure 1. The calculated effects of i_a, i_c, Q_a/Q_c and T_a on the throwing power are presented in figures 2-5. It is seen that the most important parameter for improving the throwing power is i_c. Like in direct current plating the throwing power is improved with decreasing cathodic current density. The throwing power is also improved by increasing Q_a/Q_c. The minor effects of i_a and T_a could be due to non-steady-state conditions in the anodic period.

From the results presented in figures 2-5 the best throwing power was expected for i_a = 1.6 A/dm^2, i_c = 0.4 A/dm^2, Q_a/Q_c = 40 % and T_a = 1 s. Carring out this experiment a throwing power of 0.98 was obtained, representing a nearly perfect material distribution.

Throwing Power on Complex Geometries

The validity of eq. (4a) was tested by two experiments using Assaf panels, a direct current experiment with i_{DC} = 0.75 A/dm^2 and a pulse reversal current experiment with $i_c = i_a$ = 0.75 A/dm^2. If eq. (4a) is valid and the assumptions are fulfilled the same material distribution is expected in the two experiments. The data in table 2 show a fair accordance between theory and results.

The experimental plan and results from plating on Assaf panels are shown in table 3. In these experiments i_c was fixed at 0.8 A/dm^2, since attention was paid to the three parameters that have shown minor effects on the material distribution. The calculated effects of i_a, Q_a/Q_c and T_a are presented in figures 6-8. Q_a/Q_c has the largest influence on the throwing power among these parameters. The throwing power is increased with increasing Q_a/Q_c. Again, i_a and T_a seem to have only minor influence on the throwing power, but with the same tendency as in the previous experiments.

The best back to front thickness ratio was expected for i_a = 2 A/dm^2, Q_a/Q_c = 60 % and T_a = 1.2 s. The expectation was confirmed by the experiment, which gives a back to front thickness ratio of 0.95.

Passivation

Under the pulse reversal plating conditions described above no passivation of the silver surface was observed, but at lower anodic current densities (e.g. 0.4 A/dm^2) an adherent layer of white silver cyanide precipitates on the surface. At even lower anodic current densities the situation is changed again - no precipitate is formed.

Vielstich and Gerischer [6] have suggested two mechanisms for oxidation of silver in cyanide containing solutions depending on the concentration of cyanide.

A) For [CN$^-$] > 0.2 M:

$$Ag + 2\,CN^- \rightarrow [Ag(CN)_2]^- + e^-$$
$$[Ag(CN)_2]^- + CN^- \leftrightarrow [Ag(CN)_3]^{2-}$$

B) For [CN$^-$] < 0.1 M:

$$Ag + CN^- \rightarrow [AgCN] + e^-$$
$$[AgCN] + 2\,CN^- \leftrightarrow [Ag(CN)_3]^{2-}$$

In the plating solution used in this investigation the concentration of free cyanide was 0.4 M (assuming that all silver is present as $[Ag(CN)_3]^{2-}$).

At low anodic current densities no depletion of cyanide occures at the surface, and silver is oxidised according to mechanism A. At medium anodic current densities cyanide is partly depleted at the surface and silver is then oxidised according to mechanism B with the formation of solid silver cyanide on the surface. At high anodic current densities a third mechanism can be considered, assuming total depletion of cyanide at the surface.

C) For [CN$^-$] ≈ 0 M at the surface:

$$Ag \rightarrow Ag^+ + e^-$$
$$Ag^+ + 3\,CN^- \leftrightarrow [Ag(CN)_3]^{2-}$$

The model suggested above for silver oxidation during the anodic period as a function of the current density is illustrated in figure 9.

Conclusions

It has been shown that the throwing power can be controlled on different geometries in a silver cyanide bath by combining periods of electrodeposition with periods of electrodissolution in a low frequency pulse reversal current process.

The most important parameter for increasing the relative thickness in the low current density areas is i_c, but Q_a/Q_c is important too. i_a and T_a seem to have only minor influence on the throwing power, but they are probably having an interacting influence, too, due to non-steady-state conditions in the anodic period.

A model for silver oxidation during the anodic period as a function of the current density has been suggested. The conditions resulting in silver cyanide precipitation during the anodic periods should be studied in more details to avoid passivation during the plating proces. In addition to current density and cyanide concentration it is evident that the hydrodynamic conditions are of importance.

Acknowledgement

The authors are gratefull to Mr. A. Marquorodt and Mr. K. Hofschneider, University of Hannover, Germany for their contributions.

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Experiment	i_a A/dm^2	i_c A/dm^2	Q_a/Q_c %	T_a ms	T_c ms	Cycles	Throwing power
PR1	1.2	0.4	10	100	3000	556	0.85
PR2	1.2	0.8	20	500	3750	250	0.81
PR3	1.2	1.2	40	1000	2500	333	0.84
PR4	1.6	0.4	20	1000	20000	94	0.95
PR5	1.6	0.8	40	100	500	2500	0.87
PR6	1.6	1.2	10	500	6667	83	0.82
PR7	2.0	0.4	40	500	6250	400	0.93
PR8	2.0	0.8	10	1000	25000	33	0.82
PR9	2.0	1.2	20	100	833	750	0.79

Table 1: Experimental plan and results from plating on samples with simple geometry.

Current type	$i_{DC} = i_c$ A/dm^2	i_a A/dm^2	Back to front thickness ratio
DC	0.75	-	0.62
PR	0.75	0.75	0.56

Table 2: Experiments supporting the validity of eq. (4).
$T_c = 4$ s and $T_a = 1$ s for the PR experiment.

Experiment	i_a A/dm^2	i_c A/dm^2	Q_a/Q_c %	T_a ms	T_c ms	Cycles	Throwing power
DC11	-	0.8	0	-	-	-	0.49
PR11	1.6	0.8	40	400	2000	893	0.64
PR12	1.6	0.8	50	800	3200	670	072
PR13	1.6	0.8	60	1200	4000	670	0.84
PR14	2.0	0.8	50	1200	5829	368	083
PR15	2.0	0.8	60	400	1619	1654	0.82
PR16	2.0	0.8	40	800	4857	368	0.65
PR17	2.4	0.8	60	800	3810	703	077
PR18	2.4	0.8	40	1200	8572	208	0.70
PR19	2.4	0.8	50	400	2286	938	0.67

Table 3: Experimental plan and results from plating on Assaf panels.

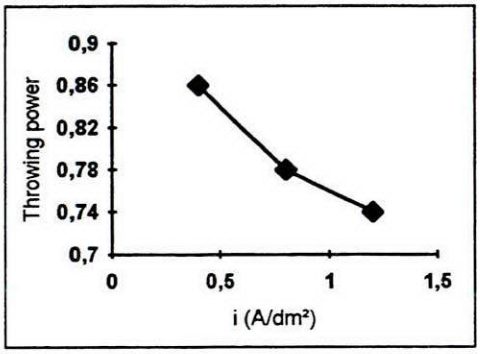

Figure 1: The influence of current density on the throwing power under direct current conditions.

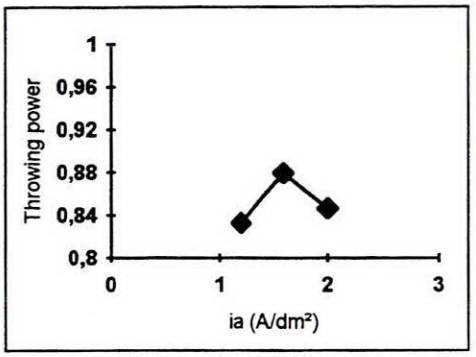

Figure 2: The calculated effect of i_a on the throwing power.

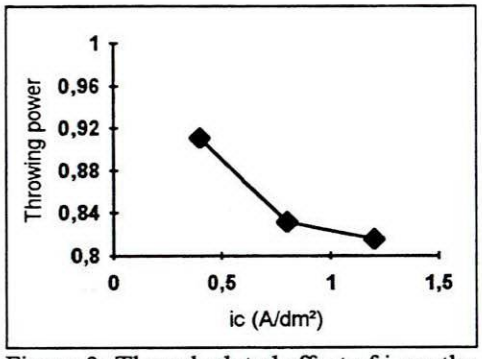

Figure 3: The calculated effect of i_c on the throwing power.

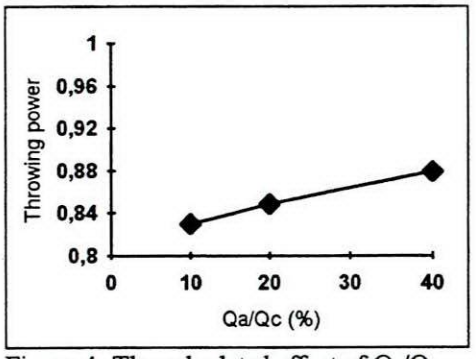

Figure 4: The calculated effect of Q_a/Q_c on the throwing power.

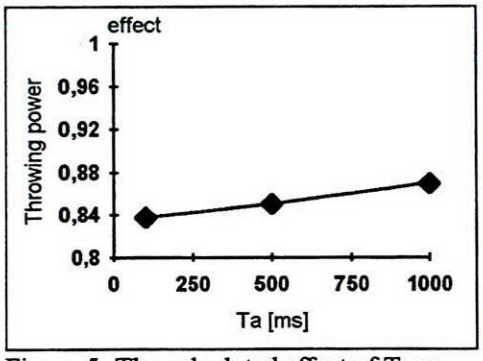

Figure 5: The calculated effect of T_a on the throwing power.

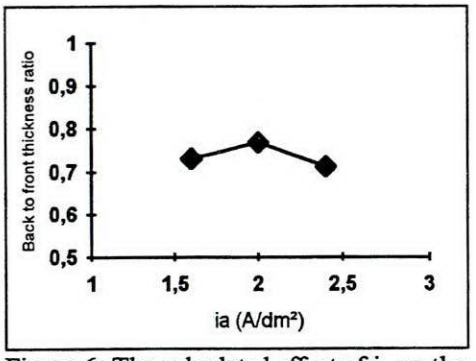

Figure 6: The calculated effect of i_a on the back to front thickness ratio.

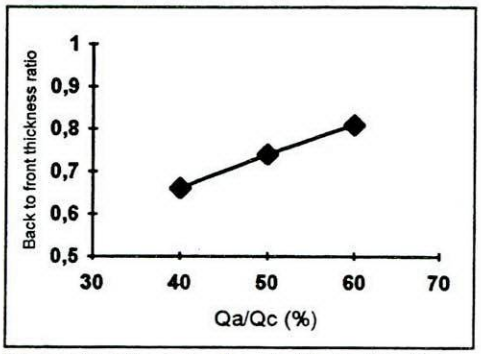

Figure 7: The calculated effect of Q_a/Q_c on the back to front thickness ratio.

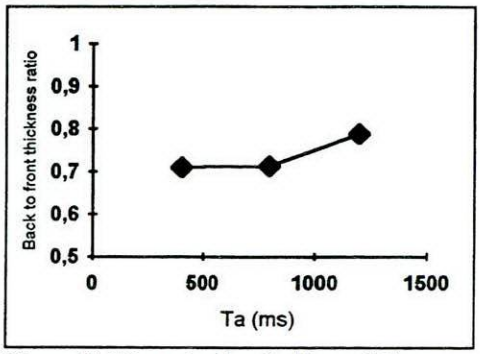

Figure 8: The calculated effect of Ta on the bact to front thickness ratio.

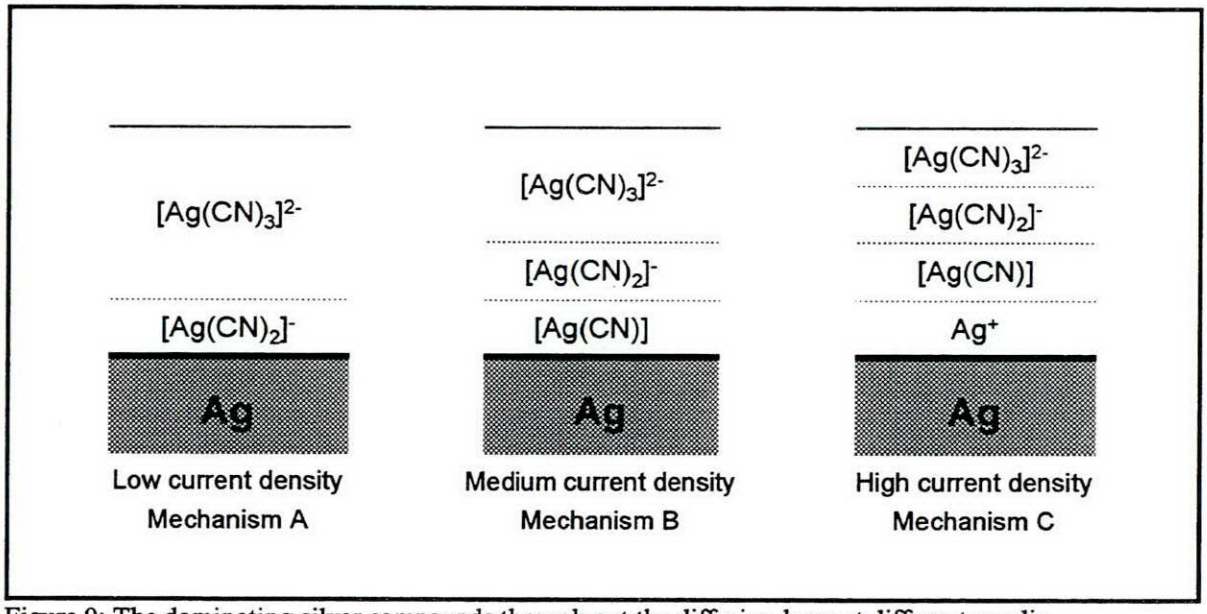

Figure 9: The dominating silver compounds through out the diffusion layer at different anodic current densities.

THE INVESTIGATIONS AND CHARACTERISATIONS OF COBALT MULTILAYER METAL NANOSTRUCTURES

D.M.A. NabiRahni*, P.T. Tang, P. Leisner
Technical University of Denmark, Centre of Advanced Electroplating, Lyngby, Denmark

* A Fulbright Senior Scholar on Leave from: Pace University, Department of Chemistry, Pleasantville, NY 10570 U.S.A., to whom correspondence should be addressed.

Multilayer films of Co, and Co-Cu, in the thickness range of several manometers up to 1 μm, have been electroplated using a single, and a recently developed automated multibath systems. Electroplating bath constituent, pH, temperature, agitation, etc. as well as galvanostatic modes, i.e. direct current versus pulse and/or pulse reverse, were investigated, optimised, and will henceforth be reported. Nanostructures of up to over a thousand layers, with varying thicknesses if desired, were produced in an automated system developed recently in our laboratory. The structures were characterized for composition, texture, magnetic and mechanical properties with optical microscopy, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-ray fluorescence and diffraction spectroscopies. For cobalt deposition, a combination of direct and pulsating currents under mild air agitation resulted in the best specimens. Compositionally modulated alloys (CMA) of cobalt-copper were obtained employing a combination of alternating current amplitudes and agitation modes. Nanostructures such as those reported herein will have promising applications in a wide area of high tech manufacturing enterprises due to their unique electronic, mechanic, and magnetic properties.

Introduction

Although the electrodeposition of multilayered metals was introduced in the 20's by Blum [1] employing a manual dual bath system, their optimised manufacturing processes and full potential applications are yet to be realised. This has been in part due to the lack of consistency among the samples for mass device fabrication, and limitations in "nanomizing" the thickness of the deposits. However, the enhancement of tensile strength has been observed for laminated structures in the sub-micrometer dimension, when compared to the bulk metal of comparable thickness. It was shown[2] that a "supermodulus effect" is observed for such structures, when the thickness of Au-Ni and Cu-Pd laminated structures fall below 10-nm. For instance, a four-fold anisotropic effect of an electrodeposited Co/Cu CMA, in the several nanometer thickness ranges, has been observed[3]. The origin of such changes in magnetic properties is not however established yet[4], mainly due to poor quality of the specimen produced by currently employed processes such as Chemical/Physical Vapour Depositions.

CMAs and multilaminated ultra-thin metal structures, as produced in a single electroplating bath on a rotating disk substrate, have provided high quality alternative deposits with sharp boundaries[5-8]. A rotating disk electrode with a well defined and controllable hydrodynamic mass transport and potential, as it is commonly used, is not, however, an ideal tool in a manufacturing scenario, even though excellent work reported based on such a system was necessary to fully characterise and thus control the bath conditions[9]. We herein describe two complementary methods of generating such structures in a semi-industrial approach: first, employing a single bath containing

optimised constituents for the co-deposition of Cobalt and Copper, by modulation of DC vs. pulse currents and agitation; second, by the use of an automated multibath system recently developed in our laboratory, where multilaminated thin structures of Cobalt-Copper, and Cobalt-Copper-Nickel, in varying thicknesses of nano- to micrometer ranges and of up to several thousand layers, are produced with great precision..

Experimental Section

I. Materials

1. Chemicals: Chemicals used were either reagent grade and/or the manufacturing grade of high purity.
2. Apparatus: The following instruments were used in our investigations: Perkin-Elmer Atomic Absorption spectrometer, Hitachi Scanning Electron Microscope, Siemens D 5000 X-ray diffractometer, and SQUID from Cryogenic Consultants Ltd. Series BP2.

II. Sample preparation

1. Single bath: The bath was a modification of an earlier reported system[8]. The concentration of the more noble metal, copper, was maintained in the order of 0.65 %(w/w) to 0.30 % of the less noble metal, cobalt. The bath was composed of reagent grade materials (g/litre) as follows: cobalt sulphate heptahydrate (330), cobalt chloride hexahydrate (40), Boric acid (30), and the equivalent of 0.25 to 0.5 g copper as desired, from a copper sulphate, chloride, or sulphamate salt. The bulk pH was adjusted periodically to 4.50, with sodium hydroxide or hydrogen chloride. The cobalt bath current efficiency was found to be ~90 %. The bath was run at 45 °C under mild aeration, unless otherwise noted. Employing a Computer-Aided Pulse Plating System (CAPP) developed in our laboratory, several galvanostatic programs were executed to supply the total current to an activated steel St. 37 panel of 300 cm^2. The most commonly employed applied current programs are depicted in Figure 1: ramp of 0.00 to 4.0 A in 60 seconds to deposit primarily cobalt as an underlayer on an activated steel substrate, followed by a DC current of 0.320 s of 4.0 A, followed by 10.0 s of pulses 0.040 A amplitude for copper deposition (Fig 1A). The other three programs depicted follow the same analogy. A modified version of the above program resulted in micrometer thickness CMAs and/or polylaminated metal structures; in such cases, the agitation was employed during the electrodeposition of copper so as to replenish its concentration in the diffusion layer, whilst the bath remained stagnant during the cobalt electrodeposition.

2. Dual bath: The cobalt bath in this deposition mode was the same as above, except that the copper salt was absent. The separate copper bath was composed of 20 g/l Cu ($CuSO_4$), 200 g/l H_2SO_4, and commercial brightening agents, typically of less than 1 g/l concentrations. The substrate was activated in a citric acid bath, 20g/L, followed by rinsing in a double distilled, deionised water (18 Ω M-cm), before it was inserted into any of the above two baths.

Results and Discussions

Figure 2 illustrates the result of a series of Hull cell experiments. The metal distributions were determined with X-ray Fluorescence spectroscopy, and confirmed with in-situ atomic absorption spectroscopy. One notes that percent composition of copper was decreased as a function of increasing current density, whilst the percent cobalt was increased. It is based on such experiments that the current densities to preferentially deposit copper and/or cobalt were pre-selected. Figure 3 illustrates the feature of a cobalt-copper laminated nanostructures obtained with Scanning Electron Microscopy. It is a sample produced in our automated dual bath system. The lighter areas are ~100-nm cobalt layer, followed by three consecutive sub-layers of ~30-nm

cobalt, all interspaced with 100-nm copper layers that have been etched away for SEM preparations. It is admitted that we are still working with various levelling and brightening agents to smooth out the layers. Figure 4 illustrates the x-ray diffraction spectra for laminated 30-100-nanometer structures of cobalt interspaced with 100-nm copper, for a total of 80 sub-layers of each metal present. The substrate was pre-zincated aluminium plate. Figure 4 illustrates a series of x-ray diffraction patterns obtained from direct exposure of the deposits. It is interesting to note that below 50-nm thickness, even though cobalt is still present, it nevertheless takes the crystal structure of copper which is present in higher thickness of 100-nm.

Magnetic characterisation of the specimen based on SQUID techniques to observe the magnetisation as a function of varying applied magnetic field, and temperature are being currently investigated, and will therefore be reported during the presentation; however, preliminary data indicates a change from "in-phase", i.e. negative anisotropy, to an "out-of-Phase", i.e. positive anisotropy when the thickness of cobalt layer is decreased to below ~30-nm. We are currently engaged in further optimising the bath systems and processes in order to generate thinner, more levelled laminated structures. A more thorough characterisation of such specimens is also our other main focus, with emphases on magnetic and electrical properties.

Acknowledgement

Some technical assistance for the operation of X-ray diffractometer, provided by Dr. John Evans of the Univ. Oxford, UK, is appreciated.

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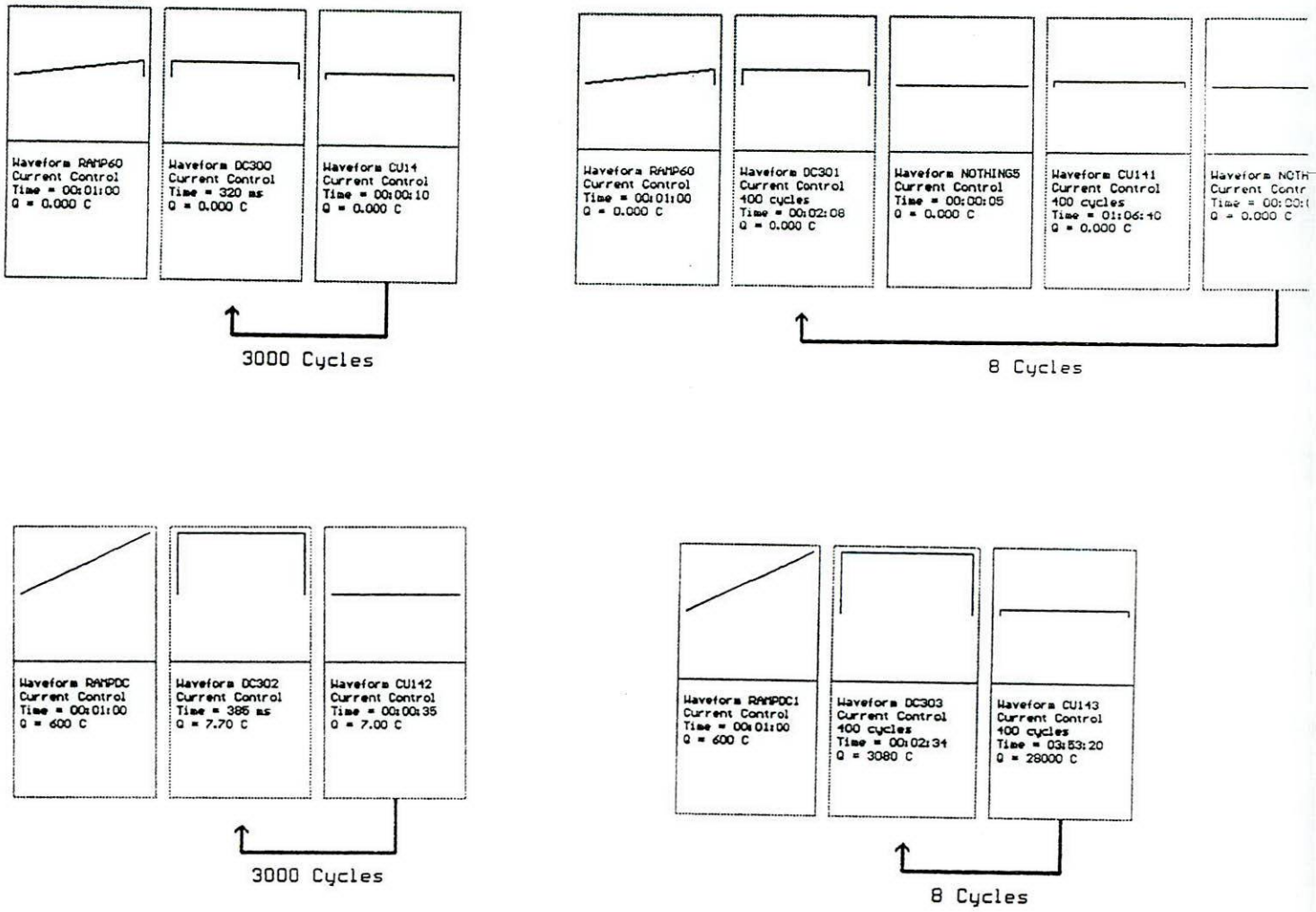

Figure 1: Typical applied current programs based on computer assisted pulse plating software.

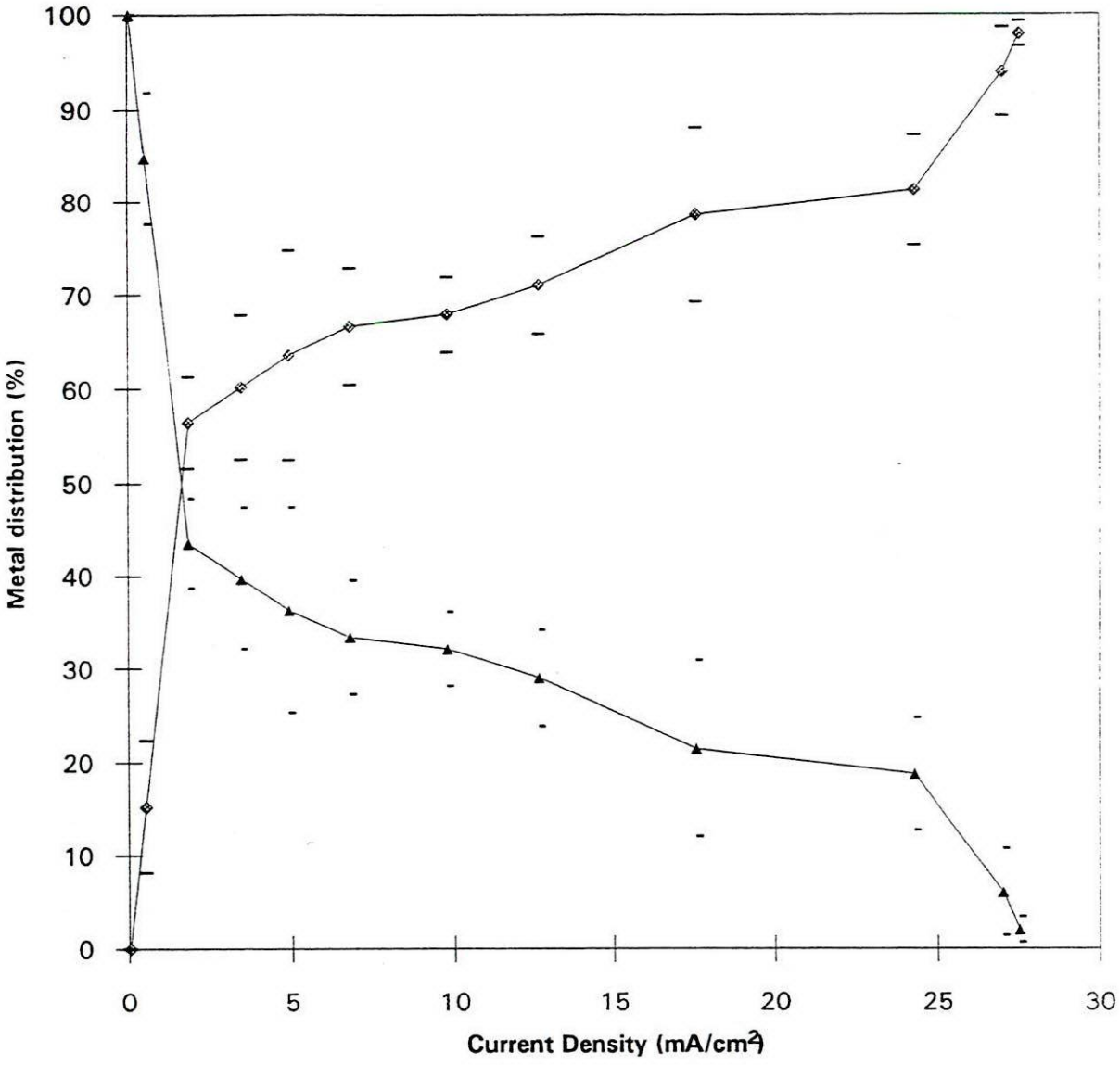

Figure 2: Cobalt-copper distribution as a function of current density (▲ copper; ◆ cobalt), each an average of five measurements, where horizontal bars indicate the standard derivations.

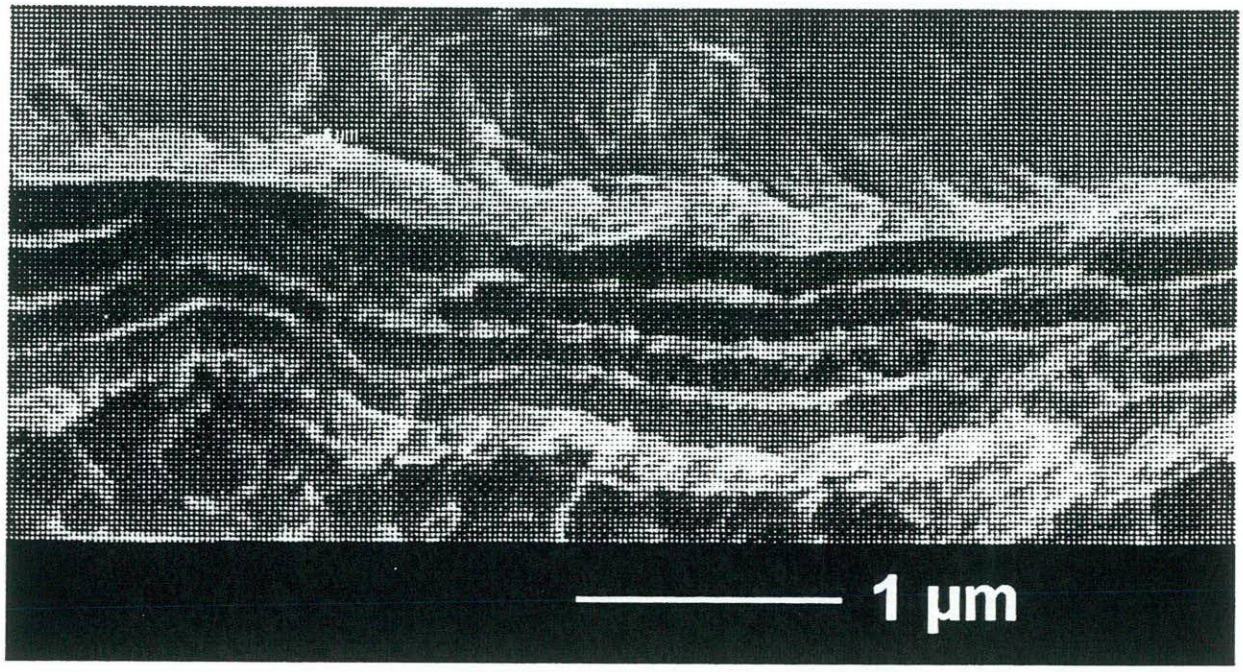

Figure 3: Scanning electron microscopic image of a cobalt-copper laminated structure, in nanometer dimension.

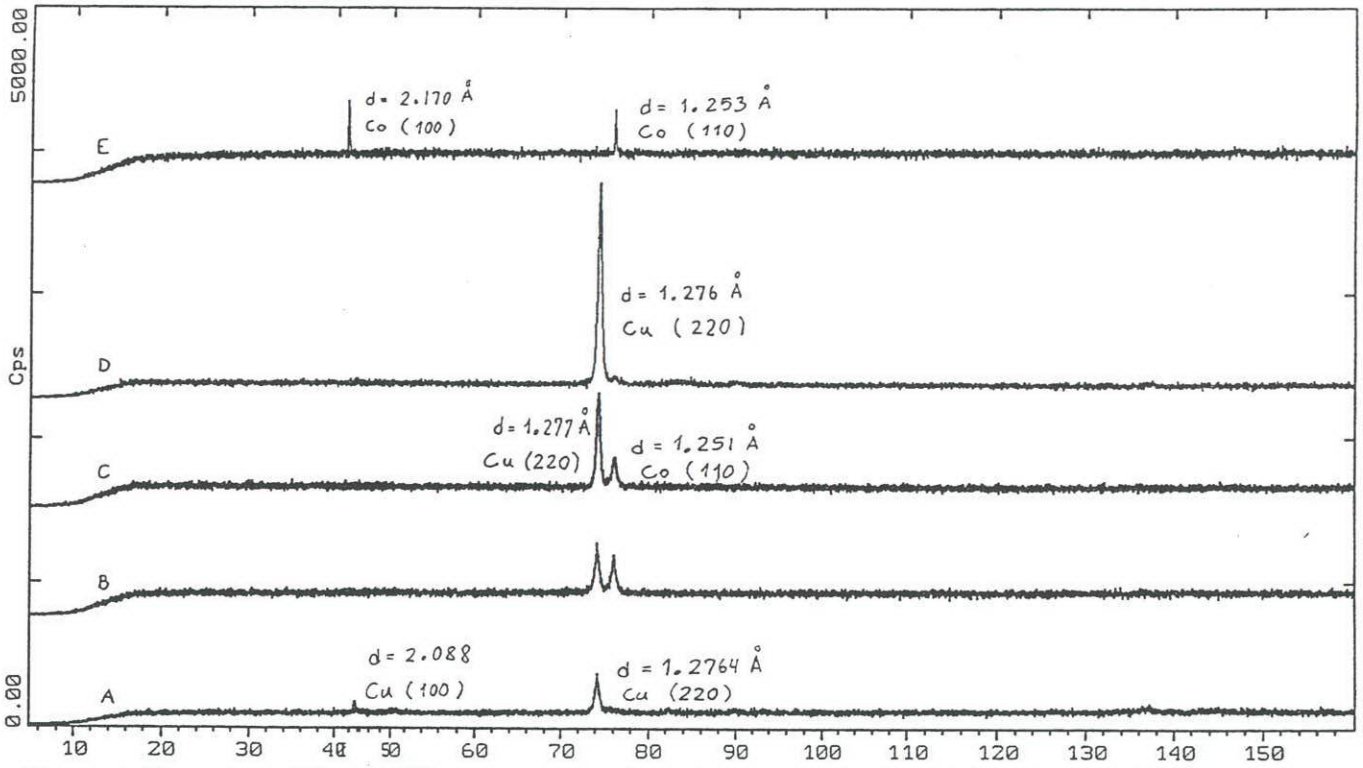

Figure 4: Examples of X-ray diffraction patterns for cobalt-copper laminated deposits; A) Cobalt below 30 nm, copper 100 nm; B) 100 nm of each with a levelling agent normaly used for nickel plating (OXY 0.5 ml/l); C) Cobalt 50 nm, copper 100 nm; D) 100 nm of each; E) ~8 µm cobalt deposited under pulse mode and agitation.

DEVELOPMENT AND CHARACTERIZATION OF TIN CAPPED GOLD BUMPS IN TAB

F. Carney, G. Carney, J. Heckman,

M. Nagarkar, J. Schaper, M. Seddon, E. Woolsey

Advanced Packaging Design and Automation Center

LATG Advanced Technology

Motorola, Inc

Chandler, Arizona

Abstract

Motorola ASIC employs a Sn-Au eutectic gang bonding technique for TAB interconnect. This methodology allows the reliable bonding of high lead count devices at very fine pitch. Advantages include low bonding temperatures, low bonding pressures, and a visual metric of bond integrity. Disadvantages include problems with Sn plating thickness reproducibility and Sn whisker growth on Sn-plated Cu tape. Using reflowed Sn-capped gold bumps, first developed by Siemens, a robust bonding technique using Au tape to achieve Sn-Au eutectic bonds has been developed. The Sn-capped process was characterized with respect to Sn plating thickness on the Au bump, heat treatment conditions for eutectic formation, metallurgical changes after thermal aging, bonding conditions, and reliability.

TAB Interconnect Technology

Tape Automated Bonding (TAB) of Application Specific Integrated Circuits (ASICs) began at Motorola in 1988. TAB bonding was chosen for certain ASIC applications due to its small footprint, excellent electrical performance, and ability to bond very high lead count devices with 100 µm pad pitch[1]. Standard TAB technology uses Au bumps bonded to Cu leads that are plated with either Au or Sn. Au plated tape is normally bonded to a Au bump using thermocompression bonding. Sn plated tape uses the Au-Sn eutectic alloy as the means of interconnect. A Sn plated TAB lead bonded to a Au bump using the eutectic alloy bonding technique is illustrated in Fig. 1. The thermocompression bonding process has the advantage of using Au plated TAB tape that does not exhibit the problems associated with Sn tape. The principal problems associated with Sn tape are Sn plating reproducibility, Sn thickness measurement accuracy in the 0.5 µm thickness range, thermal treatments to inhibit Sn whiskers, and Sn whisker formation with time. Shelf life issues due to the interdiffusion of Cu and Sn is also a major problem[2]. The Sn-Au eutectic bonding process has the advantage of lower bonding pressures and temperatures as compared to thermocompression bonding. This process has historically required Sn plated TAB tape.

The TAB gang-bonding technique in which all leads on the tape are bonded simultaneously was chosen over single point bonding. Gang bonding offered the speed and alignment accuracy that was necessary to bond the ASIC Mosaic III 100µm pitch.

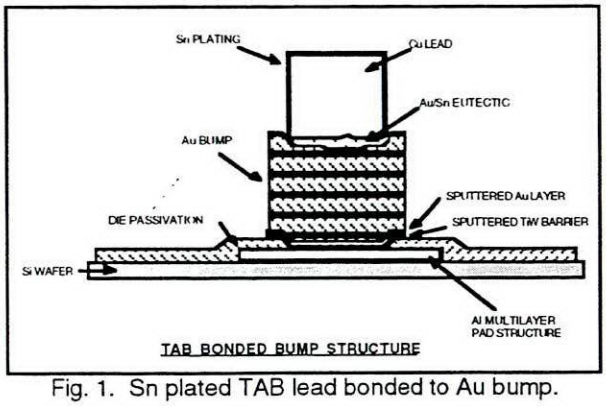

Fig. 1. Sn plated TAB lead bonded to Au bump.

Comparison of Bonding Techniques

Plating of Sn on the top of Au bumps for TAB applications was first reported by Hitachi in 1983 although they did not propose the reflow of the Au bumps prior to bonding. Reflow of the Sn cap bump was first reported by Siemens in a VLSI and packaging workshop in 1990 [3]. Work on the Sn-cap bumping process has also been conducted at the Technical University of Berlin[4]. The TAB Engineering Department started Motorola's development on the Sn-cap bumping

process in 1992. This process was developed to accommodate the needs of ASIC customers for Au plated TAB tape.

Standard TAB technology uses thermocompression bonding to bond Au tape to Au bumps. The ASIC Mosaic III die, with its three layer Al pad structure and polyimide passivation, could not withstand the high temperatures and pressures that are required for Au/Au thermocompression bonding. The pressures and temperatures used in thermocompression bonding cause barrier layer cracking between the Au bump and Al pad. Once this barrier layer is cracked there is Al-Au diffusion during high temperature storage that degrades the adhesion between the Au bump and Al pad. This loss of adhesion causes bump lift failures. The Sn-cap bonding process offered the reliability of Au tape without sacrificing the lower bonding pressures and temperatures characteristic of Au/Sn eutectic bonding. Fig. 2 compares the three types of bonding techniques over several critical parameters associated with the TAB process. It can be seen from the comparison that the bonding force necessary for the Sn-cap process is 4X less then that needed for standard Sn-Au eutectic bonding, and 10X less then thermocompression bonding. This reduction in the bonding force has the distinct advantage of eliminating TiW barrier cracking. The main disadvantage of the Sn-cap bonding process is the two step bump plating process necessary for the formation of the Sn-cap bump. This two step plating process requires greater Au bump plating control because of the diffuculty in measuring the Au bump height prior to the Sn plating step.

BONDING TECHNIQUE COMPARISONS

	Au/Au Tin Cap	Sn/Au Eutectic	Au/Au Thermocompression
• Bonding Force	5.5 -10 g/lead	22 - 30 g/lead	50 - 70 g/lead
• Bonding Temperature	400 - 500°C	450 - 525 °C	450 - 525°C
• Bump Plating Process	2 step Au then Sn	1 step Au	1 step Au
• Tape Metallurgy (ILB)	Au or Sn	Sn	Au
• Bonding Type	Gang	Gang	Gang
• Bonding Equipment	Anorad	Anorad	Anorad
- Bond Reliability	Excellent	Good	Average
• Sn Whiskers	No	Possible	No
• TAB Tape Consistency	Good	Poor	Good
• Reliability of Tape	Excellent	Average	Excellent
- TiW Barrier Damage	No	Possible	Yes

Fig. 2. Comparison of TAB bonding techniques.

Tin-Cap Process

The Sn-cap bumping process consists of plating a standard Au bump to 18 μm and adding a layer of Sn. The production flow for a standard Au bump is to first sputter TiW across the wafer which acts as the barrier and adhesion layers between the Al pad and Au bump. The Au seed layer is then sputtered that will serve as a conductive layer for the Au plating step, and an oxidation barrier for the TiW. At this stage the entire wafer is coated with approximately 30 μm of photoresist and via's are developed out over the bond pads for the Au bump plating process. The 18 μm Au bumps are then plated in the photoresist via's with their size being defined by the original opening of the via. Once the Au plating is completed the wafers are transferred to the Sn plating bath where the layer of Sn is deposited on the top surface of the Au. The photoresist, Au seed layer, TiW adhesion layer, and TiWNx barrier layer are then chemically removed from the entire wafer surface using the Au bumps as a mask. A metallographic cross section of a completed Sn-cap bump prior to reflow is shown in Fig. 3. The plated Sn layer can be seen on the top of the Au bump.

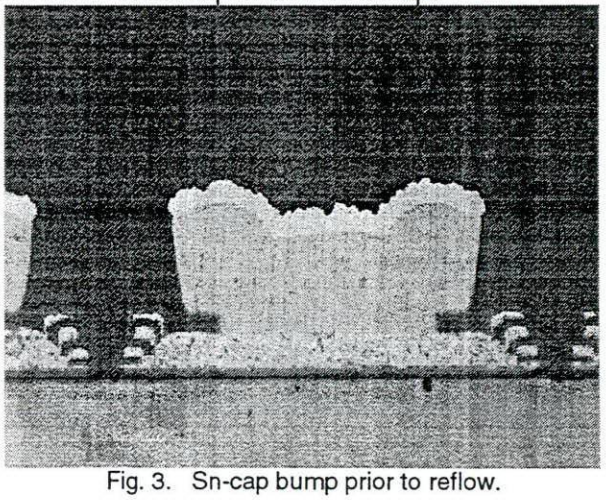

Fig. 3. Sn-cap bump prior to reflow.

The completed Sn-cap bumps are now heat treated in a convection furnace containing an inert atmosphere. The current process uses a heat treatment in nitrogen. Fig. 4 shows the reflowed Sn-cap bumps after heat treatment. The top layer of the reflowed bump is Au-Sn eutectic alloy composed of Au_5Sn and AuSn having a melting point of 280°C. The Au-Sn phase diagram showing the eutectic alloy is shown in Fig. 5 . A metallographic cross section of a reflowed Sn-cap bump showing the domed Au-Sn eutectic alloy having a composition of 80 wt. % (71 at. %) Au and 20 wt. % (29 at. %) Sn is shown in Fig.6. Below the eutectic alloy dome the ζ' phase and pure Au layer can be seen.

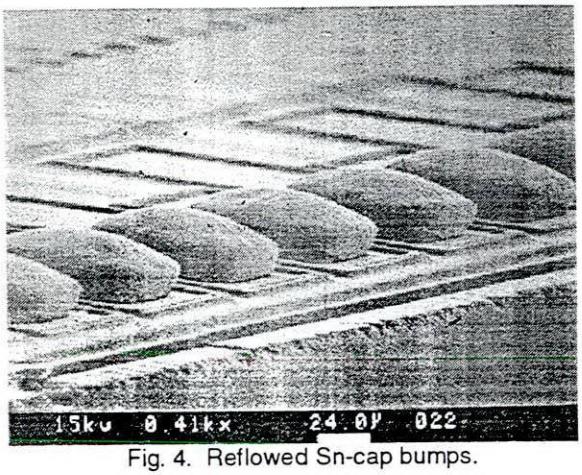

Fig. 4. Reflowed Sn-cap bumps.

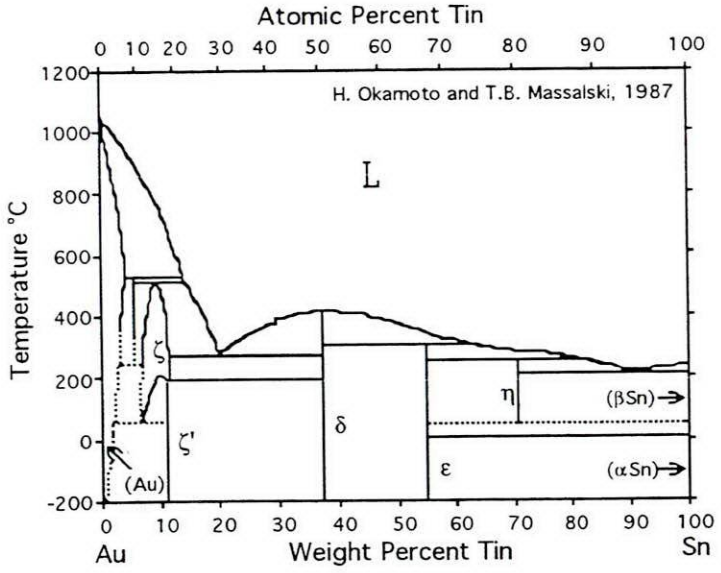

Fig. 5. Gold-tin equilibrium phase diagram.

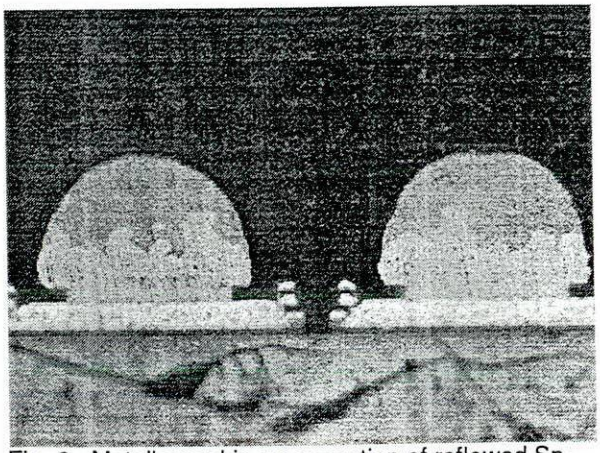
Fig. 6. Metallographic cross section of reflowed Sn-cap bump.

Once the Sn-cap bumps are formed the sample is bonded according to the parameters shown for the Sn-cap process in Fig.1. A comparison between standard eutectic bonding using Sn plated TAB tape, and Sn-cap eutectic bonding using Au tape can be seen in Fig. 7 and Fig. 8 respectively. Fig. 7 is a SEM micrograph showing the eutectic alloy flow that connects the TAB lead to the Au bump. The flow can be seen completely covering the top of the Au bump and extending partially up the Sn plated Cu TAB lead Fig. 8. shows a Au lead bonded to the Sn-cap bump and the improved eutectic alloy wetting to the TAB lead is readily observed.

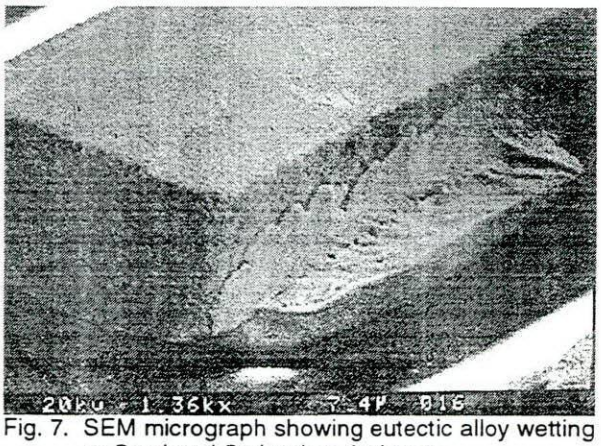

Fig. 7. SEM micrograph showing eutectic alloy wetting to Sn plated Cu lead on Au bump.

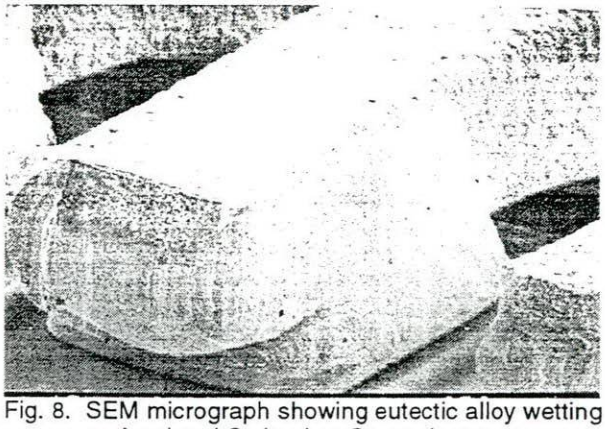

Fig. 8. SEM micrograph showing eutectic alloy wetting to Au plated Cu lead on Sn-cap bump.

A metallographic cross section showing a Au plated Cu lead bonded to a Sn-cap bump is shown in Fig. 9. The eutectic alloy flows completely up the side of the TAB lead and all of the Au is dissolved off the sides and bottom of the Cu lead. The ζ' can be seen below the lead, and this phase acts as a diffusion barrier which inhibits pour formation associated with Cu diffusion[5].

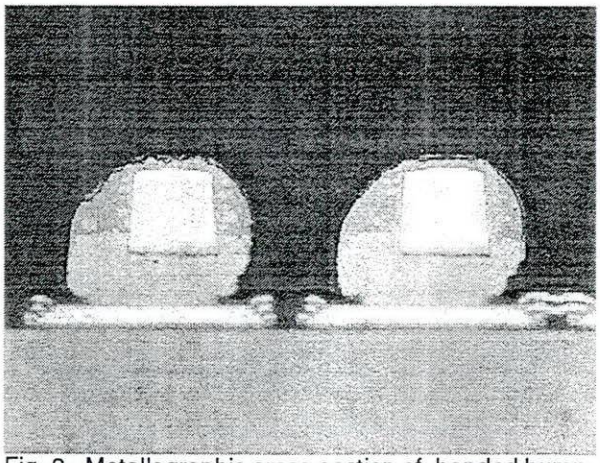

Fig. 9. Metallographic cross section of bonded bump.

RELIABILITY

In order to check the reliability of the bonded Sn-cap bumps, both electrical and mechanical evaluations are employed. The electrical portion of the evaluation uses live die that have been bonded to TAB tape. Stress testing is performed on bonded samples and an electrical test is used to determine if the samples are still functional. The stress testing for the Sn-cap TAB bonding evaluation consisted of 1000 cycles of condition C thermal shock (-65°C - 150°C), 1000 cycles of condition C temperature cycle, and 1000 hours of high temperature storage at 150°C. The mechanical portion of the evaluation uses identical stress conditions but the leads are destructively pulled to evaluate Cu lead strength, lead to bump integrity, and bump to pad adhesion strength. The data is reported in a "Form 8" format. The "Form 8" evaluation consists of 28 leads pulled per die, 4 leads at each corner and 3 leads in the center of each quadrant. There are a total of 8 die pulled for each "Form 8". Figures 10,11,12, and 13 show the "Form 8" data of the control parts before stress testing, 1000 cycles condition C thermal shock, 1000 cycles condition C temperature cycle, and 1008 hours of high temperature storage at 150°C respectively. The reliability of the bonded units far exceeds the ASIC TAB qualification requirements of 200 cycles for thermal shock and 300 cycles of temperature cycle.

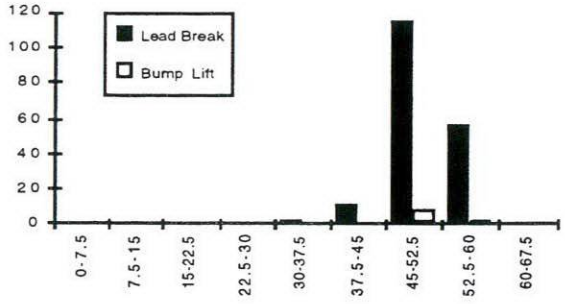

Fig. 10. Control bond pulls before stress testing.

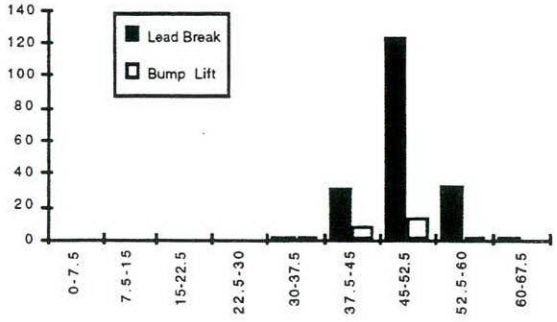

Fig. 11. 1000 cycles of condition C (-65°C-150°C) thermal shock.

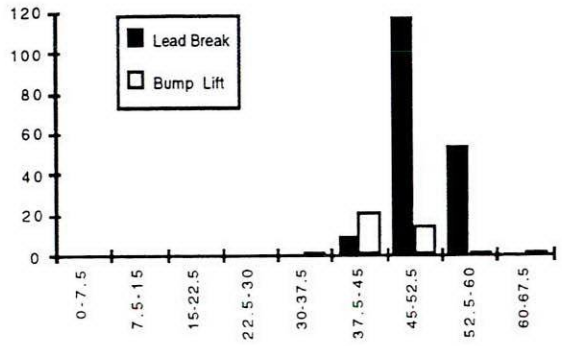

Fig. 12. 1000 cycles of condition C (-65°C-150°C) temperature cycle.

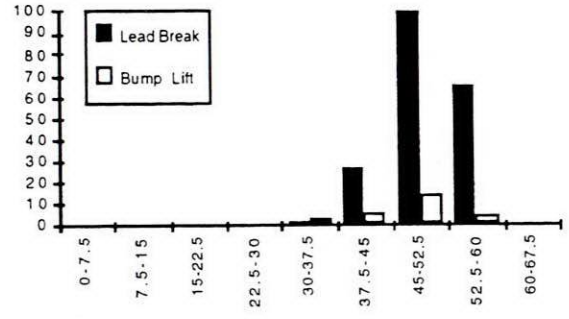

Fig. 13. 1008 hrs. of 150°C life storage.

Kinetics

To study the growth kinetics of the zeta' (ζ') phase, tin-capped bumps were aged at 100-250°C for 300 seconds to 36 hours after the initial standard heat treatment. After aging, die were mounted in epoxy, cross sectioned, and etched with an HF/HCl mixture to reveal the Au/Sn metallurgical structures. These cross sections enabled area and width measurements of the ζ' phase to be taken. The etchant attacks the AuSn compound, delineating the eutectic alloy phase, while not having any effect on the pure Au or the white Au_5Sn. A video camera attached to a microscope was used to scan the metallographic images into a computer. Using Macintosh MacCanvas software it was then possible to measure the average area of the ζ' phase. An example of the scanned image from which the area was caculated is shown in Fig. 13. Dividing the area by the average phase width yields thickness values for the ζ' phase.

The growth rate of an intermetallic compound during interdiffusion follows a parabolic rate law as follows:

$$x = kt^{0.5}$$

where x is the compound thickness, t is the aging time, and k is the rate constant. A plot of zeta' phase thickness as a function of the square root of aging time at 100°, 150°, 200°, and 250°C is shown in Fig. 14. The plots demonstrate the accelerated growth rate at 200° and 250°. The micrographs also show the increased formation of ζ' phase at these temperatures. The activation energy can be determined by using the Arrhenius equation:

$$k = A_o \exp(-Ea/RT)$$

where A_o is the pre-exponential factor, Ea is the activation energy, R is the gas constant, and T is the temperature. From a plot of the ln of the rate constant vs. inverse aging temperature as shown in Fig. 15, an activation energy of 0.63 eV was calculated for Au_5Sn. This value is close to the published value for AuSn of 0.59 eV[6].

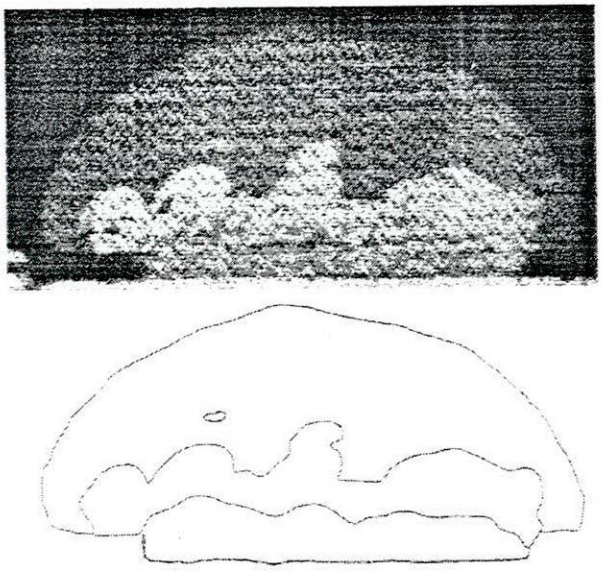

Fig. 13. Mac Canvas area analysis technique.

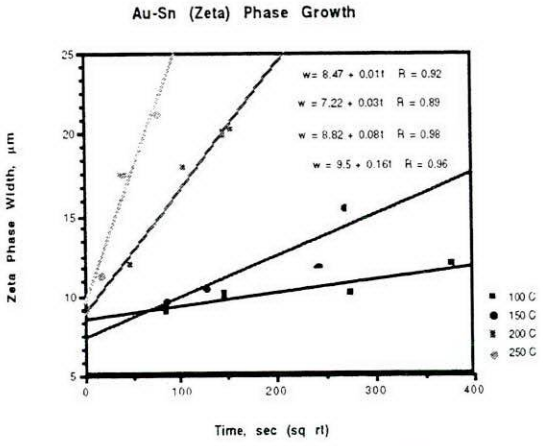

Fig. 14. Thickness vs. time curves.

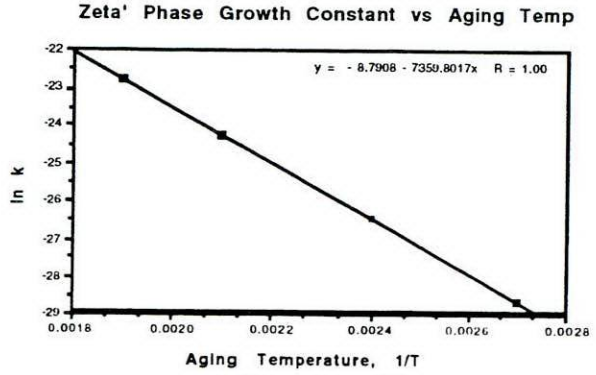

Fig. 11 - ln k vs. 1/T

Conclusion

The Sn cap bonding process can be used to bond Au tape to Au bumps on ASIC die using the Au-Sn eutectic bonding system. The Sn cap bonding process uses lower temperature and pressure to achieve reliable bonds when compared to either thermocompression or standard Au-Sn eutectic bonding. The Sn cap bonding process offers increased reliability when bonding ASIC die to Au tape due to the complete elimination of TiW barrier cracking. The reflowed Sn cap bumping process has applications in both flip-chip and TAB bonding applications.

Acknowledgments

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Laser Direct Writing of Palladium on Pyroceram and Polyimide

Zuzhan Yu, Xin Zeng, Yamei Wang,
Department of Chemistry, Fudan University, Shanghai 200433, China
Guoqing Zhao
Department of Nuclear Science, Fudan University, Shanghai 200433,China

Based on the spin-coated thin palladium acetate films and focused cw Ar^+ and He-Ne laser, Pd was rapidly deposited on pyroceram and polyimide substrates on the laser -irradiated zones, Pd lines with good adhesion were obtained. The dependence of deposit composition and structure on laser power, wavelength and scan speed was studied using SEM, AES, XPS and RBS, and deposition mechanism on two different substrates was also discussed.

Introduction

Laser direct-write metallization on integrated circuit microfabrication has generated much interest and research. Metal deposition by the laser- induced decomposition of spin- coated organometallic polymer precursors offers the advantages of increased safety and ease of handling, and a wide variety of metals can be incorporated in the synthesis of organometallic polymers,tailing them to specific applications[1,2,3].

Palladium acetate(PdAc) is a nonpolymeric metallo-organic compound that forms homogeneous, noncrystalline films when spin coated from chloroform solution, and deposition of Pd from PdAc/$CHCl_3$ precursors can be done with very highly writing speeds on various substrates, such as quartz, silicon etc. , as has been described by several authors[4,5,6]. In this paper we presented results of work on the fabrication of Pd lines based on PdAc precursor on pyroceram and polyimide(KAPTON,Du Pont, including PI(A) and PI(B) substrates.

Results and Discusion

Both PdAc precursor and PI substrates have lower absorbance at longer wavelength, as shown in Fig.1, and PI(A) would have higher absorbance

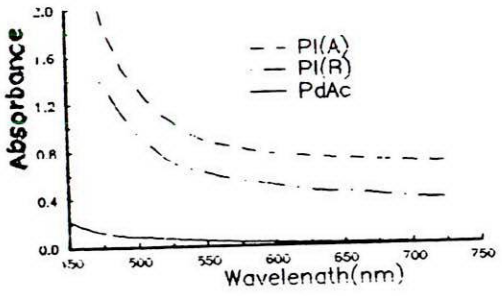


Fig. 1 Optical absorption spectra of PdAc and PI Substrates

than PI(B) at the same wavelength between 400 and 700nm wavelength.

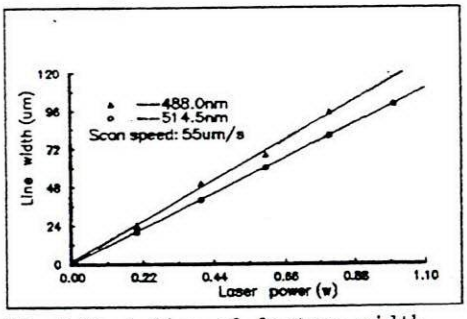


Fig. 2 Variation of feature width with laser power

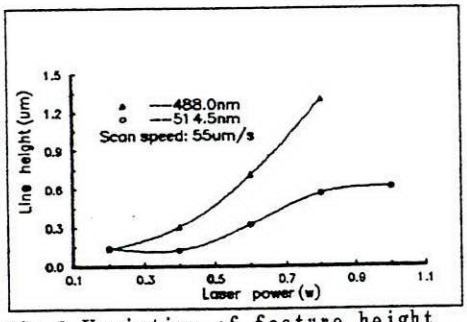


Fig. 3 Variation of feature height with Laser Power

Fig.2 and 3 show the width and height of the obtained Pd lines on pyroceram substrate as a function of the laser power at scan speed of 55 um/s for two Ar^+ laser radiation wavelengths, and the average thickness of the precursor is 6um. Both the line width and line height increase with the laser power, and a linear dependence of the line width on laser power is found, especially. Fig.4 and 5 show the width and height of the

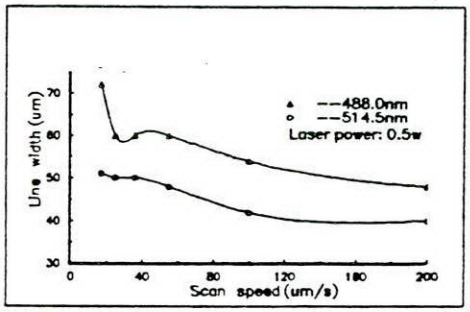


Fig. 4 Variation of feature width with scan speed

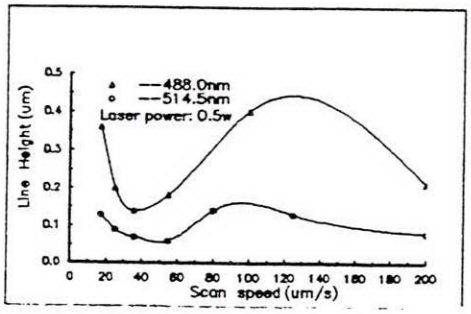


Fig. 5 Variation of feature height with scan speed

lines on pyroceram as a function of the scan speed at laser power of 0. 5w for two Ar^+ laser radiation wavelengths, as can be seen, the lines turn narrower as scan speed grows, and surprisingly, the line heights present a more complicated behaviour with the scan speed. This is probably due to the "explosive" phenomenon that will be discussed below. As narrow as 20um of the minimum width of the deposited Pd features was obtained in our work, which is much smaller than the laser spot diameter(~35um) used. Because the optical absorbance of PdAc precursor decrease with the wavelength, the features resulting from 488. 0nm irradiation are wider and thicker than those from 514.5nm.

Fig.6 and 7 show the width and height of the Pd lines on PI as a function of the scan speed at

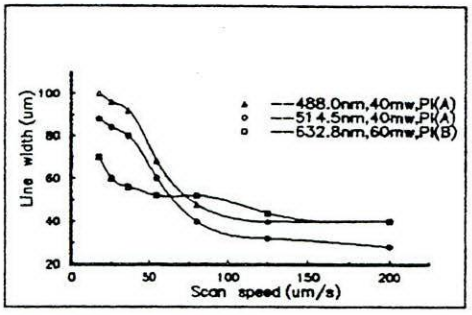


Fig. 6 Variation of feature width with scan speed

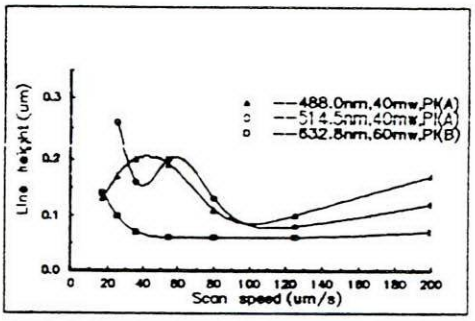


Fig. 7 Variation of feature height with scan speed

the average precursor thickness of 4um for three kinds of laser radiation wavelength, including two Ar+laser wavelengths(488.0nm and 514.5nm) at laser power of 40mw irradiated on PI(A) and one He-Ne laser wavelength(632.8nm) at power of 60mw irradiated on PI(B). As scan speed increasing, the line width decreases, and it will be falloff when scan speed is above 100um s. Scan speed has greater influence upon width of Pd line written on PI(A) induced by Ar+laser than that on PI(B) induced by He-Ne laser. Little dependence of Pd line height on scan speed is found, which is similar to the result obtained on pyroceram substrate. As can be seen from Fig.1, the optical absorbance of PdAc films and PI substrates decrease with the increasing wavelength, and PI(A) has higher absorbance than PI (B) at the same wavelength, so the width of Pd lines on PI(A) induced by Ar+ laser resembles that on PI(B) induced by He-Ne laser, and the height of the former is much larger than the latter, although the used power of Ar+ laser is lower than that of He-Ne laser by 20mw.

The deposition rate is an important issue to

which much care should be taken. In our process, the approximate deposition rate of Pd is calculated to be about 150～5000um³/s, clearly much higher than what is observed in general electroless and electroplating processes. The deposition rate of Pd on PI substrates is estimated between 150 and 600um³/s, which is much smaller than that on pyroceram substrate.

Auger analysis established that deposits on irradiated zones of pyroceram substrate consisted of Pd、C、O、Cl and slight amounts of Si、Al, as shown in Fig.8 (a). Based on the AES data,we can

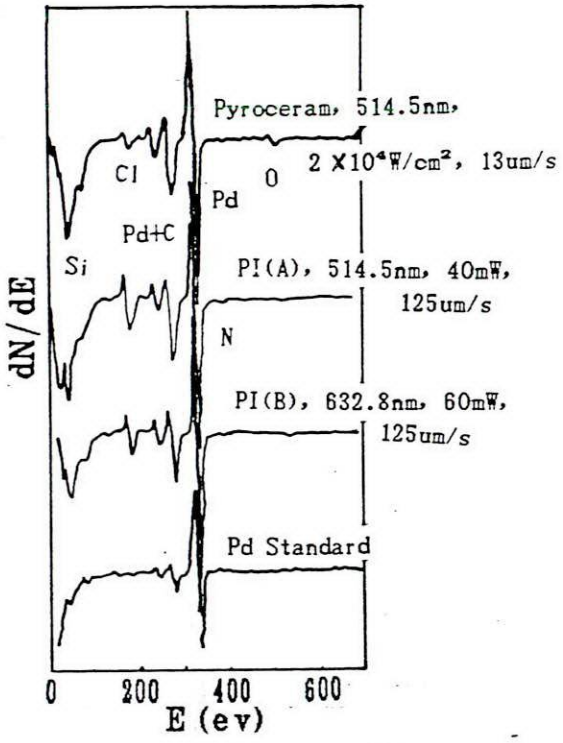


Fig. 8 AES of Pd features written on pyroceram and PI substrates

obtain the element percentages of Pd features: 65.5%Pd, 6.0%O, 25.8%C, 2.7% Cl. Fig.8 (b) shows that deposits on irradiated zones of two different PI substrates consisted of Pd、C、Cl and small amounts of N、O etc.

XPS studies showed that the deposits on pyroceram consisted of Pd、C、O、Si、Al,shown in Fig.9 (a), and deposits on PI consisted of Pd、C、N、O etc, shown in Fig. 9 (b), which were consistent with the AES results.

Based on the XPS data, we could conclude palladium was predominantly in the form of elemental Pd, chlorine was found in all features, presumably resulting from palladium chloride

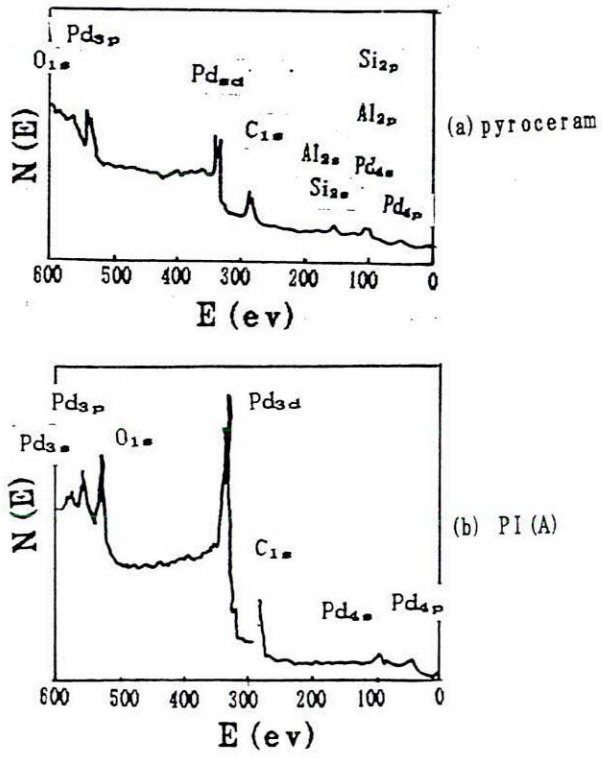


Fig. 9 XPS of Pd features written on pyroceram and PI (A) Substrates the wave length is 514.5nm

contamination of the acetate. on features of pyroceram substrate,carbon was also in the form of elemental C, and oxygen was observed in the form of SiO_2、Al_2O_3 from the pyroceram substrate However,complex carbon and oxygen species were found in the features on PI substrates.

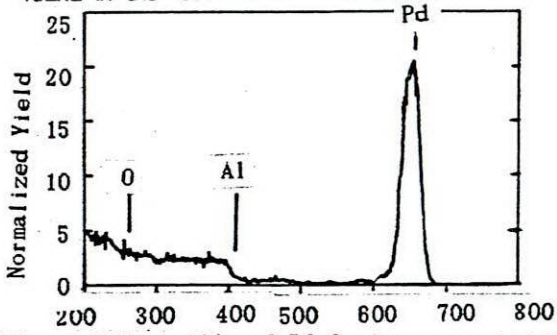


Fig. 10 RBS profile of Pd feature on pyroceram substrate (Experimental conditon as in Fig. 9)

Fig.10 shows a typical RBS spectrum of Pd feature on pyroceram,Pd and small amounts of O、Al、Si etc were detected in the deposit, which supported the AES and XPS results. Based on the that, RBS spectrum,we also found that Pd had diffused into the substrate, indicating that surface melting of pyroceram substrate was associated with the deposition mechanism proposed below.

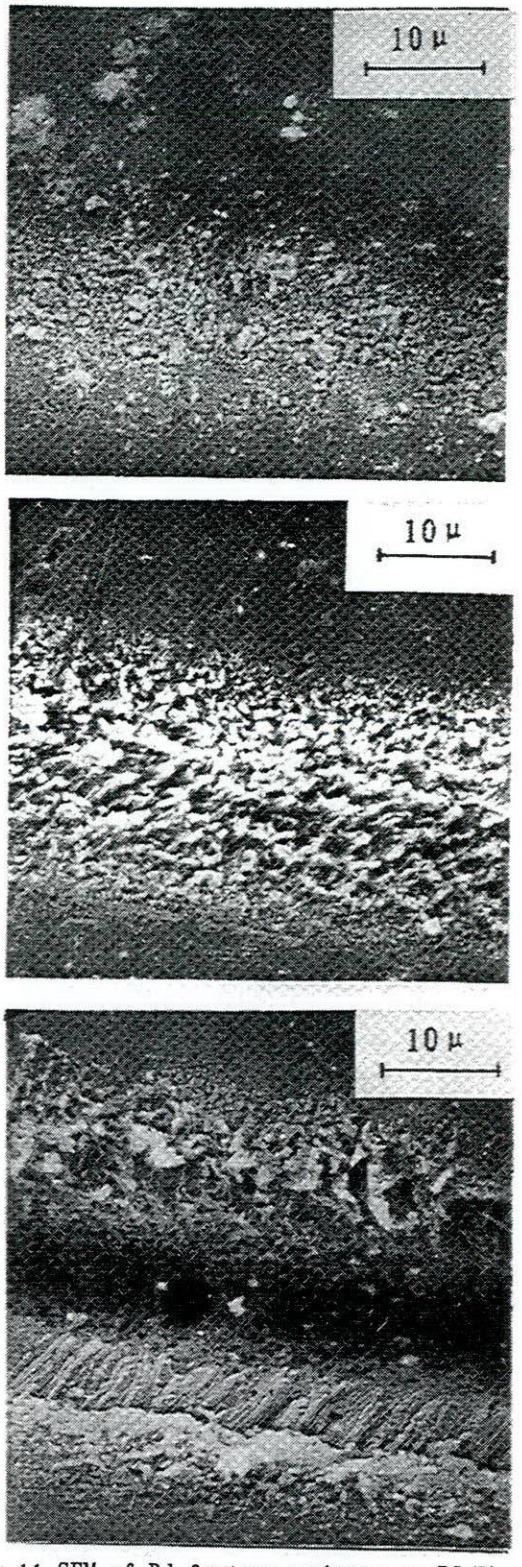
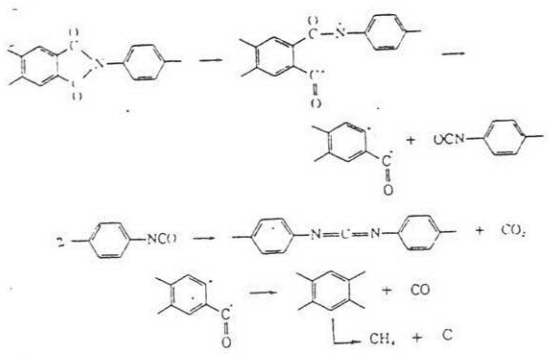


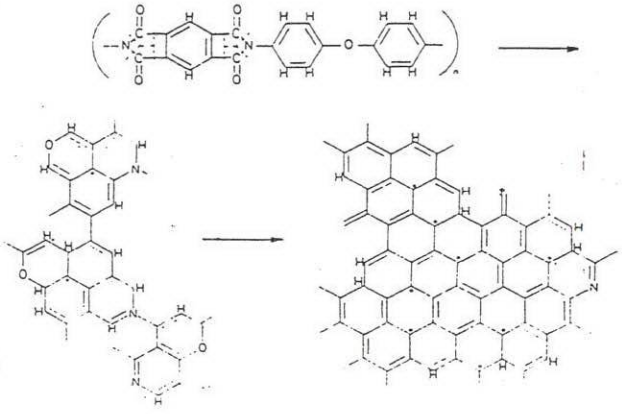
Fig. 11 SEM of Pd feature written on PI(B) at different scan speeds, cw He-Ne Laser--60mW, 632.8nm
(a) 200um/s (b) 36um/s (c) 17um/s

Deposit has fine Pd crystal at faster scan speed(see Fig.11a) and a rougher deposit is obtained at slower scan speed(see Fig. 11b) . Reducing scan speed to 17um/s brings about "carbon craters" in the middle of the Pd lines, and the fine Pd crystalline grain turns into coarse fernleaf crystal, this factor may result in the irregularity of the Pd line heights with various scan speeds.

On the basis of the measurements by thermal -couple analytical technique, we estimate the maximum temperature of PI substrate surface on the laser-irradiated zones at slow scan speed is higher than 600℃, while the stable temperature of PI is about 400 ℃, so as the power level increases or scan speed decreases, laser- induced local heating may cause deformation of PI substrate. The major decomposition reaction process can be written as follows:



As scan speed slows down rapidly, laser induced local heat-accumulating is high enough to cause decomposition and even crosslinking of PI, according to the report of Bruck[7], the pyrolytic conversion of PI to semiconducting products may occurred as follow[8]:



So, we believe,on the laser-irradiated zones of PI substrate,PdAc precursors may take place not only thermal decomposition,but also chemical reduction to metal Pd by the capture of electrons generated during the PI to semiconducting products transformation. The postulated mechanism for laser-induced deposition on PI substrates must be further tested.

Conclusions

Pd lines could be deposited directly on pyroceram and polyimide substrates by a cw laser direct-write process in thin palladium acetate precursors. Experimental results indicated that laser irradiation gived rise to local temperature increase, which resulted in the thermal decomposition of palladium acetate on the directly irradiated zones. We also investigated and discussed the mechanism responsible for the laser-induced decomposition of metallo- organic films on two different substrates, as a result of experiments, it showed that deposits had good qualities at lower laser power and faster scan speeds, while at higher power and slower scan speeds, Pd deposits on pyroceram would have a "explosive" structure, and polyimide substrate itself would take place carbonization and polymerization which resulted in poor deposits.

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ENVIRONMENTAL LIABILITY: OLD INSURANCE POLICIES MAY PAY

John S. Vishneski III
KECK, MAHIN & CATE
77 West Wacker Drive, 49th Floor
Chicago, Illinois 60601

I. INTRODUCTION

As the U.S. EPA continues to utilize the Superfund Law to clean up America's polluted sites, Electroplaters continue to incur liability for long past practices. Old Comprehensive General Liability Policies may pay for this liability. This paper provides first an overview of legal issues such as how the pollution exclusion is interpreted and the emerging theory of coverage under personal injury provisions. It then deals with practical issues involved in collecting insurance proceeds for Superfund Liability such as where to sue, which policies apply, what limits may be available and the expense of litigating with insurance companies.

II. COVERAGE UNDER THE PROPERTY DAMAGE PROVISIONS OF GENERAL LIABILITY INSURANCE POLICIES

The property damage coverage of standard-form Comprehensive General Liability policies may cover modern environmental liability. The two most important provisions of standard CGL policies with respect to environmental liability are the coverage clause and the pollution exclusion. The standard coverage clause in CGL policies reads:

"The company will pay on behalf of the insured all sums which the insured shall become legally obligated to pay as damages because of

A. bodily injury or
B. property damage

to which this insurance applies, caused by an occurrence ..."

....

"'occurrence' means an accident, including continuous or repeated exposure to conditions, which results [during the policy period] in bodily injury or property damage neither expected nor intended from the standpoint of the insured." See Environmental Liability Insurance Law: An Analysis of Toxic Tort and Hazardous Waste Insurance Coverage Issues, Kenneth S. Abraham (Prentice Hall Law & Business 1991), pp. 288, 291. This version has been in use with little variation since 1966.

The most striking aspect of this provision is the set of events it designates as triggering coverage. Under this provision, the event or circumstance that triggers coverage is bodily injury or property damage that happens during the policy period. For example, if a CGL policy has an effective period of one year from January 1, 1979 to January 1, 1980, it covers liability arising from events of bodily injury or property damage that happen during that year. Moreover, this is true regardless of when the

event that caused the injury or damage happened.

This aspect of the standard-form CGL policy has important consequences with respect to coverage of CERCLA environmental liability. As noted above CERCLA liability is usually imposed today for events that happened long ago. For example, the mismanagement of a waste site that resulted in soil contamination may have happened in the 1960s or 1970s. In that case, since the damage to the property happened in the 1960s or 1970s, coverage would be provided by CGL policies from the 1960s and 1970s. Thus, the question of whether insurance coverage exists for CERCLA environmental liability often involves the interpretation of old CGL policies, usually from the 1960s and 1970s.

The primary defense put forward by insurance companies to a claim for coverage of CERCLA-type environmental liability is the 1970 standard-form pollution exclusion. This exclusion, placed in most standard-form CGL policies from 1970 through 1986, reads as follows:

"This insurance does not apply ... to bodily injury or property damage arising out of the discharge, dispersal, release or escape of smoke, vapors, soot, fumes, acids, alkalis, toxic chemicals, liquids or gases, waste materials or other irritants, contaminants or pollutants into or upon land, the atmosphere or any water course or body of water; but this exclusion does not apply if such discharge, dispersal, release or escape is sudden and accidental." See Environmental Liability Insurance Law, p. 291. This exclusion is one of the most widely-litigated insurance policy provisions ever drafted.

In most cases, the controversy centers on the meaning of the exception part of the exclusion, "but this exclusion does not apply if such discharge is sudden and accidental." Policyholders seeking coverage for pollution that happened long ago, and that happened without their knowledge, argue that one reasonable meaning of the words "sudden and accidental" is unexpected and unintended. Under this interpretation, CERCLA liability for long-ago caused pollution is covered, provided the policyholder had no knowledge that the pollution was happening at the time of the events causing the pollution.

Insurance companies, on the other hand, typically argue that the only reasonable meaning of the words "sudden and accidental" is quick (or instantaneous), unexpected and unintended. Under this interpretation, coverage is only provided when the pollution from which liability arises happened all at once, such as when a tanker truck carrying hazardous substances overturns and explodes. Thus, according to insurance companies, most CERCLA liability is not covered because it is the result of waste disposal practices taking place over an extended period of time.

III. RECENT STATE SUPREME COURT OPINIONS INTERPRETING THE 1970 POLLUTION EXCLUSION

Insurance law is the province of state courts. Federal courts certainly decide a large number of coverage disputes, but they do so by applying the appropriate state law. Hence, the best indicators of the law in this controversial area are state supreme court opinions. Three recent opinions from Illinois, Florida and New Jersey demonstrate the degree of disagreement as to the proper interpretation of the 1970 standard-form pollution exclusion.

1. The Supreme Court of Illinois

The Illinois Supreme Court issued an opinion in December 1992, which was very favorable to policyholders. See Outboard Marine Corp. v. Liberty Mut. Ins. Co., 154 Ill. 2d 90, 607 N.E.2d 1204 (1992) ("Outboard Marine"). The Outboard Marine court held that liability for unexpected and unintended releases of pollutants is covered under standard-form CGL policies, and not excluded from coverage by the 1970 standard-form pollution exclusion. Under the facts of the case, releases of PCBs into Waukegan Harbor, resulting from malfunctioning of Outboard Marine's waste water control system, could be characterized as unexpected and unintended, and hence, covered releases of pollutants. The insurers argued that the only reasonable meaning of the words "sudden and accidental" is quick (or instantaneous), unexpected and unintended. Under this interpretation, coverage would not be provided in this case, where the relevant releases of PCBs took place over an extended period of time.

The Outboard Marine court found that the term "sudden" as used in the exclusion is ambiguous, having two reasonable meanings. The court noted that standard dictionaries define "sudden" both with reference to the unexpectedness of an event and with reference to quickness of an event, suggesting that both parties were asserting reasonable meanings of the term. The court also noted that profound disagreement among courts as to the meaning of "sudden" strongly suggests that it is an ambiguous term. Having found that "sudden" is an ambiguous term, the court construed it in favor of the policyholder, Outboard Marine Corporation, according to Illinois rules of insurance contract construction.

The court also noted that construing the term "sudden" with reference to the quickness of an event would create an absurdity in the pollution exclusion. The policies' definition of the term "occurrence" specifically provides that "accidents" include events of continuous or repeated exposure to conditions (i.e., gradually occurring events). If "sudden" were construed to mean quick or abrupt, then the "sudden and accidental" exception part of the pollution exclusion would apply to abrupt and gradual releases of pollutants, an absurd result.

The Outboard Marine court's holding is favorable to policyholders because interpreting the "sudden and accidental" exception to the pollution exclusion to include unexpected and unintended releases of pollutants means that the test for coverage depends on whether the policyholder was aware of the polluting event(s), a factor within the control of the policyholder. Under the insurers' interpretation, coverage would have depended on the gradualness or abruptness of the polluting release, a factor usually not within the control of the policyholder.

2. The Supreme Court of Florida

On July 1, 1993, the Supreme Court of Florida reversed its previous September 1992 decision on the 1970 pollution exclusion, which had favored policyholders. Dimmitt Chevrolet, Inc. et al. v. Southeastern Fidelity Ins. Corp., No 78293, slip op., 1993 WL 241520 (Fla. July 1, 1993). In Dimmitt, the policyholders were automobile dealers that sold used crankcase oil to a company that recycled the oil for sale as used oil. The pollution in the case was caused by releases of pollutants over a long period of time caused by the ordinary operations of the oil recycling company. The policyholders could not be said to have expected or intended the releases, but the releases could not be said to be "abrupt" or "instantaneous". Hence the case turned on whether the term "sudden" in the pollution exclusion necessarily has a temporal connotation.

In September 1992 the Florida Supreme Court decided that "sudden" was an ambiguous term and the Court considered drafting history in finding that the pollution exclusion should be interpreted in favor of coverage where pollution releases are unexpected and unintended by the policyholder. That was a four (4) to three (3) decision. The insurance company moved for rehearing and succeeded in persuading the fourth judge from the majority to change his vote. The Florida Court now holds that the pollution exclusion is unambiguous and the term "sudden" necessarily has a temporal meaning.

The short concurring opinion of the judge who changed his mind is very revealing in that it shows that more than the straightforward application of legal principles may influence the outcome of these environmental insurance coverage cases:

"I originally concurred with the position of the dissenters in this case. I have now become convinced that I relied too much on what was said to be the drafting history of the pollution clause and perhaps subconsciously upon the social premise that I would rather have insurance companies cover these losses than parties such as Dimmitt who did not actually cause the pollution damage. In so doing, I departed from the basic rule of interpretation that language should be given its plain and

ordinary meaning. Try as I will, I cannot wrench the words "sudden and accidental" to mean "gradual and accidental," which must be done in order to provide coverage in this case. Dimmitt, 1993 WL 241520 at 5.

Equally revealing is the statement of the dissenting judge who formerly wrote the majority opinion in favor of coverage. It shows just how hard the insurance industry is willing to fight to avoid coverage for environmental liability. Noting that the basis of the insurance company's motion for rehearing was so-called "new evidence " of drafting history which had actually been excluded from the record previously, he states:

"Given that the evidence being submitted by Southeastern is now inadmissible and given that a significant portion of Southeastern's argument in the petition makes reference to that evidence, I believe that the rehearing petition is improper under the rules and should be stricken. Consideration of the rehearing petition in its present form makes a mockery of the rehearing rule and effectively signals the bar that "anything goes." Apparently, the insurance industry has sought a proverbial second bite at the apple and won. Dimmitt, 1993 WL 241520 at 10-11.

3. The Supreme Court of New Jersey

Most recently, on July 21, 1993 the Supreme Court of New Jersey, in a comprehensive and thorough opinion, interpreted the 1970 pollution exclusion strongly in favor of policyholders. Morton International, Inc. v. General Accident Ins. Co. of America et al., 134 N.J. 1, 629 A.2d 831 (1993). The New Jersey Court, like the Florida Court, found that the term "sudden" necessarily has a temoral connotation. However, rather than ruling in favor of insurers on that basis, the Court conducted an extensive review of the regulatory history of the 1970 pollution exclusion and concluded that the insurance industry had misrepresented the full restrictive effect of the exclusion to state regulators in 1970.

Based on this finding, and relying on the doctrines of estoppel and the policyholder's reasonable expectations, the Court held that the pollution exclusion would only be enforced in a manner consistent with the insurance industry's representations as to its intended effect in 1970. Thus, the Court stated:

"Accordingly, we hold that notwithstanding the literal terms of the standard pollution-exclusion clause, that clause will be construed to provide coverage identical with that provided under the prior occurrence-based policy, except that the clause will be interpreted to preclude coverage in cases in which the insured intentionally discharges a known pollutant, irrespective of whether the resulting property damage was intended or expected." Morton, 629 A.2d at 875.

IV. PERSONAL INJURY COVERAGE UNDER COMPREHENSIVE GENERAL LIABILITY INSURANCE POLICIES

"Personal injury" coverage is specially defined in CGL policies to include coverage for several torts based on intentional acts committed by the policyholder, such as defamation, malicious prosecution and invasion of privacy. These provisions include liability coverage for damages resulting from the "wrongful entry or eviction, or other invasion of the right of private occupancy."

Recently, some courts have interpreted this provision covering policyholders for liability resulting from "wrongful entry or eviction, or other invasion of the right of private occupancy" as providing coverage for environmental pollution. These courts hold that the migration of contaminants onto another's property or into the groundwater constitutes an "other invasion of the right of private occupancy." There is a recent Seventh Circuit Court of Appeals decision holding that, under its interpretation of Illinois law, this language applies to environmental liability. Pipefitters Welfare Educ. Fund v. Westchester Fire, 976 F.2d 1037 (7th Cir. 1992). The Wisconsin Appellate Court has also so held. City of Edgerton v. General Cas. Co., 493 N.W.2d 768 (Wis. App. 1992).

Under this theory of coverage, a policyholder needs only to show that its liability arises from a third-party's claim that it caused an "invasion" of contaminants onto or into the third-party's property. The Wisconsin decision held that the migration of contaminants into the groundwater of neighboring property constitutes an invasion of the right of private occupancy. This theory of coverage, if accepted by a court, is quite powerful because none of the usual exclusions relating to "property damage" coverage apply to personal injury coverage. The pollution exclusion does not typically apply to this coverage; the "owned, rented or occupied" exclusion does not apply to this coverage, and the "occurrence" requirement (requiring that contamination be unexpected and unintended from the standpoint of the insured) does not apply to this coverage.

As with the Property Damage Liability theory of coverage, the Personal Injury Liability theory is controversial. Some appellate courts have held that coverage for environmental liability is not available under these provisions. See Titan Corp. v. Aetna Cas. & Sur. Co., slip op., 1994 WL 42320 (Cal. App. Feb. 10, 1994); O'Brien Energy Systems, Inc. v. American Employers' Ins. Co., 629 A.2d 957 (Pa.Super. 1993); and County of Columbia v. Continental Ins. Co., 595 N.Y.S.2d 988 (NY.App. 1993).

V. PRACTICAL CONSIDERATIONS IN EVALUATING AND PURSUING CLAIMS

The primary goal in evaluating a potential insurance claim for environmental liability is to develop enough information to decide whether to pursue the claim through negotiation, through litigation, or

not to pursue the claim at all. The initial steps in this process include researching and preparing a site chronology, collecting relevant insurance policies, and analyzing the strength of the claim.

A. Preparing the Site Chronology

The first step in pursuing an environmental claim is to develop a chronology of signiicant events at the contamiated site for which the policyolder is being held liable. This is the first step because the course of events at the site will determine, which inurance policies are applicable to the claim.

The site chronology must show when the policyholder's and others' contaminants were released into the environment and what those contaminants have done in the environment since that time. Many jurisictions hold that property damage occurs continuously from the time of release of polluants into the environment until the damaged environment is cleaned up. This is the broadst view with respect to which policies are triggered by an environmental claim, and for purposes of determining, at a preliminary stage, which policies may apply to a claim, it is the most conservative approach to take so that potential coverage is not overlooked.

The site chronology must also show how the pollutants were released into the environment. For example, the policyholder's production processes may have allowed pollutants to escape into the environment through some unknown defect in its waste control system. On the other hand, the policyholder's employees may have intentionally dumped pollutants into the environment, not knowing the ill effects of doing so at the time. The sets of polluting circumstances are many and varied.

These facts are important for determining whether there has been a covered "occurrence" and for determining whether a "pollution exclusion" may apply. Generally, the question of whether there has been a covered "occurrence" depends on whether the policyholder knew its activities were causing property damage. The applicability of most pre-1986 pollution exclusions depend on whether the policyholder knew it was releasing pollutants into the environment.

A closely related issue that the site chronology must address is the policyholder's knowledge concerning both the polluting events and threatened or actual liability claims concerning those polluting events. For example, some environmental claims arise from the polluting activities of independent contractors who the policyholder hired to dispose of its waste. Often, policyholders have no knowledge of the polluting events of potential claims concerning those events until they are named as a defendant in a lawsuit or a Potentially Responsible Party under the Superfund law. At the other extreme, some policyholders learned of a leak in their on-

site waste control system and determined at the time that it would not be cost-effective to fix the problem. They may receive threats from neighbors or the government for years before a suit is filed against them.

These facts are important for analyzing the "late notice" issue. Most CGL policies require the policyholder to give notice of a potential claim as soon as practicable. This duty is usually triggered by the policyholder's knowledge of an occurrence that could reasonably result in a claim. The question of when an occurrence becomes reasonably likely to result in a claim is often a very difficult one, and well-informed policyholders know to give notice to their insurers conservatively early so as to avoid any dispute concerning notice.

The site chronology may need to be supplemented later, but, at the initial stages, information relating to which policies are triggered, how the pollution happened, and what the policyholder knew about the pollution and any potential claims is sufficient.

B. Collecting Relevant Policies

Once the site chronology is prepared, the policyholder is in a position to determine the time period during which property damage occurred at the contaminated site, and hence, to identify the insurance policies that may provide coverage for the policyholder's liability.

It is prudent to identify the longest period of potential property damage so as not the rule out potential coverage. For example, in developing the site chronology, one may only find records showing that waste was released at the policyholder's plant beginning in 1972. However, if the plant began operations in 1960, it is best to hunt down the policies covering the period from 1960 to 1972 as well as from 1972 forward. It is always possible that evidence of earlier polluting activity will turn up later.

This task may be very easy -- or very hard. Some (relatively few) policyholders have carefully saved their old CGL and excess liability insurance policies. For them, the task of collecting policies is little more than looking in the appropriate file. Many policyholders, however, have not saved the old CGL and excess liability policies that apply to a particular environmental liability. These insureds will have to seek policies from their brokers, their insurance companies and other sources. In many cases, policies will be lost and may have to be reconstructed from secondary evidence, such as accounting records and old claim files. Insurance archeologist firms exist that can find or reconstruct policies and then act as expert witnesses at trial in proving up the existence and terms of lost insurance policies.

In some cases, first party property insurance policies may apply to a claim. These should

be found and analyzed. Also, in the late 1970s and early 1980s the insurance industry sold Environmental Impairment Liability policies and Pollution Liability policies. These too should be found and analyzed.

C. Providing Notice to Insurers

Once the site chronology is prepared, and the insurance policies are collected, the next step is to determine which insurance carriers have already been placed notice of the claim, and to collect evidence of such notice. Then, to the extent the insurers who issued other applicable policies have not been placed on notice of the claim, they should be notified immediately.

As with determining which insurance policies to hunt for, it is important to be conserative in determining which insurers to place on notice. It is best to send notice of the claim to all insurers whose policies may possibly cover the claim. Taking again the same example noted above, suppose at this point the insured only had evidence of pollutant releases at its plant during and after 1972, but the plant had opened in 1960. It is possible, and usually likely, that further investigation will turn up facts showing pollutant releases during the 1960-1972 period. If early notice was given to the pre-1972 carriers, the policyholder will be in a position to press its claims against them when the new evidence arises. Otherwise, such claims may be lost due to failure to give timely notice.

D. To Sue or Not to Sue

Once the site chronology is prepared, the policies are collected and analyzed, and the relevant insurers placed on notice, it time to determine how best to pursue the claim.

It is usually best to attempt to negotiate the claim first. The policyholder has an obligation to cooperate with the insurer in investigating the claim. This will typically mean that the parties engage in an information exchange that allows the insurers to make a determination concerning coverge. Such an information exchange can be beneficial for the policyholder as well. During this process, the insurer may voluntarily provide policy information that was otherwise lacking. The insurer may also waive some of its defenses by not specifying them in a reservation of rights. Negotiating is always less expensive than litigation.

Like any negotiation, negotiating coverage for an environmental claim should be backed up by a legitimate threat to litigate. In many cases, however, pre-suit negotiation leads to an acceptable settlement of the claim because of the large transactions costs involved in litigating environmental coverage disputes. In any case, it is usually best to try negotiation first because it may result in a settlement, and, if not, such negotiation often strengthens the policyholder's litigation position.

There are some circumstances under which it is better to sue first and ask questions later. One example is where the choice-of-law issue is important to the outcome of the claim. Suppose the policyholder has its plant in Illinois, has Illinois-issued policies, but is liable for a waste site in Michigan because an independent third-party waste hauler took it there. Further suppose that the operators of the waste site conducted their operations so as to release pollutants at the site consistently over a long period of time. But, all of this polluting activity was completely unknown to the policyholder until it received a Potentially Responsible Party letter from the U.S. government.

On these facts, the outcome of the coverage litigation is likely to be different depending on whether Michigan law or Illinois law applies to the interpretation of the insurance policies. Assuming that the standard 1970 pollution exclusion is in each of the relevant policies, Michigan's Supreme Court has held that gradual pollution is not covered regardless of whether the insured knew anything about it. The Illinois Supreme Court, on the other hand, has held that gradual pollution may be covered if unexpected and unintended by the policyholder. Consequently, the insured would be well-advised to pursue the claim so that Illinois law is most likely to apply.

In this particular example, suing the insurers in an Illinois court would be the insured's best strategy for ensuring that Illinois law will apply. If the policyholder attempts to negotiate the claim first, the insurers may seek to obtain an advantage by filing a declaratory judgment action in Michigan and beating the policyholder to the courthouse. This could be a disastrous result. Of course, negotiation is always possible after suit has been filed, and may be more effective in this example where the insurers are facing the likely application of Illinois law to the claim.

VI. CONCLUSION

Although the area of insurance coverage for environmental liability is a controversial one, a great many policyholders have been successful in recovering some or all of their loss from their insurers. When faced with environmental liability, Electroplaters and Surface Finishers should take a look at those old policies ... they may pay.

ELECTROLYTIC METAL RECOVERY WITH A PACKED-BED CATHODE

C.-D. Zhou, E.J. Taylor, R.P. Renz, and M.K. Sunkara
Faraday Technology, Inc.
3155 Research Blvd.
Dayton, OH 45420

ABSTRACT

Recovery of metals from plating waste waters by electrowinning is limited by low current efficiency and high effluent concentration. The approach to improve the electrowinning process is to enhance mass transfer rate and effective electrode surface area. In this study, we are conducting experiments to recover copper from copper plating waste waters using pulse current (PC) to enhance mass transfer rate and packed-bed cathode to increase electrode surface area. We are studying various effects of flow by configuration along with the effects of pulse current waveform parameters such as duty cycle, frequency, and peak current. The results are also compared with DC electrolysis.

INTRODUCTION

Metals are used in a broad range of industrial processes and products, including 1) metal plating, 2) paint additives, 3) ore processing and 4) the manufacture of photographic films. Metal waste sources and their characteristics are listed in several literature.[1,2] Rinse water, contaminated with bath dragout from workpieces, accounts for the large majority of waste produced in electroplating shops. Spent cleaning and plating baths are another waste source. Waste water containing heavy metals must be adequately treated before being discharged. The U.S. Environmental Protection Agency published its regulations for waste water discharge from electroplating and metal finishing industries.

Conventional methods for metal removal/recovery include precipitation, ion-exchange, reverse-osmosis, evaporation and freeze crystallization. Precipitation often inadequately detoxifies waste water and generates undesirable sludge as a by-product, which creates new waste disposal problem. The ion-exchange, reverse osmosis, evaporation and freeze crystallization technologies can provide water with low metal concentration for discharge. However, the concentrated stream generated needs further treatment. The electrochemical method for metal recovery has an advantage over the conventional methods. It can recover metal as a metallic form for recycle and purify waste water for reuse as a rinse water.

For dilute solutions, such as plating rinse water, electrolytic recovery of metal is not efficient because of mass transfer limitation and low reaction rate per unit electrode area. A number of electrolytic cells have been designed with the electrodes that either enhance mass transfer rate or have a large surface area. Some of these designs are: porous electrode,[3] concentric cylinder,[3] rotating cylinder,[4] packed-bed,[5-8] fluidized-bed,[8-10] and carbon fibre.[11] The porous electrode, packed-bed, and carbon fibre provide a large surface area; whereas the concentric and rotating cylinders have a high mass transfer rate. The fluidized bed offers a large surface area and a high mass transfer rate; however, it has a high electric resistivity because electrode particles lose contact with the current collector during the fluidization movement.

This study examines the feasibility of using pulse current (PC) to enhance mass transfer rate and utilizing packed-bed to increase electrode surface area for metal recovery. The effects of cell current, solution flow rate, and PC parameters on the electrolytic treatment of waste copper solution were studied.

EXPERIMENTAL

Test Solution

Experiments were carried out to recover copper from a waste acid copper sulfate solution. Because the electrochemical cell used in experiments consisted of a cathode and an anode compartment, 10 liters of 0.012 M $CuSO_4$ (or 700 - 800 ppm copper ion) and 0.01 M H_2SO_4 were used as the catholyte (the simulated waste solution), and 10 liters of 0.01 M H_2SO_4 were used as the anolyte.

Electrochemical Cell

The structure of the electrochemical cell used in experiments is shown in Figure 1. The cell size is 0.12 m^2. It includes three cell modules and each module has two compartments, a cathode compartment and an anode compartment. There is a membrane between the cathode and the anode to separate the catholyte and the anolyte. Electrolyte distributing frames are used at the inlet of the cathode compartment and anode compartment, respectively. The electrolyte volume in the cell is approximately 3 liters. The cathode is a packed-bed electrode. It is packed with irregular graphite particles with the equivalent diameter of 1-2 mm. The void fraction is about 0.5. The packing depth is 9 mm. The anode is DSA/O_2, pH below 2 electrode (Electrode Corporation, Chardon, OH). The membrane is NE450 (Dupont Limited). The distance between the anode surface and the membrane is approximately 2.5 mm. The packed-bed cathode almost reaches the membrane on the other side. A thin net between the cathode and the membrane serves as a turbulence promoter for the catholyte flow channel.

Experimental Setup

Experiments were conducted to recover copper with a batchwise recirculation operation. The experimental setup is schematically shown in Figure 2. The system consisted of an electrochemical cell, a power supply, a catholyte holding tank, an anolyte holding tank, two metering pumps, two pH meters, two temperature meters and a voltammeter. The electrochemical cell, pumps, and holding tanks were connected with Tygon tubes. Two HDPE tanks were used as the catholyte and anolyte holding tanks. One metering pump (Masterflex I/P, Model 7529, Cole-Parmer, Niles, IL) with a flow range of 0.12 to 13 l/min was used to recirculate catholyte between the cathode compartment of the electrochemical cell and the catholyte holding tank. Another metering pump (the same model) was used to recirculate anolyte between the anode compartment of the electrochemical cell and the anolyte holding tank. Two pH meters (Model 5656-00, Cole-Parmer, Niles, IL) were used to monitor pH of the catholyte and anolyte during the experiment. Catholyte/Anolyte temperature were measured by two temperature meters (Model 2427, Westcon Corporation, Marion, OH). Two mixers (Model 6000, Arrow Engineering Co., Inc., Hillside, NJ) were used to stir catholyte and anolyte in the holding tanks during the experiment. A pulse reverse power supply (Model DPR20-100-400, Kraft Dynatronix Inc., Amery, WI) was used to supply either a constant current or a pulsed current to the electrochemical cell. A voltammeter (Model AP-101, Asahi Keiki Co., Ltd., Ohta-ku, Tokyo, Japan) was used to monitor the cathode-to-anode voltage during the experiment.

Experimental Procedure

For each run, the electrochemical cell and holding tanks were cleaned before the experiment. The acid copper sulfate solution and sulfuric acid solution were put in the catholyte and anolyte holding tanks, respectively. The mixers were turned on to stir the solution and two metering pumps were turned on to recirculate catholyte and anolyte between the electrochemical cell and holding tanks at the same flow rate. After several minutes, a sample was taken from the catholyte holding tank to analyze copper concentration. Afterwards, a current from the power supply was applied to the cell. During the electrolysis, 10 ml of aliquots were taken from the catholyte holding tank every 15 minutes and copper concentration was analyzed with a cyclic voltammetry method and an anodic stripping voltammetry method. A run was terminated when copper concentration dropped below 2 ppm.

RESULTS AND DISCUSSION

Experiments were carried out using direct current (DC) as a baseline. The effects of cell current and solution flow rate on electrolytic treatment of an acid copper sulfate solution were studied. Pulse current (PC) electrolysis was also compared with DC electrolysis.

The Effect of Cell Current

To examine the effect of cell current on the electrolytic treatment of an acid copper sulfate solution, three DC cell currents were used; they were: 5A, 10A, 15A. The corresponding apparent current densities were: 4.2, 8.3, and 12.5 mA/cm^2. The cell was operated in a batch mode, with the catholyte/anolyte recirculation between the cathode compartment/anode compartment of the cell and the catholyte/anolyte holding tanks at a rate of 2.5 l/min. The catholyte and anolyte temperature varied from 67 to 71°F. The pH of the catholyte and anolyte was constant during the experiment at 2.1. The cathode-to-anode voltage increased with electrolysis time. Figure 3 shows the copper concentration change with the electrolysis time for the three runs. As shown in the figure, the copper concentration decreased faster with higher cell current. The average current efficiency was 42%, 39%, and 27%, and energy consumption was 3.6, 4.3, and 7.2 kWh/kg Cu for the cell current of 5 A, 10 A, and 15 A, respectively. Therefore, at low cell current, the average current efficiency was high and energy consumption was low. The instantaneous cathodic current efficiency and energy consumption per kilogram of copper recovered for the three runs are plotted against copper ion concentration in Figures 4 and 5. As shown in the figures, the cathodic current efficiency and energy consumption were approximately equal for the three runs when copper concentration was above 100 ppm. However, when copper concentration dropped below 50 ppm, the current efficiency became less than 20% and energy consumption was above 10 kWh/kg Cu for the cell current of 5 A, and the current efficiency became less than 10% and energy consumption was above 50 kWh/kg Cu for the cell current of 15 A. This was due to a large fraction of cell current used for the hydrogen evolution side reaction at low copper ion concentration. The results indicate that: 1) low cell current is more efficient than high cell current, especially when copper concentration is low; 2) DC method is not efficient for the treatment of waste copper sulfate solution when copper ion concentration was below 50 ppm.

The Effect of Solution Flow Rate

Experiments were carried out at a cell current of 20 A (DC) with two solution flow rates of 2.5 l/min and 6 l/min. The other operating conditions were the same as described above. Figure 6 shows the instantaneous current efficiency vs. copper ion concentration for the two runs. As shown in the figures, with the high solution flow rate, the current efficiency was high. The better performance at high solution flow rate was due to the high mass transfer rate at the high flow rate.

Comparison of PC and DC Results

Experiments were conducted with pulse current (PC) electrolysis at different frequencies, duty cycles, and peak currents. The results were compared with DC electrolysis at the same average cell current. Depending upon the PC parameters, some PC runs improved the electrolytic treatment of waste copper sulfate solution compared to DC electrolysis, and the improvement was especially obvious when copper concentration was below 100 ppm. Figure 7 shows the copper concentration vs. electrolysis time from 800 ppm to below 2 ppm for the DC run of 5A and PC run of 10 Hz frequency, 10% duty cycle, and 5A average current. Two runs were carried out at a solution flow rate of 2.5 l/min. As shown in the figure, when the copper concentration was above 100 ppm, PC and DC had similar results. However, when the copper concentration dropped below 100 ppm, it took less time for PC to decrease the copper concentration. Figure 8 shows the copper concentration change with electrolysis time from 100 ppm to less than 2 ppm for this DC and PC operation. As shown in the figure, PC improved the electrolytic process compared with DC when copper concentration was below 100 ppm. In Figure 9, DC was 5 A and PC was 100 Hz frequency, 2% duty cycle, and 5A average current. As shown in this figure, PC also had

better performance than DC when the copper concentration was below 100 ppm. PC had about 19% improvement for copper concentration dropping from 100 ppm to 1 ppm.

The reason can be explained as follows. When copper concentration is high, the electrolytic process of waste copper treatment is not limited by mass transfer. In this case, PC does not show its advantage (high mass transfer rate) over DC. When copper concentration becomes low, the process is limited by the transport of copper ions from bulk to the electrode surface. In this case, high mass transfer rate is needed, and PC does show its advantage over DC. According to Chin's study[12], mass transfer rate can be increased by one to three orders of magnitude with PC electrolysis at high frequency and low duty cycle. We expect more improvement with PC electrolysis in our copper recovery experiment, especially at high frequency and low duty cycle. However, we did not see such a improvement. This is because throwing power is smaller for PC compared to DC in our experiment, especially at low duty cycle[13], resulting in smaller active (utilized) electrode surface area in PC electrolysis.

CONCLUSIONS

A study has been made to electrolytically treat waste copper sulfate solution with a packed-bed cathode using DC and PC electrolysis. Copper concentration was reduced from 800 ppm to below 2 ppm with average current efficiency of 25% - 45%, and average energy consumption of 3 - 10 kWh/kg Cu, depending upon the operating conditions. The effect of cell current and solution flow rate on the electrolytic treatment of waste copper solution was studied. The high current efficiency and low energy consumption were obtained with low cell current and high solution flow rate. PC results were compared with DC results at the same average current. PC does not improve the electrolytic process of waste copper treatment when copper concentration was above 100 ppm; however, it improves the process when copper concentration was below 100 ppm.

ACKNOWLEDGMENT

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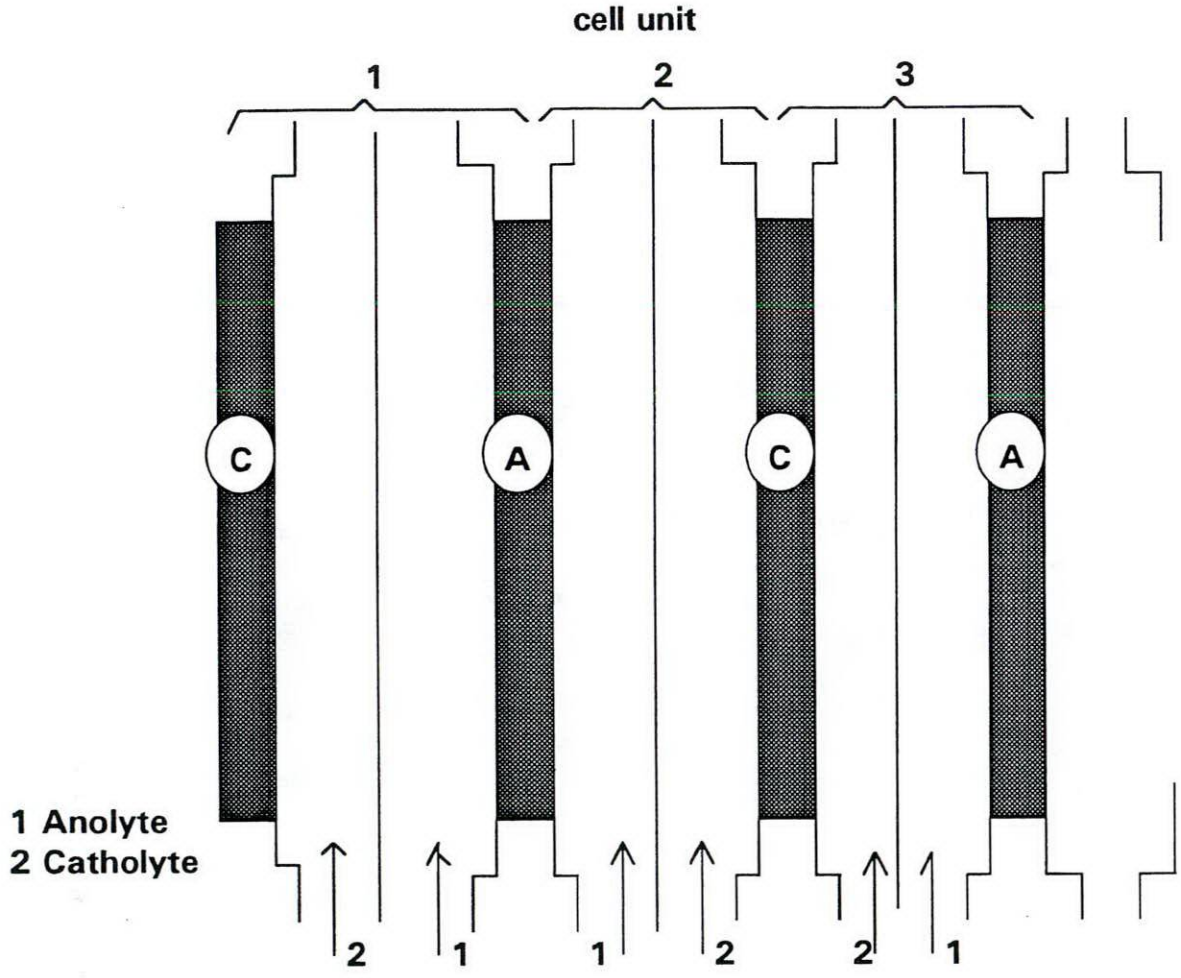


Figure 1: The structure of electrochemical cell.

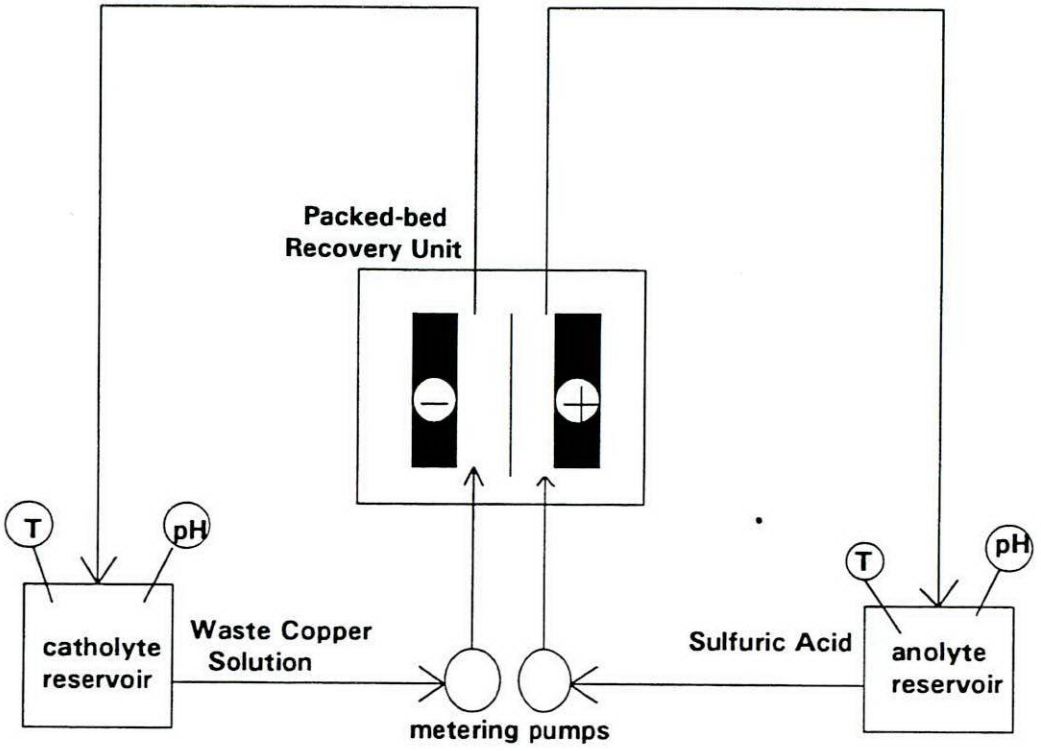


Figure 2: Schematic of experimental setup.

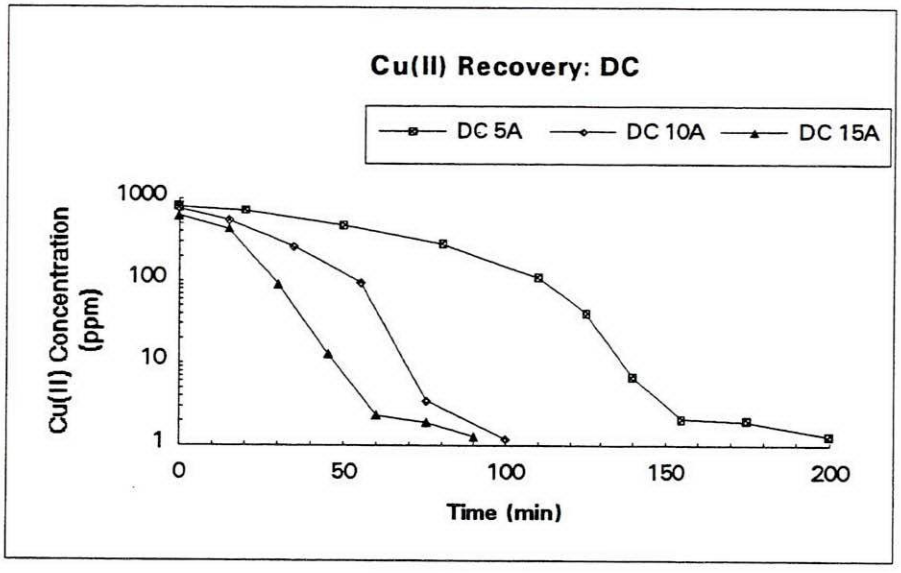
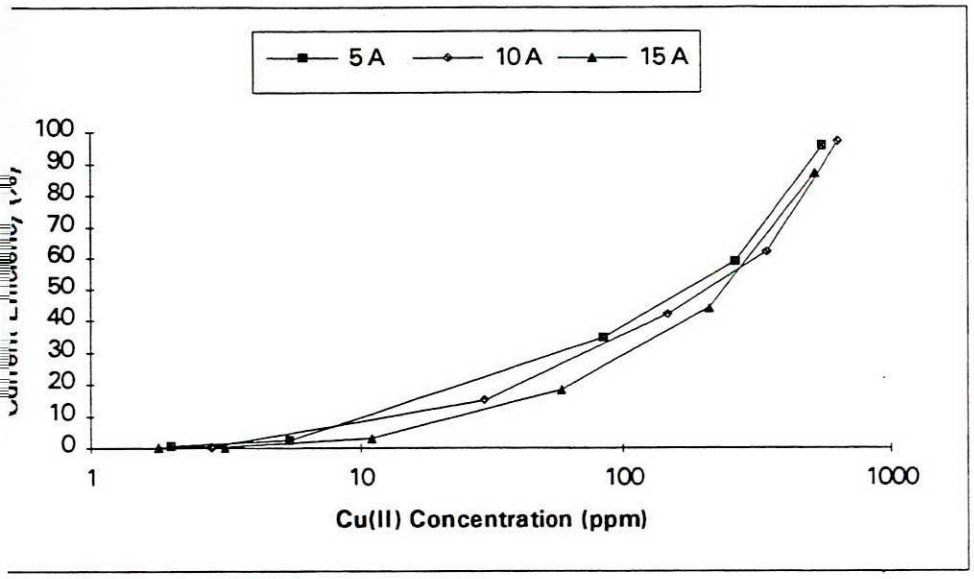
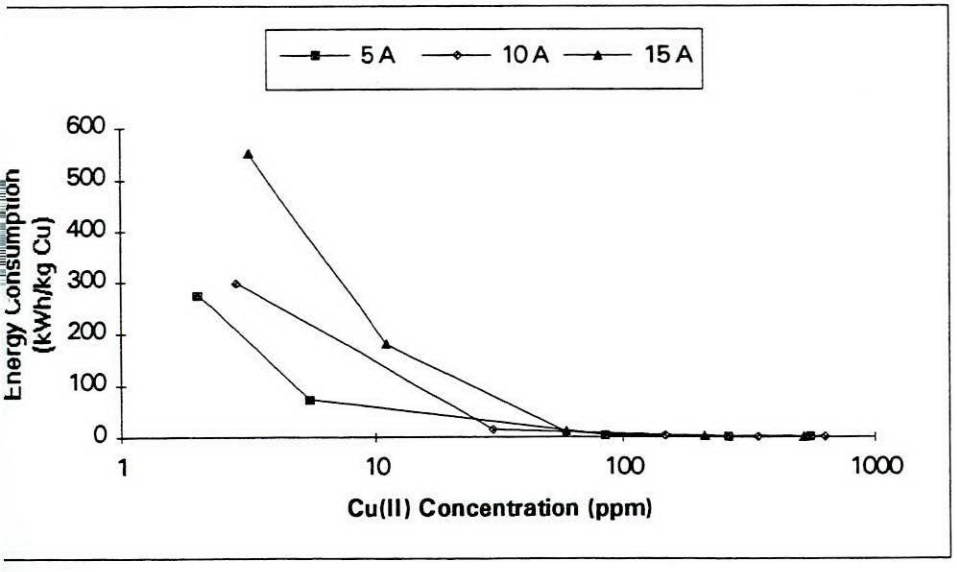


Figure 3: Copper concentration vs. electrolysis time for the treatment of waste copper solution at three DC currents of 5 A, 10 A, and 15 A.



re 4: Cathodic current efficiency vs. copper concentration

at the three DC currents of 5 A, 10 A, and 15 A.



ıre 5: Electric energy consumption vs. copper concentration at the three DC currents of 5 A, 10

ınd 15 A.

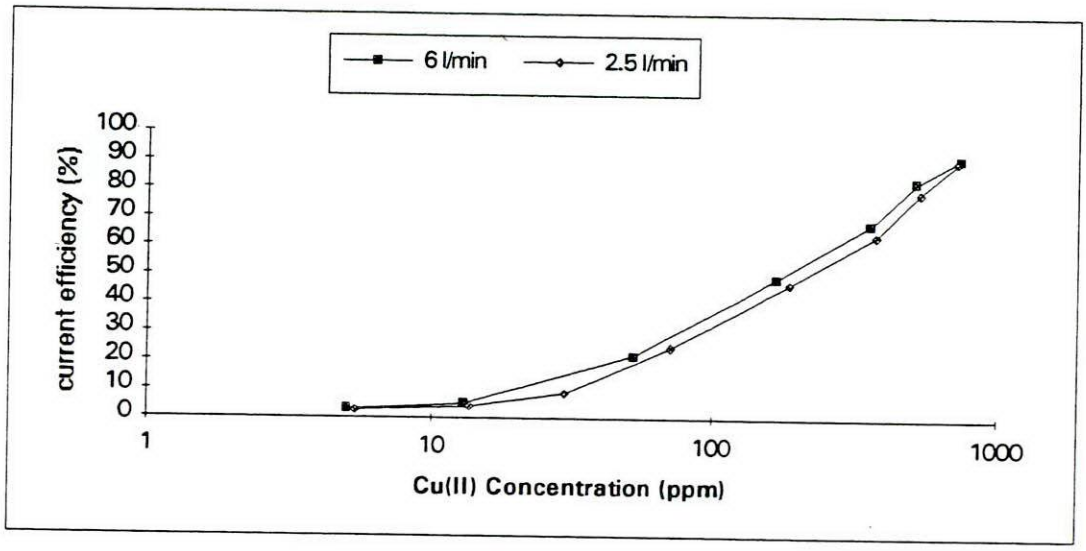


Figure 6: Current efficiency vs. copper concentration at a cell current of 20 A and two solution flow rates of 2.5 l/min and 6 l/min.

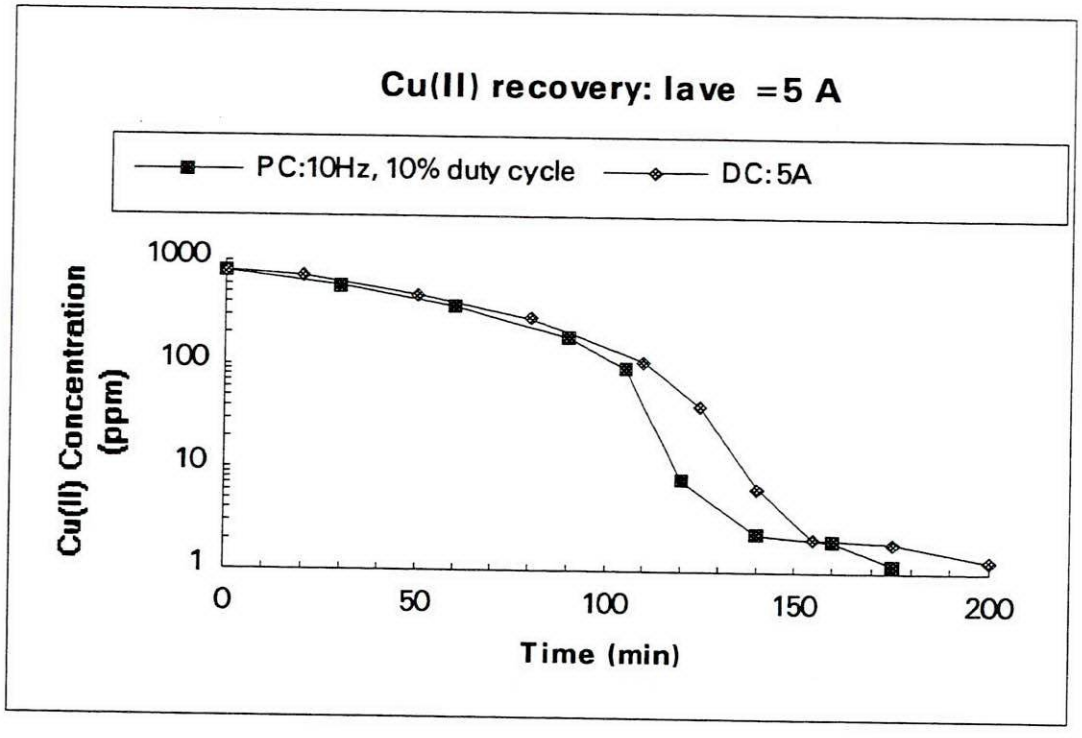


Figure 7: Copper concentration change with electrolysis time from 800 ppm to below 2 ppm for DC 5 A and PC of 10 Hz frequency, 10% duty cycle, and 5A average current.

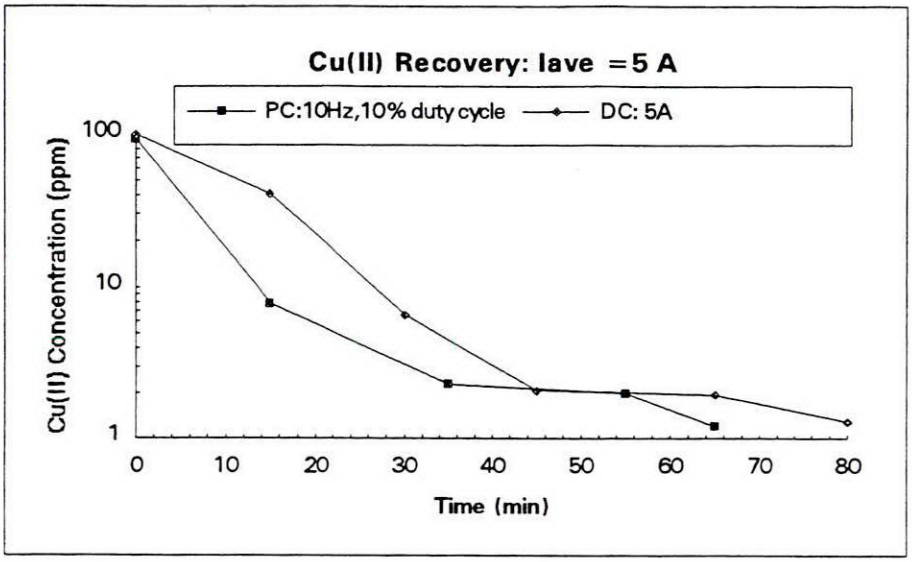


Figure 8: Copper concentration change with electrolysis time from 100 ppm to below 2 ppm for DC 5 A and PC of 10 Hz frequency, 10% duty cycle, and 5A average current.

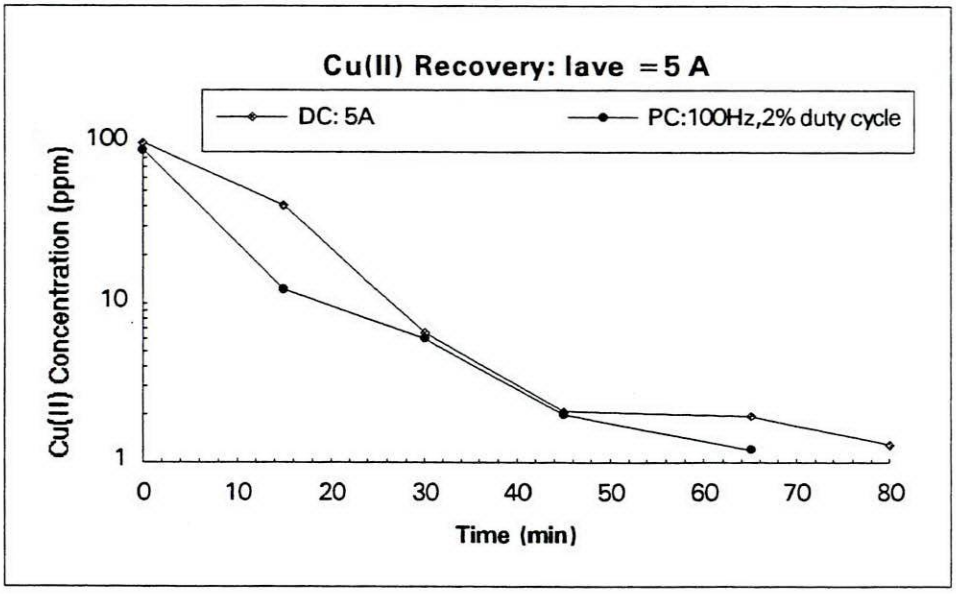


Figure 9: Copper concentration change with electrolysis time from 100 ppm to below 2 ppm for DC 5 A and PC of 100 Hz frequency, 2% duty cycle, and 5A average current.

PRACTICAL RECOMMENDATIONS FOR COMPLIANCE WITH THE CLEAN AIR ACT AMENDMENTS

American Electroplaters and Surface Finishers Society
SUR/FIN '94

GEOFFREY A. GLANDERS
August Mack Environmental, Inc.
Indianapolis, Indiana ~ Chicago, Illinois ~ Columbus, Ohio
1-800-837-6363

Regulatory Determinations, Exemptions and Fees

I. State Construction Permit Requirements
(Minor Sources of Criteria Pollutants Only)

A. Based on State "Allowable Emissions" Which is the Lowest of:
1. Maximum Facility Capacity (8,760 hours)
2. Most Stringent Regulations (NSPS, NESHAP, SIP, etc.)
3. Federally Enforceable Operational Limits
4. Emission Rates
5. Without Controls

B. Preconstruction Permits
1. Indiana Construction Permits
   a. All Sources Must Apply
   b. $500 Filing/Registration fee
   c. IDEM Determines Exempt, Register or State Permit
2. Ohio Permits to Install
   a. Sources >10 lb/day must apply
   b. Some Sources Exempt
   c. Emission Rates Determine Registration or PTI

C. Operating Permits
1. Obtain Operating Permit
   a. Prepare Application
   b. $75 - $30,000 Annual Operating Permit Fees
   c. Multi-Year Permit
2. Emission Control Dictated by Source Type and Location
   a. New Source Performance Standard (NSPS)
   b. Reasonably Available Control Technology (RACT)
   c. State Best Available Control Technology (BACT) for VOCs
   d. State Synthetic Minor

II. State New Source Review Construction Permits
(Major Sources of Criteria Pollutants Only)

A. Based on Federal "Potential to Emit"
1. Considers Operational Restrictions
2. Considers Emission Control Equipment

B. Attainment Areas
1. Obtain PSD Permit
a. $12,500 - $30,000+ Permit Fee
b. Emission Controls Obtained by:
i. New Source Performance Standards (NSPS)
ii. Best Demonstrated Technology (BDT)
iii. Best Available Control Technology (BACT)
2. Federal Synthetic Minor
a. Eliminates PSD Permitting
b. State Permit Imposes Operating Restrictions
i. Operating Schedule Limitations
ii. Material Use/Throughput Limitations
iii. Emission Control Equipment

C. Non-Attainment Areas
1. Obtain Emission Offset
a. $12,500 - $30,000+ Permit Fee
b. Emission Controls Obtained by:
i. Emission Offsets
ii. Lowest Achievable Emission Rate (LAER)
2. Federal Synthetic Minor

III. State Administered Federal Part 70 Operating Permits
(Major and Affected Sources of Criteria Pollutants & HAPs)

A. Based on Federal "Potential to Emit"
1. Considers FESOP Operational Restrictions
2. Considers FESOP Emission Control Equipment

B. Parallel Construction Permit Program
1. Enhanced New Source Review
2. Becomes Initial Part 70 Permit

C. Obtain Part 70 Permit
1. Existing Sources Apply Before November 15, 1995
2. IDEM Must Respond by May 15,1997
3. New Sources Apply within 1 Year of Start up
4. Renewals Within 9 Months of Expiration
5. $7,300 - $184,700 Annual Fees
6. Emission Controls Obtained by:
a. PSD or Offset Controls for Criteria Pollutants

b. Maximum Available Control Technology (MACT) for HAPs

D. Federally Enforceable State Operating Permit (FESOP)
   1. Application Schedule Same as Part 70
   2. $3,500 Application Fee
   3. Small Annual Operating Fee
   4. Emission Controls Obtained by:
      a. Operating Schedule Limitations
      b. Material Use/Throughput Limitations
      c. Emission Control Equipment

E. Source Specific Permit-By-Rule (General Permits)
   1. Permitted Upon Request
   2. Minimal Permit Fee
   3. Emissions Controlled by:
      a. Operating Requirements
      b. Recordkeeping & Reporting Requirements

F. Non-Major Area Sources
   1. Presently Deferred
   2. Generally Available Control Technology (GACT)

How to Prepare

I. Air Emission Audits

- A. Level 1 - Inventory
- B. Level 2 - Mass Balance
- C. Level 3 - Emission Factor Estimates
- D. Level 4 - Stack Testing

II. Level 1 HAP Inventories

- A. Identify HAP Products
- B. Estimate HAP Contents
- C. Obtain Purchase Volumes
- D. Multiply Purchase Volumes by HAP Content
- E. Compare to Thresholds

III. Level 2 - HAP Mass Balance

- A. Diagram Production Processes
- B. Identify Input/Output Stream
- C. Estimate Input/Output Compositions
- D. Determine Air Emissions from Output

IV. Level 3 - Emission Factor Estimates

- A. U.S. EPA Publications
- B. Trade Associations
- C. Industry Sources

V. Level 4 - Stack Testing

COMPLYING WITH THE NEW AIR TOXICS REGULATIONS UNDER THE 1990 CLEAN AIR ACT AMENDMENT

Geoffrey A. Glanders
August Mack Environmental, Inc.

INTRODUCTION

The passage of the 1990 Amendments to the Clean Air Act (CAA) will greatly increase the number of businesses that will have to control and permit air emissions associated with their operations. This increase will primarily be a result of the air toxic provisions that will expand the number of regulated hazardous air pollutants (HAPs) from seven to 189 chemical constituents. Previous versions of the CAA had focused on regulating conventional pollutant emissions (i.e. VOCs, particulate, carbon monoxide, nitrogen oxides, sulfur dioxide, etc.) from "heavy industries" such as automotive, iron and steel, utilities, petroleum refining and petrochemical. These industries will continue to receive the brunt of the regulatory burden but the new air toxic provisions will also regulate several smaller industries such as printers, dry cleaners, metal working shops, commercial bakeries and service stations. The economic impact associated with the 1990 CAA amendments has not been fully assessed but some analysts have predicted that the total impact will range from $7 to $60 billion annually.

HAP EMISSION AUDITS

In order to minimize these impacts and to develop a strategy for future compliance, air emission planning is necessary. One planning tool currently being used by large and small industries is an air emission audit. The audit is used to estimate the type and amounts of HAPs that are emitted to determine if a facility is a major or minor emission source. The new air toxic regulations require permits for any new or existing source that emits greater than 10 tons per year (tpy) of any one HAP or greater than 25 tpy of all HAPs combined. Sources that emit HAPs in excess of these threshold rates will be classified as "major" emission sources and will likely have to install pollution control equipment. Major sources which voluntarily reduce their emissions by 90% over 1987 levels prior to 1994 will be given a six year extension to install this equipment. Minor sources are required to register with the appropriate regulatory authorities but will probably not have to install control equipment.

There are four auditing techniques that can be used to estimate emission rates. The four techniques are: Level 1 - HAP Inventory; Level 2 - HAP Mass Balance; Level 3 - Emission Factor Estimate, and; Level 4 - HAP Stack Testing. The appropriate technique is chosen according to the complexity of the industrial process and the proximity of the emission rate to the regulatory threshold. Typically, these auditing techniques are performed sequentially until an adequate HAP emission estimate is generated.

Level 1 - HAP Inventory

The HAP inventory is a screening procedure used to determine if the regulations will apply to a particular facility or operation. The inventory involves determining the amount of HAPs utilized at the facility and can commonly be performed by facility personnel. The inventory is conducted by reviewing purchase records and material safety data sheets (MSDSs) for all products and raw materials used at the facility. The MSDS review will indicate the products which contain HAPs and the percentage of HAPs in each. Multiplying the annual purchase quantity of HAP containing products by the percentage of HAP in each will yield the amount of HAP handled at the facility. If the facility purchases less than 10 tpy of any one HAP or a total of less than 25 tpy, then it cannot be considered a major source.

Level 2 - HAP Mass Balance

If the HAP inventory indicates that the facility utilizes more than the threshold amounts, a mass balance should be conducted. The mass balance estimates the amount of the purchased HAP that is emitted from the manufacturing process by reviewing facility processes and performing engineering calculations. The process review involves: inspecting and preparing flow diagrams for all production processes; identifying associated HAP containing raw materials; documenting the changes that occur to each material during processing, and; identifying each source of air emissions. A typical process includes a raw material input and finished product and waste outputs. Waste outputs often include liquid discharges (i.e. wastewater), solid wastes or air emissions. In order to perform the mass balance, the HAP content of each output stream, except air emissions, must be known. The HAP emissions are then estimated by subtraction. This is an effective means of estimating air emissions from simple processes, however, care must be taken to understand the impacts the process may have on HAP generation. Many processes involve extreme conditions of heat and/or pressure which can produce or destroy HAPs which must be accounted for during the mass balance computation.

Level 3 - Emission Factor Estimates

If the mass balance approach indicates emission rates above the threshold quantities, or if insufficient information is available to compute the mass balance, emission estimates can be prepared using emission factors established by United States Environmental Protection Agency (USEPA) or other industry sources. In this method, emission rates are estimated by multiplying published emission factors by facility production or throughput rates.

Two USEPA documents that are commonly used to estimate emissions are: "Compilation Of Air Pollutant Emission Factors, AP-42, Fourth Addition", (AP-42), and; "Aerometric Information Retrieval System, Facility Subsystem Source Classification Codes and Emission Factor Listing For Criteria Air Pollutants" (AIRS). These documents contain emission factors for conventional pollutant emissions associated with a wide variety of sources including: Dry Cleaning; Surface Coating (painting); Printing; Pharmaceutical Production; Bread Baking; Iron and Steel Production; Petroleum Refining, etc. If the percentage of HAP associated with a conventional pollutant is known, then these documents can be used to estimate HAP emissions. For example, if a paint solvent contains 75% toluene (which is a VOC and HAP) and 25% other VOCs which are not HAPs, the HAP emission rate would be 75% of the VOC emission as determined by the USEPA emission factor for VOCs.

There are two main disadvantages with the use of USEPA emission factors. First, emission factorshave not yet been established for HAPs and the example noted above can only be applied to simple processes. Second, the USEPA emission factors tend to be very conservative and, as a result, overestimate the emission rate. In order to compensate for these limitations, many suppliers of HAP containing raw materials or products are developing emission factors for their products which can aid in estimating HAP emission rates. The suitability of these industry supplied emission factors in demonstrating compliance has not yet been proven, however.

Level 4 - HAP Stack Testing

If the first three audit steps yield results which are over the threshold limits or if insufficient information is available to use these techniques, then HAP stack testing should be considered. Stack testing is the most accurate means of estimating HAP emissions, however, it is the most costly. The testing procedures used and the associated costs depend on the stack characteristics and the HAP parameters. Some of the more unique HAPs do not have USEPA approved test methods and, as such, research and development is necessary to test for these parameters.

SUMMARY

The 1990 CAA amendments will dramatically expand the number and type of industries that will require air emission permitting and installation of air pollution control equipment. The most expansive amendment provision relates to the regulation of air toxics. A cost effective way to determine if a facility will be regulated is to perform a HAP audit. The Level 1 inventory may be capable of demonstrating that small operations do not require permits or may indicate areas where material substitution could eliminate permitting. Other facilities may require more sophisticated audit techniques such as mass balance, emission factor estimates or stack testing to determine the compliance status. Performing the first three audit procedures can effectively reduce HAP stack testing costs by enabling the facility to concentrate on those sources which have the greatest potential for HAP emissions. This can substantially reduce the number of stacks which require testing. Regardless of the technique used, the audit results will aid in developing a plan for complying with the air toxics provisions of the 1990 CAA amendments.

Practical Pollution Prevention Techniques for Platers

Thomas Allegretti, Amerdec, Inc., Waukegan, IL

CLEANERS - As in plating, we make up the cleaners with deionized water, use a deionized spray as s Keep Full and wash the cleaner back for re use. The cleaners are filtered at high flow and last indefinitely. Since the D.I. spray removes most of the cleaner, recycling the rinse is only a few dollars a month. There is no water to drain and about 90% re use of the cleaners.

ETCH - We are testing a very simple bag filter for the etch. We expect to keep the solution relatively free of aluminate. Again we use a spray to wash to the Etch back into its tank As in plating where there are 2 rinses, the first rinse has a deionized spray and the 1st rinse supplies the spray for the spray over the Etch. As a result, almost all of the Etch is re used - but more important - there is no water to drain. Where there is only one rinse, that rinse can be recycled since the spray washes most of the solution into the Etch tank

DE OX or DESMUT - We do nothing to this tank. When there is only one rinse, we use a spray over the 1st rinse and recycle the anodizing rinse and use that as the 2nd rinse.

ANODIZE - The acid is recycled to maintain a low level of Aluminum in the acid. We use an Ion exchange to replace the aluminum for an hydrogen ion to form sulphuric acid. This method reduces large amounts of water to drain.

APU or acid purification units may cost 20 times the Cation method. Amerdec's purpose is to reduce water to drain and to reduce costs so that the Metal Finishing Industry can compete with the rest of the world. Converting the Aluminum Sulphate to acid can reduce the acid to drain by a high percentage.

Rinses- Where there are single rinses, we use the Desmut or Deoxidizer rinse as a tap spray rinse and recycle the anodizing rinse. Therefore, in Desmut, you will have a spray over the Desmut rinse and then go to the recycled anodizing rinse. From there the next station is the Anodizing for which the 1st rinse is the Desmut with the spray and then back to the recycled anodizing line.

By using the above system the results are:
1. Instead of flowing rinses, the only water used is a 5 - 7 second spray when the bar leaves that rinse station, yet you have a high purity recycled rinse in the anodizing.
2. In the whole line, the only water to drain is two timed sprays, from Desmut and Anodizing.
3. The last rinse is high purity and does not contaminate the seal.

DYES - Most of the dyes are at high temperature. I recommend a deionized spray as the parts leave the dye and hen go into a recycled rinse. In this way you get your dye back with no water to drain.

In Anodizing you can recycle 400 gpm for as little as $300.00 per month. The usual recycling cost for anodizing is .037/1000 gallons of high purity water.

PRINTED CIRCUIT - This is handled in the same manner as in plating. The only problem in Printed circuits is the Electroless Copper with EDTA. Using ion exchange, the EDTA replaces the copper on the resins hence the copper is not picked up. This is especially true on Final Heavy Metal Removers, where the copper goes to drain. Amerdec uses its special patent applied for cooling towers to evaporate the solution so that all of the electroless copper goes back into the copper tank for re use. There is no water to drain from this station. The cooling towers are used on all ambient solutions.

Most Printed Circuit plants should be able to recycle their rinses for about $200.00 per month and have unlimited amounts of water for re use. Sprays are the answer to the Printed Circuit rinse problems.

To conclude - I feel that future regulations in smaller towns and cities will be far more stringent and it is for this reason that the Amerdec Systems tend toward almost complete re use.

These systems can be installed with no investment. Actually, since they pay for themselves and are on a Lease/Sale basis, the rental is deductible and the savings pay for the rental.

As a rule, there is little or no water to drain in the Cleaner Station. The big savings are the cleaners themselves. Wh there are 2 rinses almost 95% of the cleaner cost is saved.

The next station is the ACID. Where actual acids are used instead of acid salts, the acids are never dumped. There are 2 ways of removing metals from an acid tank.

Where Muriatic acid is involved, we use an ANION resin. This resin uses an amine in its manufacture. Many mete mostly copper, zinc, cadmium and iron will complex with the resin. The acid is simply recycled for a few hours and pic up the metals. What is so remarkable about the resin is that only water is necessary to wash off the metals, to collection point.

Other acids - with 20% or less by volume - use a CATION resin. Since we are dealing with an acid solution, the me pick up is not as efficient. What actually happens is that the metal ions exchange with the loosely held Hydrogen ions the resin. If we are recycling Sulphuric, with copper in it, the copper is there as a sulphate. When the copper stays the resin the molecule becomes Sulphuric acid. One of the advantages of this system is that you can regenerate with less expensive acid.

During recycling some of the copper ions stay on the resins and the hydrogen ion comes off thus changing the copp sulphate to acid reducing the percentage of copper in the acid tank. Since copper sulphate is always forming, you m recycle the acid on a set timer basis - enough to maintain a low copper content.

When it is worth while, MURIATIC ACID can regenerate the resins. However, the resins must be rinsed to get rid of t chlorides. Whereas if the same acid that is recycled is used to regenerate, there is no rinsing.

As a rule your acid savings are in the 70% range. There is no need to decant and you maintain the strength of the aci

As to rinsing - the first acid rinse goes directly to either waste treatment or metal pick up. The second rinse is recycle In a HAND or HOIST rack line, we use a deionized water spray rinse unless softened water is used.

BARREL LINE- We usually use 2 gpm in the 1st rinse. The 2nd rinse is recycled, filtered and deionized. Where there but one rinse we can use one rinse for 2 or 3 solutions and the recycled rinse for 2 or 3 solutions. In any case there is great savings in acid costs. This is only possible on a hoist line - the Barrel may go to a recycled cleaner rinse o recycled plating rinse.

PLATING SOLUTIONS - In hot solutions 140°F chrome, copper or nickel, we use a deionized spray over the soluti and recycle the rinses. Where there is a BARREL NICKEL I suggest three rinses so that the first 2 can counterfl back to the plating tank The rinse is recycled and deionized. To re use plating solutions, 3 rinses are far more efficien

When you are plating Tin, Cadmium, Zinc or one of the zinc alloys, we use special cooling towers for which a Pate has been filed. Some Alloys cannot use the towers since they form carbonates too readily.

Where the towers can be used almost all of the solution can be re used with NO WATER TO DRAIN. This makes t use of cyanide more practical - there is no need for oxidation of the cyanides and precipitation. It is especially import. In the Amerdec System where we pick up all of the metals by ion exchange to less than 0.5 ppm.

As a rule, there are no solids other than the filters, 99% of the water is used at a cost of .06 - .07 per i000 gallons, with pay back usually in one year.

Most of the time, the savings on the solutions , cleaners, acids and plating solutions pay for the rinsing - N POLLUTION and unlimited water usage are free. The system is exceedingly simple - just re use almost everything. Usually, on a Rack line we go to drain with about 10 gph and recycle 100 gpm for less than $ 100.00 monthly. On Barrel line we go to drain with 120 gph and recycle 200 gpm for about $200.00 monthly. and recycle 200 gpm approximately $200.00 monthly

In ANODIZING.- You only go to drain with 2 sprays, usually 5 - 7 seconds and recycle all the water you want at abo .037/1000 gallons. We recycle the sulphuric acid to maintain a low level of aluminum. The sprays going to drain are fr the Desmut and the Anodizing. If there is no drain we can completely close the line with nothing to drain. We wou have to use our cooling towers. I do not think the savings warrant the cost when you can go into the city sewers Remember, the safest place to discharge is the city sewers. Pollution is the easiest to handle if you re use.

MERDEC, INC 90 le Baron Waukegan, IL 60085 708 623 6650 (FAX) 708 623 636

The Metal Finishing Industry was guilty of more waste and pollution than any other industry with the exception, perhaps, of atomic energy. Then came the EPA, it not only continued the waste and pollution but also wasted a lot of money on precipitation in an attempt to comply with the EPA regulations.

The EPA was equally guilty, regulations were haphazard as was most of the enforcement. Yet, I feel, that t the Finishing ndustry should bow their heads in thanks. At least the EPA caused the Industry to seek answers to problems, waste, re ise and pollution.

City Sanitary Districts, next to the Federal Government, the mines and the farmers are probably the next greater polluters. If the MSD could prevent heavy metals in their solids, they most would have a market for their compacted sewage

Because American Industry is competing with the World, businesses must reduce their costs and remain viable in their approach to success. Soon, Mexico will be a large factor as competition. The simplest way to reduce costs in Metal Finishing is re use. Actually, what percentage of your solutions are consumed in plating? If you can reduce your costs to actual usage, what would the savings be?

This lecture is about re using Cleaners, Acids and other surface finishing materials. Let's start with PLATING - Hand, Barrel and Rack and what we intend to re use

CLEANERS - there is never any reason to dump a Cleaner. You have - A caustic solution with some wetting agents and silicates— 1) Let us start by using deionized water for Make Up and Keep Full. Normally a cleaner solution uses tap water for Make Up. In most cities the tap water has about 200 ppm of dissolved solids. At about 180°, you will average a 10% evaporation. The second day, the Total Dissolved Solids would increase by 10% and so on.

If you keep the solution for 2 weeks or a month, your TDS becomes high enough to interfere with the cleaning. In addition to the dissolved solids, you have oil, dirt and heavy metals to aid and abet the decreasing efficiency of the bath.

If you use Deionized water for Make Up we have, for all practical purposes, ZERO dissolved solids except the cleaning solution. One result is greater efficiency of the cleaner. If we use deionized water for Make Up we add no dissolved solids to the bath, the bath remains like new.

The next step is to filter. In filtration we must remove dirt, oil and heavy metals. The filter removes the solids and the oil including precipitated metals. The dissolved metals, usually chrome, zinc and cadmium, we remove by ion exchange - an inexpensive method.

Remember, in a week a cleaner on the zinc line can have 20,000 ppm. You can drop this 90% for a few cents.
Other metals are not as soluble except Cadmium, yet, Trichrome will also be present and removed.

The Electro and Soak are handled in the same manner except the Electro; filter is smaller, there are less solids to pick up.

RACK LINE - In an automatic rack line we use a deionized spray as the parts leave the surface of the Electro Cleaner. This spray is equal to the evaporation of the Soak Cleaner and the Electro.

Where there is only one rinse, the prior spray removes enough solution so as to make recycling the rinse practical. This allows us to recycle the rinse.

BARREL LINE - In a barrel line, sprays are useless. If there is only one rinse on an automatic line, we can do nothing

CLEANER - If the barrel line is a hoist, we can use the 1st acid rinse as a prior rinse for both the cleaner and the acid. We would recycle and deionize the cleaner rinse. It is not the best, yet, though a few minutes are lost, we have a recycled rinse for both the acid and the cleaner. The pH of the rinse is in the 5.3 area, therefore, the acid is not neutralized and the following solution is not compromised. The ideal situation is for 2 rinses on Racks and 3 rinses for Barrel cleaners.



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WILL THE REGULATORS BELIEVE YOU?

"The $25,000 Question"

Thomas H. Martin, CEF

Delta Compliance Consultants, Div.
Delta Chemicals & Equipment, Inc.
3675 Newgate Lane
Indianapolis, IN 46236
(317) 898-6446

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Thomas H. Martin, CEF

Delta Compliance Consultants
Division of
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Abstract

The metal finishing industry has spent billions of dollars on pollution control and abatement during the past two decades. However, platers were once polluters and regulatory agencies still view electroplating operations as "suspect." Therefore, platers are frequently targeted by regulators for compliance inspections and enforcement actions. Fortunately, metal finishers can take positive steps to increase the likelihood of a favorable outcome during an inspection. This paper presents actions that platers can take to increase credibility and avoid the "red flags" that cause regulators to distrust metal finishers.

Key Words: compliance, credibility, electroplating, enforcement, inspection

Introduction

Small, family owned plating shops are easy targets for compliance inspections and enforcement actions. This is because small shops cannot afford to have a full time person on staff to be responsible for regulatory compliance. Also, large amounts of capital are not available to spend on legal council and law suits. However, the numerous regulations of the Clean Air Act (CAA), Clean Water Act (CWA), Dept. of Transportation (DOT), Occupational Safety and Health Administration (OSHA) and the Resource Conservation & Recovery Act (RCRA) still must be complied with.

Years ago, platers were polluters, and metal finishers were one of the first industries to be regulated by "categorical standards." Although electroplaters have spent millions of dollars on pollution control and abatement, little effort has been made to raise the credibility of the metal finishing industry. However, there are a few platers that enjoy the benefits of high credibility with the regulatory agencies. Some of these benefits are a better rapport with regulators and a de-emphasis on enforcement actions. This paper discusses some of the techniques these firms have used

to increase their credibility.

The key idea that this paper presents is metal finishers can increase their credibility with regulators. Here are three (3) techniques that have been successful:

1. Make a good first impression
2. Know regulations and waste treatment
3. Sharpen communication skills

However, before learning how to increase credibility we must learn about the components of credibility. Then specific techniques may be applied to each of the components.

What is Credibility?

Credibility is a perception, much like the attribute of charisma, which can be created in the mind of another person. There are three kinds of credibility which include initial, derived and terminal.[1]

Initial credibility is based upon past reputation. For example, a bad compliance record will lower initial credibility and vice versa. Also, a person's position or status in the organization, as well as title such as Dr. or Professor, will increase initial credibility.

Derived credibility results from face to face interviews and involves the total communication process which includes both verbal and nonverbal behaviors. We are influenced not only by words, but by eye contact, gestures, personal appearance and even office decorations.

Terminal credibility is the product of initial and derived credibility, and has a direct influence on future initial credibility.[2] For example, will a person's "believability index" go up or down after the interview is concluded? Therefore, to improve this index, one should work hard to improve both initial and derived credibility.

Improving Initial Credibility

As the saying goes, "you only get one chance to make a good first impression." However, chances are very likely that the inspector will already have an impression before visiting the regulated industry. This is because most regulators will review compliance records before making an

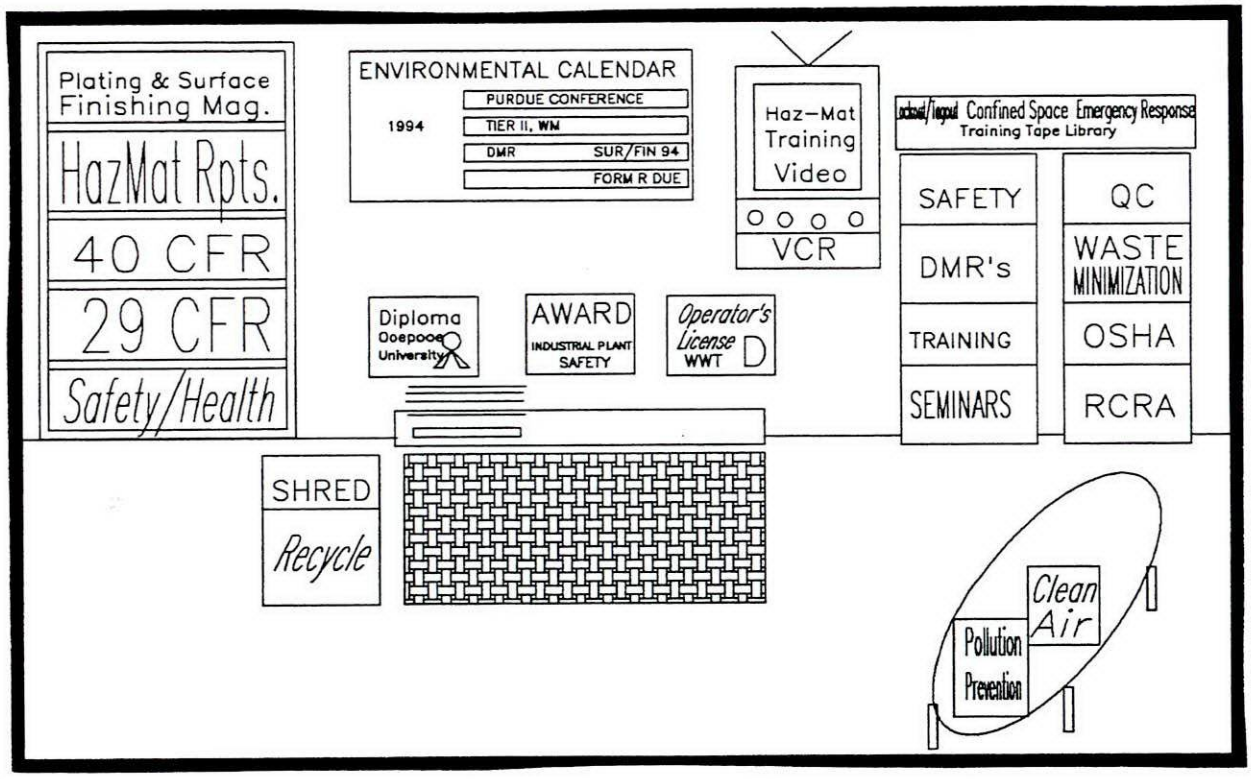
inspection. Therefore, initial credibility will be based on past history to a large extent. In light of this, a company with a good compliance record will probably benefit from higher initial credibility.

However, a good compliance record involves more than not having any violations on discharge monitoring reports (DMR's). The newspapers are full of stories about people being fined and put in jail for falsifying DMR's and tampering with monitoring devices. All reports must be accurate, factual and filed in a timely manner. Also, most platers have several reports to file annually which become public record. One such report, SARA Title III, Tier I and II requires reporting hazardous chemicals on hand above threshold planning quantities by March 1 each year. This information is accessible by the community under "Right to Know" laws. Another report also due on March 1 and required of large quantity generators (LQG), is the Biannual Hazardous Waste Report. In addition to these two reports is the U.S. EPA Toxic Chemical Release Reporting (Form R) which is due on July 1. With all this reporting, there is an abundance of information available to both the regulator and the general public as well.

Initial credibility can also be decreased by the improper handling of a Notice of Violation (NOV). Most cities or states are required by the EPA to send a NOV whenever the company is in non compliance. The recipient is required by law to respond to the NOV promptly. A letter must be sent summarizing the cause of the excursion(s) and the corrective action being taken to prevent future violations. Also, spills and permit violations must be reported within twenty-four hours to the regulatory authority.

Furthermore, the construction of privately owned waste treatment systems is usually a matter of public record. This is because most states require permits for construction of wastewater treatment facilities. Therefore, regulatory compliance inspectors will be familiar with the kind of equipment and chemical processes that are used to treat electroplating wastestreams. For example, most shops discharging over 10,000 GPD will have a continuous, flow-through system using conventional hydroxide precipitation chemistry to remove heavy metals. Since much of this information is stored on a computer data base, a regulator can learn a great deal about a company in a very short period of time. In fact, at least 50% of the company's initial credibility has been determined before the regulator leaves his or her office. An opinion has already been formed before the company has even been inspected. The personal interview will either reinforce or minimize these preconceived beliefs.[3]

Compliance inspectors are trained to be astute observers, have excellent memories and are generally fair in their dealings. Therefore, all is not lost if a company's compliance record is somewhat blemished. There are several techniques to improve initial credibility during the interview and inspection. For one thing, good personal appearance and good grammar are always a "plus." Also, office adornments such as certificates and awards displayed reflect underlying attitudes concerning the environment as well as professional development.[4] In fact, if one were to design an office for maximizing initial credibility with the regulators, it might look much like the following illustration.



Granted, this might be a bit overdone, but everything the manager needs is close at hand. For example, three ring binders with copies of DMR's, SARA Title III reports and U.S. EPA Form R are available for inspection. Also, certificates, diplomas and licenses are prominently displayed, as well as plaques and awards. The "library" contains reference books such as 40 CFR and several binders from professional compliance seminars.

Although the purpose of this office decor may not be readily apparent, every item makes a statement about the occupant. For instance, there may be an "ice breaker" which would tend to

promote "common ground" with the regulator, such as a school, associations or hobbies. Also, the regulator may be so impressed the company representative's ability to organize materials that he or she will presume that the facility is being managed in an environmentally responsible manner. Psychologists call this the "halo" effect which increases initial credibility dramatically.[5]

Improving Derived Credibility

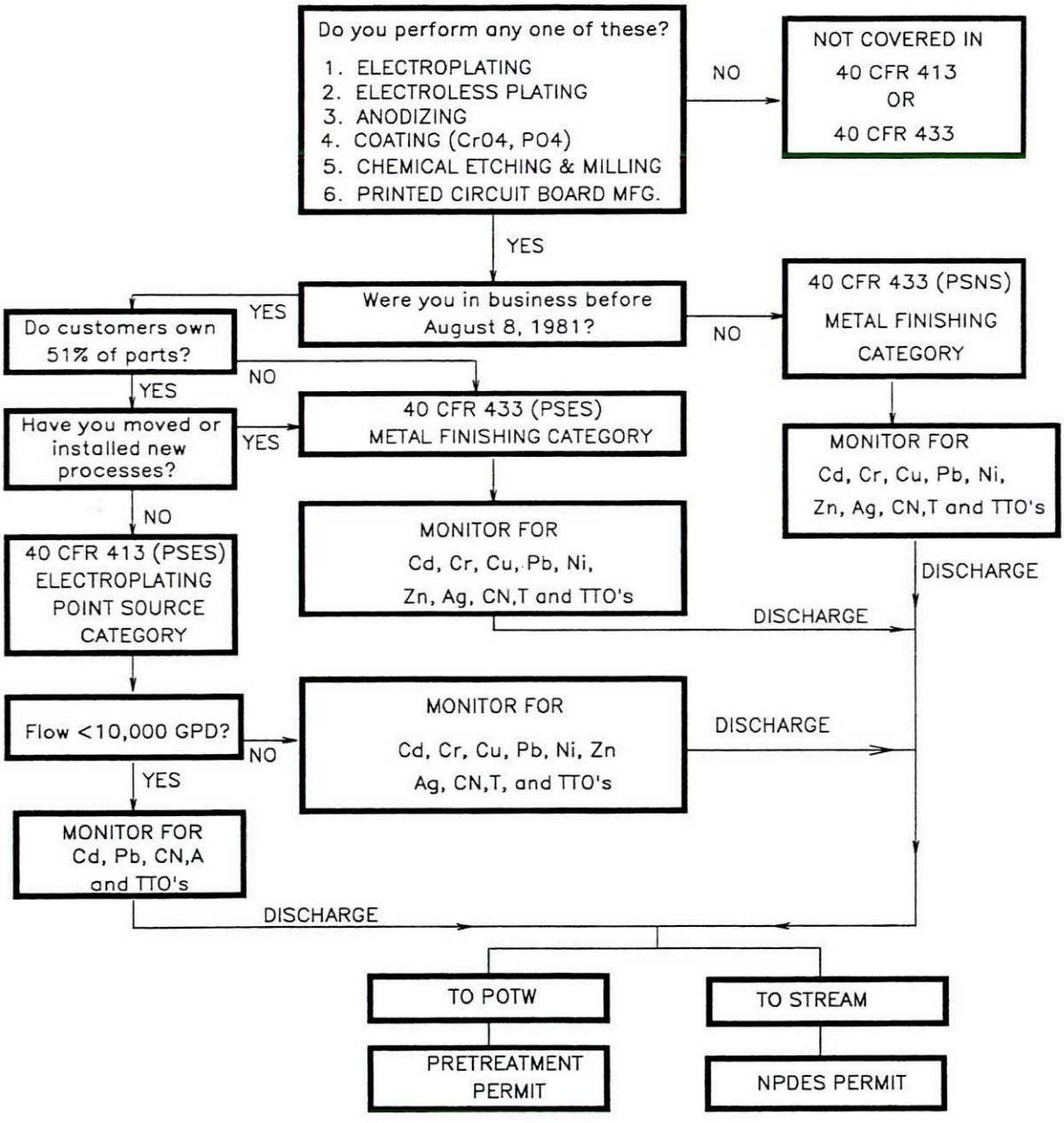
Derived credibility results from the effective interaction between the company representative and the inspector during the "face to face" interview. Being able to speak the regulation's language will help increase derived credibility. This means knowing and understanding the basic regulations of the metal finishing industry and how wastes are treated. Memorizing key parts of Title 40 of the Code of Federal Regulations (CFR's) would be impressive, but is not necessary. However, every electroplater should at least know if the company is regulated under 40 CFR Part 413 or Part 433 or both.

For example, if a company has been in the plating business for a long time, it is probably classified as a "electroplater" and falls under the Part 413 Categorical Standards. Part 413 is more commonly known as the "grandfather" clause. However, the customers must own at least 51% of the work being plated and if the company moves or installs new processes, it may be reclassified. The "electroplating" preexisting source standards are very desirable, because they have the most liberal discharge limitations. Also, the monitoring requirements are reduced for discharges less than 10,000 GPD.

On the other hand, if the electroplating operations were put in service after August 8, 1981, the process is classified as a "new source" and is regulated under the "metal finishing" categorical standards. These regulations are published in 40 CFR Part 433 and have much stricter limitations on the effluent being discharged.

Much confusion exists concerning the classification of facilities. There could be four electroplating shops on one city block and they could all have different discharge limitations. The following flow chart should help eliminate some of the confusion.

SURFACE FINISHING REGULATION FLOW CHART

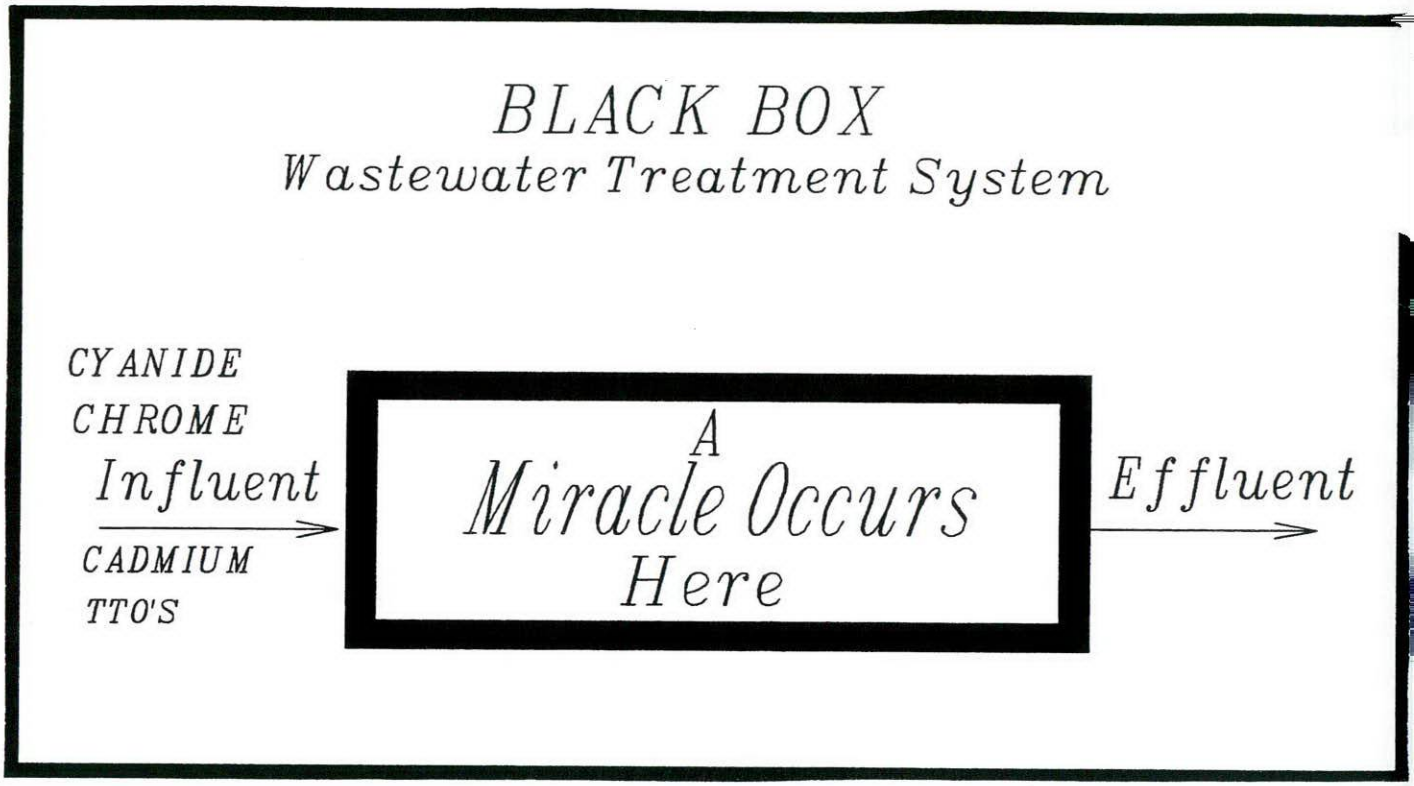


COMPILED BY
THOMAS H. MARTIN
DELTA COMPLIANCE CONSULTANTS
DELTA CHEMICALS & EQUIP., INC.

TOTAL METALS — Cu, Ni, Cr, Pb
(PSNS) PRETREATMENT STANDARDS NEW SOURCES
(PSES) PRETREATMENT STANDARDS EXISTING SOURCES

During the inspection, a copy of the pretreatment permit or National Pollutant Discharge Elimination System (NPDES) permit may be requested. Locating a copy during the pressure of the inspection can be difficult. It's a good idea to keep a copy of the permit in the same file with the monthly monitoring reports.

Generally speaking, the regulator will be familiar with processes used to treat electroplating wastestreams and will not appreciate evasive or inaccurate explanations of the system. Being knowledgable about how the company treats wastes will help increase derived credibility. An excellent way to learn about the system is with a flow diagram and some help from the certified operator. However, be prepared for much skepticism from the inspector if the flow diagram looks like the following illustration.



Typical electroplating wastewater treatment processes include chromium reduction, cyanide oxidation and the removal of heavy metals by hydroxide precipitation chemistry. Since the process produces sludge, it usually is regulated as a hazardous waste. Therefore, be prepared to produce manifests and answer any questions about disposal practices. Even if the sludge is not "listed" and is non hazardous, many states require a permit for disposal. For example, Indiana classifies sludge which is non hazardous waste as "special waste" and disposal is only permitted in specific landfills.

Perhaps one of the best credibility building "tools" available is effective communication during the interview. The better the regulator feels during the interview, the less prone he or she will be to "nit pick" while inspecting the facility. During the initial contact, work hard to develop rapport with the inspector. Keep interruptions to a minimum by having the secretary hold all calls and visitors. Remember that the communication process involves both the spoken word as well as non verbal behaviors such as eye contact and gestures. Ideally, the verbal and nonverbal communication should convey the same message. However, if the signals are crossed, the inspector will tend to believe the non verbal message.[6] It's important to maintain good eye contact when answering questions and avoid obvious manifestations of nervousness such as clicking a pen, biting fingernails, or fidgeting. Derived credibility is increased by giving straight forward answers to questions and never playing "stupid." If the question can't be answered directly, tell the inspector, "I don't know, but I'll find out." And then, make yourself a note to follow up on the information request.

Improving Terminal Credibility

Terminal credibility is the product of initial and derived credibility and has a direct influence on future credibility. This is why it is so important to "follow up" on any promises made during the interview and inspection. Also, it helps to get to know the regulator on a "first name" basis so he or she may be telephoned about regulatory matters. For instance, terminal credibility is increased when the inspector receives a phone call that is not the result of an enforcement action, but perhaps a request for information.

Conclusion

Metal finishers can learn how to increase their credibility with regulators. Foremost, make a good "first impression" by having a good compliance record. Install waste treatment equipment that is the standard of the industry. Organize the company office to reflect that the business is being managed in an environmentally safe and responsible manner. Learn to speak the inspector's language by being familiar with regulations and the treatment of electroplating wastes. During the inspection, work hard to develop rapport and strive to make verbal and nonverbal communication convey the same message. Give straight forward answers and don't be afraid to say "I don't know, but I'll find out." Be sure to "follow up" on any promises made during the interview and inspection. Also, try to get to know the regulator on a first name basis and don't be afraid to contact him or her personally when you need information.

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The Diffusion of Technology during Seventy Years of Anodizing

Arthur W Brace

Consultant, Stonehouse, Glos., England

Synopsis:

The development of anodizing technology since the granting of the patent for chromic acid anodizing in 1924 is reviewed. The relation between anodizing technology, materials and market requirements is examined with particular reference to the development of markets for automobile bright trim, architectural anodizing and hard anodizing. A detailed study is presented of the marketing strategy for anodized finishes used by a major aluminium producer. These developments are presented with particular reference to the author's involvement in them in the United Kingdom.

The means by which the information and technology involved have been diffused to anodizers is examined in some detail, with particular reference to the methods of communication used and the role of an Industry Association in the development of quality standards.

This paper is primarily a personal account of the development of anodizing arising from a professional involvement in the industry which commenced in the 1950's. It is also based on experiences initially gained mainly in the United Kingdom, but with ongoing and increasing contact over the years with colleagues in a number of countries, particularly the U.S.A.

The Early Commercial Development of Anodizing

The patent for chromic acid anodizing was granted in 1924 to J D Bengough and J D Stuart, working at the National Physical Laboratory, Teddington, England. It effectively established anodizing as a commercial process, with 1994 as the 70th. anniversary of the discovery of the process. However, it was the patenting of sulphuric acid anodizing in 1927 which provided the foundation for the growth of an industry whose world-wide turnover is now billions of dollars. The 70th. anniversary of the first commercial process is an appropriate occasion on which to look back and record how this growth took place.

In the 1930's there was a limited output of anodized aluminium, with early applications of its use for shop fronts, windows and doors. The colour anodizing of aluminium had been developed and markets for various anodized consumer goods had been established. The technology for electro-brightening reflectors and similar items had also been developed. The techniques for the production of silk screen and photographic reproduction of designs and lettering were developed in Germany in the 1930's and became firmly established as a result of their use during the 1939-45 war. Anodizing was widely used during World War II, but the technology employed was largely inappropriate to civilian markets.

The Development of Markets for Anodized Products

The basis of anodizing technology was established in the 1930's. An examination of the patent literature shows that patents for sealing in boiling water, nickel acetate and dichromate solutions, the use of electrobrightening, and silk screen printing, all date from that period. World War II saw the development of electropolishing, but otherwise did not give rise to any significant new technology (see Table 1). In the early post-war years anodizing was an infant industry. which began to grow rapidly once the economies of the industrialised countries had switched to meeting post-war needs. It is instructive to examine the development of anodizing technology as it developed to meet the needs of the major post-war markets.

Bright Trim: The Korean conflict in the early 1950's served as a warning of the instability of the post-war world. With it came a shortage of nickel, which lead to the use of bright anodized aluminium trim for automobiles, because of the poor reputation of nickel-chromium plating on automobile trim which resulted from the use of thin nickel coatings. The pioneering work in this application was a result of the recommencement of automobile production in Germany. Faced with the

Table 1: Important Patents relating to Anodizing and Related Processes

Patent No.	Year	Process
Brit. Pat. 223,994	1924	Chromic acid anodizing
Brit. Pat. 223,995	1924	Dyeing anodic coatings
Brit. Pat. 290,291	1927	Sulphuric acid anodizing
Brit. Pat. 388,787	1931	Sealing using nickel salts
Brit. Pat. 393,996	1931	Dichromate sealing
Brit. Pat. 406,999	1932	Water sealing
Brit. Pat. 407,457	1932	Water sealing
Brit. Pat. 413,814	1933	Nickel acetate sealing
Brit. Pat. 433,484	1934	Alzak ™ electrobrightening
Brit. Pat. 449,162	1934	Brytal™ electrobrightening
Brit. Pat. 496,436	1938	Steam sealing
Brit. Pat 613,478	1940	Phosphoric acid electropolishing
Brit. Pat. 612,???	1946	Phosphoric acid electropolishing
Brit. Pat. 659,747	1947	R5 chemical polishing
Brit. Pat. 675,444	1950	H_3PO_4–H_2SO_4–HNO_3 chemical polishing
U.S. Pat. 2,550,544	1951	Battelle electropolish
Brit. Pat. 716,759	1952	D.C. + A.C. hard anodizing
Brit. Pat. 701,390	1953	M.H.C. hard anodizing process
Brit. Pat. 850,576	1959	Kalcolor process
Brit. Pat. 1.022,927	1968	Asada electrolytic colouring
Brit. Pat. 1,265,424	1972	Sealing smut remover
Brit. Pat. 2,012,814	1979	Interference colouring
Eur. Pat. 0,101,830Al	1984	Cold Sealing

current shortage of nickel, Volkswagon responded firstly by limiting the amount of trim used, and secondly by introducing bright anodized aluminium trim where practical [1].

A major factor in its sucess was the availability of an adequate quantity of 99,99% aluminium from a small smelter still operational in Germany, which took primary aluminium and further refined it. To overcome its low strength, it was alloyed with either 0.5% or 1.0% magnesium. When the occupying powers allowed the reconstruction of German aluminium smelters, their improved technology and high purity sources of bauxite enabled them to select batches of the metal produced which were of 99.9% purity, thus giving a reduction in the raw material price, enabling aluminium trim to remain competitive even when nickel became freely available at the end of the Korean war.

The good performance of the Volkswagon trim [1] led to its use by Mercedes, B.M.W. and other German producers. However, in the United States there was much resistance to introducing aluminium trim. Price competition was intense and thinly anodized aluminium, some of only 99.2% purity, was used initially for trim, which hardly enhanced its

reputation. However, after some time, the superior performance of anodized aluminium compared with nickel-chromium plating became accepted by the automobile industry. With it also came the recognition that aluminium of at least 99.7% purity was needed if an acceptable brightness was to be achieved in conjunction with a film thickness sufficient to ensure the required durability in service.

However, this background is still reflected in the bright trim material specifications in Germany as against the United States, as can be seen from the Table II.

Table II: Comparison of German and U.S.A. bright trim materials

Germany:	Bright Trim Alloys			
Designation	**Nominal Composition %**			
AlRMg0.5	Mg 0.35–0.6,	Si 0.01,	Fe 0.008,	Zn 0.01
AlRMg1	Mg 0.8–1.1,	Si 0.01	Fe 0.008,	Zn 0.01
Al99.9Mg0.5	Mg 0.35–0.6	Si 0.06	Fe 0.04,	Zn 0.04
Al99.9Mg1	Mg 0.8–1.1,	Si 0.06,	Fe 0.04,	Zn 0.04
Al99.85Mg0.5	Mg 0.30–0.6,	Si 0.08,	Fe 0.08,	Zn 0.05
Al99.85Mg1.0	Mg 0.7–1.1	Si 0.08,	Fe 0.08,	Zn 0.05
Al99.9MgSi	Mg 0.35–0.7	Si 0.35–0.7,	Fe 0.04,	Zn 0.04
Al99.85MgSi	Mg 0.35–0.7,	Si 0.35–0.7,	Fe 0.08,	Zn 0.05
Al99.8ZnMg	Mg 0.7–1.2,	Si 0.10,	Fe 0.10,	Zn 3.8–4.8
United States	**Bright Trim Alloys**			
Designation	**Nominal Composition %**			
5657	Mg 0.3–0.8 ,	Si 0.10,	Fe 0.10,	Mn+Cu 0.35
5457	Mg 0.8–1.2,	Si 0.08,	Fe 0.10,	Mn 0.15–0.45
6463	Mg 0.45–0.9,	Si 0.20–0.6,	Fe 0.15,	Cu 0.20
7016	Mg 0.8–1.4,	Si 0.10,	Fe 0.12,	Zn 4.0–5.0

The acceptance of anodized automobile trim had important consequences for anodizers. Not only did it demonstrate its good performance, and establish itself in the automobile industry, but this led to its use as a finish on a wide range of consumer durables. These developments also proved that anodized aluminium could be mass produced. For example, in the U.K. the first automatic anodizing plant was installed by Hoover Washing Machines in 1954 [2] for etched and anodized washing machine tubs and bright anodized and blue dyed lids.

Architectural Anodizing: This period also saw the beginnings of another major market for anodized aluminium. The aluminium producers were devoting a significant marketing effort to selling aluminium to the architectural market. To demonstrate its faith in aluminium, the new headquarters building of Alcoa, erected in Pittsburgh, used much aluminium in its construction. Anodized aluminium was used for the windows, facia panels, fittings and many other items. Other aluminium companies later followed Alcoa's lead.

However, developing this market was not simple, especially since architectural components were large. In the United Kingdom in the early 1950's the main capacity available was amongst the trade anodizers, and was initially restricted to tanks of 12 - 15 ft. in length and 3000 amperes capacity. In-line installations were unknown in these plants and immense manipulative feats were performed in moving work around. However, by the end of the 1950's two window manufacturers had installed in-line plants and trade anodizers had installed larger tanks. The introduction of mechanical joints for window manufacture in the 1960's saw large in-line plants handling lengths of extrusions becoming the norm.

At that time around 95% of the output was of "natural" anodizing, with the aluminium companies introducing an aluminium-5% silicon alloy which anodized to a grey colour. A small amount of work was produced using ferric ammonium oxalate to produce gold shades and black by dyeing in Aluminium Deep Black MLW.

A major boost to architectural anodizing came with the introduction of Kalcolor by Kaiser Aluminum Corporation, which had been developed in the late 1950's, although it was the 1960's which saw its widespread use. With the bronze shades and dark greys provided by Kalcolor, architects were able to achieve aesthetic effects with aluminium which had previously been unobtainable. Its success stimulated a large number of imitations, e.g. Alcanodox, Duranodic, Veroxal, Peranodic, etc,

In anodizing, as in other industrial technologies, external factors can occasionally have a dramatic impact. The energy crisis following the 1974 Arab-Israeli War caused anodizers to look critically at energy costs. The high voltages used in the Kalcolor process meant that total energy consumption in anodizing was 2 - 5 times that of conventional sulphuric acid anodizing which stimulated a search for a viable alternative process.

In Japan, a process had been developed by Dr Asada which was to revolutionize colouring techniques. In this process the anodized parts are placed in a solution of metallic salts and an alternating current passed. This results in the deposition of metallic particles at the base of the pores in the coating which, because of their random size distribution, produce bronze shades - the depth depending on the colouring time. The process is widely known as "electrolytic colouring", but the term "two-step coloring" is more commonly used in the U.S.A. The patent rights for its use outside of Japan were

acquired by Alcan Aluminium Ltd. and the process was licensed under the trade name "Anolok". The process originally used nickel salts, later replaced by cobalt salts, which were found to give a better black.

Meanwhile in Germany, Henkel Chemicals in collaboration with Josef Gartner & Co., (a large architectural aluminium company), developed a similar process using tin salts, which has been omitted from the patent claims for Anolok. Henkel also took the view that since the principle of electrolytic colouring had been disclosed in patents granted in the 1930's, the principle of electrolytic colouring was "prior art". The development of Henkel's "Almecolor" was accompanied by the other chemical supply companies announcing tin-based processes, which now account for a major part of the architectural market.

The success of electrolytic colouring is now a matter of history, although the range of colours available is still growing. Much of its success is due to its controllability, particularly as a result of the specially developed power units and controls.

The rapid growth of architectural anodizing during the '60s and '70s stimulated interest in process development, such as over-dyeing and spray dyeing. Alcan's Banbury Laboratories support for research at Manchester University Institute of Science and Technology undertaken by Prof. Wood's team led to the development of interference colouring.

Apart from anodizing, the major power consumption in the process is that required to maintain the sealing tank at 95-100°C (200-212°F). The development in Italy by Dr Walter dalla Barba of cold sealing using nickel fluoride based solutions provided an attractive possibility of energy saving. It has found widespread use in a number of plants. More recently, attention has been given to developing low nickel or nickel-free cold seals to meet the environmental objections to the use of nickel salts.

Hard Anodizing: The development of hard anodizing has been primarily a consequence of the demands for increased performance from components for the Defence and Space programmes, in which hard anodizing has been crucial to meeting these requirements. The fact that the hardness of anodic coatings was significantly higher if they were produced at low electrolyte temperatures and higher than normal concentrations had been established in the late 1930's. However, it was the pioneering work of the Glenn Martin Aircraft Co. in developing the M.H.C. process, as well as the pioneering work of W J Campbell of Hard Aluminium Surfaces in the U.K., in developing very high current density anodizing with D.C. plus A.C., that laid the foundation for the large scale production of the coating.

Over the years there have been, of course, other allied contributions, e.g. the development of additives, such as those from Sandford Process Corp. and Alpha Process Systems. Power sources and the development of automatic controls have also been important in achieving success

with difficult alloys. The use of pulse current is now well established, and other sophisticated power sources find use in special applications.

Another important contribution has been the development by hard anodizers of effective masking techniques. These has meant evolving suitable masking lacquers and tapes and specialised techniques for producing custom masking inserts when necessary.

An important supplement to the proporties of hard anodic coatings has been the combination of hard anodic coatings with solid film lubricants, such as polytetrafluoethylene dispersions and molybdenum disulphide. Silicone oils have also been employed where high dielectric properties, such as resistance to high voltage breakdown, are required.

The Diffusion of Anodizing Technology

Much of the success of an industrial economy depends upon the rate at which new technology can be introduced and diffused amongst the multiplicity of plants and personnel that are essential to its success. The term "diffusion of technology" is used here in preference to the term "transfer of technology" which is currently associated with the transfer of technology from an advanced economy to a developing economy, often with a different culture.

The process of the diffusion of anodizing technology since its invention is instructive in terms illustrating some of the mechanisms of the diffusion of technology in an industrial sector made up mainly of small and medium sized businesses.

The Diffusion of Chromic Acid Anodizing Technology: The chromic acid anodizing process was licensed to firms by the D.S.I.R. Initially, this was done through staff employed at the National Physical Laboratory at Teddington, where Bengough has originally worked. Later, because apart from one trade anodizer, the users were entirely in the aircraft industry, this function was passed on to the Royal Aircraft Establishment, Farnborough, where Dr H Sutton (who had worked with Bengough) was then employed.

Since its primary use was for protecting aircraft components, quality assurance was the responsibility of the Aeronautical Inspection Directorate, Accordingly, a process specification (DTD 910) was drawn up for their inspectors to refer to and ensure that the process was being correctly operated. This specification later also covered sulphuric acid anodizing. The was further supplemented by Technical Instruction Sheets which were issued by the Aeronautical Inspection Directorate for the guidance of their inspectors.

The Diffusion of Sulphuric Acid Anodizing Technology: Although the process of sulphuric acid anodizing was invented in the United Kingdom, the rights were ultimately acquired by the Aluminum Company of America (Alcoa) who saw anodizing as a means of expanding the market for aluminium.

They adopted the following means for the diffusion of anodizing technology to licensees:

1. Provision of a detailed process instruction manual.
2. Technical support in licensees plants by qualified personnel.
3. Establishing a facility in which components could be processed to demonstrate processing techniques.
4. The availability of production anodizing experience from a subsidiary holloware company in New Kensington.
5. A significant research and development effort devoted to understanding the anodizing process, particularly at the metal/oxide interface.

So successful was this that even today the "Alumilite" process is almost universally used in the U.S.A. for decorative and protective anodizing. This contrasts with the United Kingdom where, even now, variations in the anodizing electrolyte concentration from 90 - 450 g/l of sulphuric acid are permitted in the current defence specification [3], reflecting the variety of conditions used in the early years because of the confused patent situation.

In the late 1930's Alcoa granted a license to a British businessman who set up Alumilite and Alzak Ltd., with a plant in London. A patent "pool" was also created, which resulted in the sharing of patents and information between licencees in Germany, Switzerland, the United Kingdom and the United States. This proved particularly valuable in making available the silk screen printing technology that Siemens and Halske developed in Germany. Although World War II broke off the contact with European licensees, there was a continuing interchange of information between Alcoa and Alumilite & Alzak Ltd. in the U.K.

Although the basic patents for anodizing and sealing expired by the early 1950's (their period of protection having been extended because of World War II), many companies in the U.S.A. continued to pay an annual fee to Alcoa for use of the "Alumilite" trade name and a modest level of technical support. Elsewhere, the expiry of these patents encouraged further new entrants into anodizing.

The Diffusion of Chemical Polishing Technology

In the early 1950's chemical polishing patents were acquired by Albright and Wilson Ltd. (A & W), a specialist chemical manufacturer who was the sole U.K. source of phosphoric acid of S.G. 1.75, used in the formulation of these essentially phosphoric-sulphuric-nitric acid chemical polishing solutions. Other manufacturers of this acid did not supply this grade, but offered acid of S.G. 1.70. The difference in S.G. is accounted for by the presence of water, which affects the brightness obtained. A & W were in a position of having a virtual monopoly of the supply of the acid. Even with the expiry of the original patents, A & W have continued to be the dominant supplier in the U.K. The main response by competitors has been to modify the process chemistry to use S.G. 1.70 acid.

With this recognition that this was a practical, commercial process, a sales organisation with technical support staff was set up by A & W. The use of the process grew rapidly as interest in bright trim increased in the various user industries. In due course chemical polishing solutions, along with other products for metal finishing that the company subsequently developed, formed the basis of a separate operating company.

A & W's technical efforts were confined to the chemistry of the process. When bright anodized trim became accepted by the motor car industry, automatic plants were installed. Initially, a problem was experienced from a phenomenon referred to as "transfer etch". It was found that in the course of the time required to transfer the work from the chemical polishing bath to the first rinse, etching of the surface could occur.

A & W supported research carried out at Aston University, Birmingham, U.K., to understand the nature of the problem. It was found to be related to the ratio of phosphoric acid to sulphuric acid in the solution. As a consequence, they were able to modify the bath and patent an additive which inhibited etching. They supported further work at Aston on gassing defects, "icing" defects and the role of copper additions, thereby providing an understanding of the mechanism of the process and the role of the individual constituents [4-8].

In the U.S.A. Alcoa promoted the R5 process [9], which is based on a phosphoric-acetic-nitric acid mixture, whereas the A & W processes are based on phosphoric-sulphuric-nitric acid mixtures. In addition, there has been much use in the U.S.A. of a phosphoric-nitric acid mixture. In Europe the phosphoric-sulphuric-nitric mixtures are regarded as the better process.

The Development of Trim Materials: Over this period the aluminium industry was pursuing a different path. Alcan initially introduced 99.99% aluminium based alloys for bright trim and with it installed in their Banbury laboratories a pilot facility for chemical polishing using the "Erftwerk" process.

With the shift to 99.7% based materials (see p. 3) which cannot be polished by the "Erftwerk" process, interest shifted to Albright's proprietary "Phosbrite" processes. Facilities for bright anodizing prototype components using this process were installed in the laboratories of Alcan and British Aluminium. Part of the initial investigations at Alcan were devoted to building up an understanding of how to operate the process in production. For example, Brace and Kape[10] studied the effect of metal purity and nitric acid content of a "Phosbrite" chemical polishing bath on the brightness obtained.

In the course of supplying customers with material for bright anodizing, it was found that not only did the grain size and the inter-metallic particle size and distribution have to be carefully controlled, but the anodizing conditions also affected results. Work by

Scott [11], and later Jackson and Thomas [12] in British Aluminium's laboratories at Chalfont Park published the results of research showing how anodizing variables, such as concentration, temperature and current density affected the properties of the anodic coatings produced. Investigations of these factors was also carried out at Alcoa's research Laboratories in the U.S.A. [13]. Unpublished work by Polfreman at Alcan's Banbury Laboratories had also showed how the presence of impurities in the electrolyte, such as iron, could reduce brightness. This work, along with other contributions on the effect of heavy metal impurities, has been summarized by Brace and Sheasby[14])

An important contribution made by Cooke [15] at Alcan's Kingston Laboratories (Canada) studied the inter-relation between the nature and distribution of inter-metallic particles and their effect on the loss of brightness on anodizing. This was particularly valuable in explaining the loss of specular reflectivity on anodizing.

As can be noted from the above, the publication of research results in journals of the technical institutes, such as the Institute of Metal Finishing, and the American Electroplaters and Surface Finishing Society provided an important means of diffusion of knowledge on these new processes. In addition, both Alcan and British Aluminium had staff who gave technical support to customers and communicated information on a one-to-one basis with the relevant staff of major customers.

The Growth of Production Facilities: Although small bright anodizing facilities had been installed at the Radiators Branch of Morris Motors (using an electropolishing process) and at the Morris Singer Co, Exeter (using the Erftwerk process), the first automated plant for producing bright trim was that of the London Aluminium Co Ltd., Birmingham - an aluminium pressing and holloware company - who installed an automatic plant specifically for producing bright trim for the automobile industry. Once it became clear that the process and product was acceptable, one of the traditional suppliers of electroplated trim - Pianoforte Supplies Ltd., Northampton - also installed an automatic plant. However, other traditional trim suppliers were reluctant to commit themselves. It was the establishment of Pressweld Ltd., Gloucester, that provided three major bright trim production plants to assure adequate supply of trim.

The Diffusion of Architectural Anodizing Technology

Much of the initial development of architectural anodizing in the U.K. was a result of the marketing strategy of Alcan Aluminium Ltd., as a result of which they pioneered the introduction of architectural colour anodizing outside the U.S.A.

By the mid-1950's Alcan had decided to promote anodized finishes for use in architectural applications. The broad thrust of this strategy is set out in Table III. Part of the market development strategy was to support anodizing research and development, so as to provide a technical and technological basis for the acceptance of the finish by trade anodizers, as well as architectural fabricators.

Marketing Target	Marketing Programme
Architectural Products Manufacturers	- Assist with Design - Assist with Prototypes - Manufacturing Advice
Architects and Property Companies	Promote Aluminium by - preparing brochures - publicity in trade press - visits to leading figures
Anodizing and Anodizers	Process Development - Anodizing Techniques - Test and Select Colours - Develop Colouring Techniques - Develop Quality Tests - Disclose to Users
Aluminium Development Association	- Disclose Recommendations to the Finishes Committee - Secure Industry support for process recommendations - Jointly seek support from the Trade Anodizers for above - Publicise these recommendations - Set out Quality Requirements as basis for future British Standard

Table 3 : Marketing Strategy for Architectural Products

This latter strategy was based, in part, on the concept of the value of the "demonstration effect" [16]. The quicker a company can learn a new production technology the lower will be the cost of learning this and the sooner it will have the market advantages accruing from this. It should be appreciated that Alcan Aluminium Ltd (Canada) had a corporate marketing strategy at two levels:

(1) the development of aluminium sales internationally to increase the demand for primary aluminium, and
(2) support for the marketing activities of its U.K. semi-fabricating subsidiary directed at the markets such as bright trim and architectural applications.

In the course of the development of the bright trim market there were informal exchanges with British Aluminium Co., who were a primary customer of Alcan (Canada) but a competitor of Alcan Industries Ltd. in the semi-fanricated products market. These were necessary because the automobile industry insisted on a minimum of two sources of trim materials. Further, it was important that there should not be a conflict between the two companies as far as both materials specifications and quality recommendations for the anodized product were concerned.

When the work on Architectural Colour Anodizing had reached an advanced stage Alcan's primary products sales company authorised the disclosure of this information to a primary customer - High Duty Alloys Ltd. - where Kape had earlier carried out exposure testing of anodized panels using inorganic colouring techniques.

Establishing the Anodizing Technology: Alcan's subsequent success in promotion of architectural anodizing was fortuitously assisted by the fact that Dr George Gardam had joined Alcan's Banbury Laboratories in 1953 as Head of Chemistry Division. He had a high reputation in electroplating from his prior association with the Royal Armament Research and Development Dept., Woolwich. In 1955 he recruited Brace to head metal finishing R & D, who later added both Kape and Sheasby to the team. Both of these subsequently established a high personal reputation, which resulted in Banbury establishing itself internationally as a centre of anodizing expertise.

The primary objectives of the work carried out in the period 1955-1960 by this team were :

1. To understand anodizing and the processes associated with it, especially in terms of the factors which could cause problems in large scale production.
2. To recommend processing conditions for the production of anodized finishes for products required by Alcan customers.
3. To assess and recommend a range of colours for architectural use.
4. To develop test methods with a view to ensuring that quality standards could be drawn up for anodizing which would result in its acceptance in the market.

5. To assist Alcan companies in assessing the response of materials manufactured by them for use in anodizing.

In the U.S.A., Alcoa had acquired a background of outdoor exposure testing of the performance of anodized aluminium, which extended back to the late 1930's. Alcoa were recommending [17]) a 20 micron minimum film thickness for industrial conditions and 12 microns (minimum) for less severe environments. Alcan's Banbury Laboratories had limited experience of outdoor testing of anodized aluminium, but it made efforts to inspect actual windows and other installations in the United Kingdom and a limited number of European sites to establish the performance of the finish in these environments.

Also of concern, was the question of ensuring that the colours used were lightfast. At Alcan's Kingston Laboratories, Spooner had carried out an extensive evaluation of the outdoor light-fastness and of accelerated fading tests on a large number of dyed anodized panels.

The results of these test were subsequently published [18]) and these were taken as a starting point at Alcan's Banbury Laboratories for the assessment of possible colours for architectural use. It was suspected by Alcan (and subsequently confirmed) that an even wider range of dyed panels had been tested by Alcoa over a longer period. In earlier years Alcoa had recommended suitable dyes for anodizing use to its customers and "Alumilite" licensees. Arising from this work, Alcoa recommended a limited range of colours for architectural anodizing in the late 1950's [17]).

Although there were a number of dyestuffs in use, these were of limited light-fastness. It seemed essential to make sure that the colours recommended were lightfast, since a dramatic failure by fading would be a severe setback to the acceptance of colour anodized aluminium. Based on Alcan's testing, gold, black, two shades of blue, a yellow and a red which were recommended, plus gold from ferric ammonium oxalate and bronze shades produced by double dipping in cobalt acetate and then potassium permanganate solutions. Only the gold and black were widely used, but one large window company used this bronze process until the "Anolok" process became available.

Particular attention was paid to establishing the combination of anodizing, colouring and sealing conditions which would guarantee that a compact film of consistent properties was produced. Work was also carried out on the effect of contaminants and operating practices that might affect the consistency of the product.

The Dissemination of Technology Developed: The process of the diffusion of the anodizing technology built up by the Alcan R & D team utilized the following means:

1. Written research reports distributed initially to Alcan companies.
2. Papers based on this research were presented to the Annual Conferences and branch meetings of the Institute of Metal

Finishing and other technical institutes on various aspects of anodizing and contributions made to trade journals, such as "Light Metals", "Aluminium" (Germany).

3. A Symposium held in Banbury to summarize R & D findings for the benefit of personnel in Alcan companies with an interest in finishing and finished products to summarize experience.
4. A handbook "Recommended Practice for Architectural Colour Anodizing" was later prepared, printed and widely distributed to Alcan companies and customers.
5. Communication of such information to Alcan customers where appropriate on a one-to-one basis.

These means of communication were used both in the development of bright trim anodizing technology as well as archtectural.

The Marketing Strategy for Architectural Anodizing

In addition to selling the idea of anodized aluminium for windows, in the early years there was very limited capacity for architectural anodizing amongst window manufacturers. The industry in the U.K. realised that liaison with trade anodizers was also essential in these early days of market development, since they would be the initial source for providing anodized finishes for architectural applications to the smaller companies.

It was decided later at a high level in Alcan's headquarters, Montreal, Canada, to make available to the aluminium industry in the United Kingdom details of the Alcan recommendations on Architectural Colour Anodizing as part of the marketing strategy.

The Role of the Industry Association: In the U.K. the aluminium industry had set up the Aluminium Development Association at the end of the war to promote aluminium and co-ordinate industry development activities. The detailed work was carried out through a series of ad-hoc committees, one of which was the Finishes Committee. The aim of the Alcan strategy was to secure industry acceptance of its recommendations on architectural anodizing and to prepare the way for drawing up an industry quality standard.

Liaison with Trade Anodizers: Through the Finishes Committee the aluminium industry accepted the Alcan recommendations and later published them with minor modifications as industry recommendations. An essential element at this point was to secure the support and co-operation of trade anodizers, since it was evident that some window companies were initially not going to install captive anodizing plants, so capacity in the trade would be essential to market development.

The Finishes Committee had already met twice with an ad-hoc group of leading anodizers to exchange views and information, particularly in relation to quality testing of bright trim. With architectural anodizing there were a number of issues for which the co-operation of the trade anodizers was essential. All of these related to quality.

Establishing Quality Standards: Alcan Laboratories in Kingston and Banbury had extensive data on world-wide corrosion rates for bare aluminium. This showed that the corrosion rates in the United Kingdom were two to five times higher than most sites in the U.S.A. Work on accelerated corrosion testing using acidified salt spray was published by Brace and Pocock [19] showing a very significant increase in the time before pitting occurred as the film thickness was extended beyond 15 microns. Taking these factors into account, the industry Finishes Committee proposed a 25 micron minimum film thickness. At that time there were several plants which were producing shop front sections to a 15 micron thickness. There was some reluctance to adopt 25 microns universally, so that initially there was a provision for a 15 micron coating for less severe environments.

Another question that occupied the attention of both researchers and practical anodizers in subsequent years was the question of an acceptance test for sealing. In the mid-1950's the Anthraquinone Violet dye stain test was almost universally used as an acceptance test, but work at Banbury [19] had shown that work could pass this test yet still develop an unsightly white bloom on exposure. A later modification of the test by Edwards [20] in which the test was carried out in an improved design of cabinet with accurate control of the SO_2 concentration, resulted in this becoming an accepted test method (BS 1615;1972, Appendix H). The fact that it was a subjective test ("had it bloomed ?") resulted in other quantitative tests being developed by Kape [21] and by Alcoa investigators [22] which have subsequently been refined and accepted International Standards Organisation Tests.

In due course the Alcan recommendations became accepted and formed the basis of most British architectural anodizing practice. The existing Standard for Anodizing (BS 1615) was amended to take in to account the requirements of architectural anodizing. Later, a separate standard - BS 3987 "Anodic Coating on Aluminium for Architectural Applications" was drawn up for architectural anodizing, which provided for an anodic coating minimum thickness of 25 microns (0.0010"). Stringent sealing tests were specified - either the acidified sodium sulphite (Kape) test or the SO_2-humidity test - because of the relative aggressive environment prevailing then in the U.K.

As far as the author is aware, there have been no cases reported of failure of anodic coatings in the U.K. where the requirements of the British Standard have been met. It is likely that if this high quality standard had not been met failures would have occurred that would have had an adverse effect on the growth of the market and confidence in an anodized finish.

In the years following the setting up of the Aluminium Federation, which replaced the previous Aluminium Development Association, there was a change in emphasis, with market development being left primarily to the member companies. With individual members of the Federation installing captive anodizing plants to anodize mainly lengths of extrusions, plus a concern to ensure the maintenance of quality

standards in the architectural market, the British Anodizing Association was formed. Although nominally open to all anodizers, in practice its membership was drawn mainly from the larger trade anodizers whose main business was architectural anodizing, plus those of its members who had installed anodizing plants.

Later, the European Anodizing Association was formed, which provided a centre for co-ordination of information on technical an commercial matters of concern to the industry. In addition to undertaking a program of outdoor testing of the performance of anodized finishes, it developed "Qualanod", a quality standards organisation which awarded the "Qualanod" label to those plants who met its standard when independently inpected. Although quite well supported in some European countries, in the United Kingdom support was lukewarm.

Support for Research: The Aluminium Development Association was the vehicle for providing financial support for University research on topics which the industry considered to be a particular interest. It provided finance for a research student (Graham C Wood.) to undertake research into the sealing process. The technique used was to study changes in A.C. resistance and capacitance of the anodic film during sealing. After publication of the research [23], investigators in Germany adapted the principle so that by using A.C. admittance values could be directly measured by an instrument [24], which subsequently was sold commercially by Fischer Instruments under the trade name "Anotest".

Later the Association provided a degree of financial support for some research carried out at Battersea Polytechnic on chemical polishing, as well as for research carried out by Giles and his co-workers [25] into the mechanism of dyeing anodic coatings.

Future perspectives

It has taken 70 years for anodizing to evolve from an infant technology to a mature one. Most of the important technology has developed over the past 40 years. It is interesting to note that there appears to have been on average one major new development patented every 10 years. If one takes the view that this is now a mature industry, then it might be expected that the rate of innovation will slow.

However, much will depend upon future international industrial trends. Current views in the industry are coloured by the experiences of the recent world-wide recession and the competitive challenge from organic coatings, particularly powder coating. The writer is sufficiently optimistic about the future of anodizing to suggest that, although there is a place for alternative finishes in the architectural market, anodizing will remain a major finish. New trends in architectural aesthetics and in construction methods could well work to the favour of anodizing.

Anodizing is a finish for a multiplicity of products and markets. It is used on many products that had not been developed 40 years ago. It would be surprising if the next 40 years does not see rapid growth in

those markets where energy saving obtainable from using light weight aluminium is crucial. The environmental friendliness of the anodizing process will also be an important asset in the 21st century.

Growth in the use of specialised materials for electronic components and devices, in control systems and other high technology engineering is likely to grow healthily. There is also likely to be the development of new technology, possibly involving high purity materials and high value added devices which exploit the unique properties of the anodic coating on aluminium.

Anodizing is a world-wide business and its use is growing rapidly in the countries of the Pacific rim. Etched and anodized aluminium extrusions are a commodity already traded internationally in significant tonnages. The emerging industrial nations have the advantage of low labour costs, and often favourable energy prices. This will present an increasing challenge to the older industrialised countries. It seems likely that this will call for a raising of quality standards in the older economies, and increased concentration on those products where the advantage of their advanced technology and skills can be maximized.

To achieve this will call for a change in approach by many companies. The development of new designs and components must be based on integrating the finish with the design and planning of the manufacturing process. All too frequently it is an afterthought of designers, or anodizing shop are being asked to meet complex demands combined with same day delivery. It is a situation long overdue for change. It should be a matter for A.E.S.F.S. to consider at the highest level, since it has implications for all types of finishing.

That the future will be different to the past is certain, but anodizing seems likely to remain the major finish used on aluminium for many years to come. To those of you who may remain in anodizing for the forseeable future, I leave you with the Chinese curse:-"May you live in interesting times!".

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"*Casting for Surface Finishing*" (CSF)

A new method for surface finishing of cast aluminium alloys.

Anne Deacon Juhl, M.Sc. and Per Møller, Ph.D.
Centre of Advanced Electroplating (CAG)
Technical University of Denmark, Building 425, DK - 2800 Lyngby

Leif Højslet Christensen, Ph.D.
Department of Chemistry, Danish Technological Institute, DK - 2600 Tåstrup

Lars Feldager Hansen, M.Sc and Preben Nordgård Hansen, Ph.D.
Lab. of Thermal Processing of Materials, Technical University of Denmark

Abstract

It is well known that the grain sizes and phase distributions in the microstructure of casting are the important factors to be considered when a good surface finishing is essential and/or desired.

These microstructures can change over various parts of a casting. "*Surface metallurgy*" will, therefore, be introduced in order to characterise the microstructure near the surface of cast aluminium alloys. Employing a numerical simulation of the solidification of the casting and comparing it with the surface metallurgy, a new method for achieving on improved casting surface for surface finishing technology is established, i.e. *"Casting for Surface Finishing"*.

Introduction

Aluminium can be cast by practically any method generally accepted by foundrymen. When pressure die casting is selected a smooth surface is obtained, but even then the surface finishing may not be as uniform as wanted. The metallurgy in the "as cast" item is different when different casting techniques are used, but even in the same casting differences appear. These differences are caused by the variations in solidification and cooling rates across the casting. Therefore, control of the casting is of great importance in order to obtain a proper surface for surface finishing .

Pressure Die Casting

Pressure Die Casting is a process where molten metal is pressed under high pressure into a permanent mould. The process can be compared with chill casting as they both use a permanent mould. In chill casting the gravity will fill the mould, while pressure die casting uses pressure to fill the mould. The very high pouring rate makes it possible to cast very complex and thin castings and at the same time pressure die casting makes it possible to cast a large number of parts in a short time.

A normal pressure die casting cycle takes in general about 30 seconds for small parts and up till 4-5 minutes for big parts. This results in very high cooling rates, which causes a fine microstructure and a smooth surface.

Figure 1 shows the essential features of the cold chamber process. In this process the melt is placed

outside the casting system. The melt is poured into the pouring hole and the plunger presses the melt in the direction of the mould (die). While metal is solidified in the mould, the rest of the molten metal is liquid under high pressure. This is done for two reasons; 1) for compensation of the lost under solidification, and 2) for having the opportunity to press the porosity "out" causing a more dense casting.

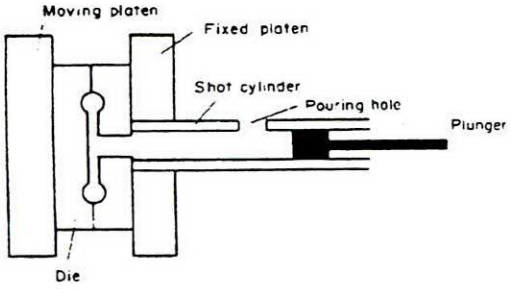

Figure 1, Diagram of the cold chamber process.[1]

During pressure die casting the heat transfer is fast, the solidification rate is high (solidification time low) and the microstructure will be fine due to a great undercooling. Such solidification rates are found at small distances from the surface of the mould, in thin sections, or at laser-remelted surfaces.[2]

Without a certain undercooling no nucleation or crystallisation will occur. At the same time, the state of undercooling, and by this nucleation ability of a melt, will determine the type of microstructure formation.[3]

A different situation prevails when the solidification rate is low (solidification time high). Here the heat transfer is low and the nuclei will continue growing and therefore the microstructure will be coarse-grained. Such microstructures are found in the central part of the mould and in thick sections.

Microstructure

It is obvious that the state of the surface is most important for the result of surface finishing, both regarding what kinds of intermetallic phases are present and how their size and distribution are.[4,5]

The form of the microstructure depends not only upon the heat transfer but also upon the alloy composition.[6] The two major growth types of a casting are the dendritic and eutectic. Both types of microstructure are present in almost every casting because of the better castability of a near-eutectic or eutectic alloy than that of any other compositions.

Pinner et al.[4] show the importance of the choice of alloys when aluminium alloys are surface treated. The content of alloying elements should not vary much, before an unsatisfactory result is obtained.

Anodic coatings formed on pure aluminium (0.05% impurities) are continuous and transparent transmitting light through thin section of the oxide coating. In coatings formed on aluminium containing 0.8% impurities dark-coloured areas are obtained. These areas contain particles of constituent and oxidation products that detract the transparency of the coating.[5] This indicates how important or rather detrimental impurities (= constituents of an alloy) are to the finish.

The distinct phases in alloyed aluminium behave differently, when anodised.[5]

Si:	*does not oxidise or dissolve*
$CuAl_2$:	*oxidises or dissolves more rapidly than Al*
β-AlMg:	*oxidises or dissolves more rapidly than Al*
$FeAl_3$:	*partly dissolves and partly remains in the coating*

This is due to the chemical composition and electrolytic behaviour of the constituents in the solution. Silicon is not oxidised or dissolved under the anodising process and will be fund at the same relative position as before

the surface finishing process. There are some disagreements about the behaviour of the other phases.[4]

Looking at the potentials (Table 1) measured in a solution containing 53 g NaCl/l and 3 g H_2O_2/l at 25°C, with reference 0.1 N Calomel electrode[7], the phases $CuAl_2$ and $FeAl_3$ might not oxidise because of the more noble potentials of these compared with the pure aluminium.

Phase	Potential (mV)
Mg_2Al_3 (Mg_5Al_8)	-1240
Al+7% Mg	-890
Al+3% Mg	-870
99.95% Al	-850
Al+1%Mg_2Si	-830
Al +1% Si	-810
Al+2% Cu	-750
$CuAl_2$	-730
$FeAl_3$	-560
Si	-260

Table 1, The potential of some intermetallic and solid phases.[7]

The difficulty with these potentials is that they have not been measured in the electrolyte used for anodising, but they may still give some indications of the electrolytic behaviour of the phases.

Quantitative Microscopy

The microstructure of alloys can be revealed using light microscopy, scanning electron microscopy (SEM), and x-ray microanalysis (EDX). However, most often the information obtained has been qualitative restricting a comparison to be a visual comparison of a limited number of micrographs.

Computer-assisted microscopy[8] provides a number of tools for quantifying the microstructure, and, thus, provides the basis for a fully quantitative comparison of data from a number of specimens. Stage automation and computer controlled microscopes allow acquisition of a sufficient number of digital micrographs to make the comparison statistical unbiased.

Surface Metallurgy

The metallurgy of the outermost surface layer, which will be exposed to the surface treatment, needs to be known and possible controlled to obtain a good and reproducible surface finishing. The surface layer should be characterised in terms of the identity of intermetallic phases, their size and spatial distribution.

Numerical simulation

By numerical simulation of the casting process[3] the solidification rates over different parts of the casting, temperature - time curves at different places in the casting, the pouring time, the filling sequence and many others casting parameters can be simulated by this program. A dramatic improvement in the quality, productivity and technical properties can be obtained when modern computer technology is used to optimise the casting.

This paper presents a new method, named ***"Casting for Surface Finishing"*** (CSF). By linking together the casting simulation, the *surface metallurgy*, and the resulting finishing a method to prepare cast aluminium parts is obtained. Preliminary results of our work are presented.

Experimental

The casting was part of a carburettor and the alloy used was SIS 4250 (AlSi9Cu3). The casting process was a cold chamber pressure die casting, where the melt was placed outside the casting system.

The casting was DC anodised in 15 (W/W)% H_2SO_4, 20°C, i_a = 2 A/dm^2, 40 minutes.

The composition (% wt) of alloy SIS 4250 was as follows:

8-11% Si	2-3.5% Cu
0.1 - 0.5% Mg	≈ 0.8% Fe
≈ 1.2% Zn	≈ 0.1 - 0.5% Mn
≈ 0.3% Ni	≈ 0.15% Ti
≈ 0.1% Sn	≈ 0.2% Pb
Bal. Al	

The two samples were taken from the carburettor. The positions of the samples are marked in figure 2. The thickness of sample I is 3 mm and that of sample II 15 mm.

The samples were prepared metallographically as cross sections perpendicular to the anodised surface. The samples were etched in Weck colour etchant prior to the light microscopy work.

The numerical simulations were carried out using the software package MAGMAsoft.

The SEM/EDX work was carried out on a Cambridge S360 microscope equipped with a Link AN10000 EDX system. The working magnification was 1.000X giving a field of view of 100 μm × 100 μm. Backscatter images and x-ray elemental maps were acquired under computer control along the oxide layer. With a grid size of 128 × 128 the "point" resolution is approximately 1 μm^2 . For each point a 100 ms x-ray spectrum was obtained providing statistical valid information for the elements Al and Si.

The backscatter image and the elemental images for each field of view were subjected to off-line image processing and graphical presentation.

Results

Figure 2 shows the solidification times of the casting when the mould is totally filled. In the dark areas the solidification time has been slow and in the light areas it has been fast.

Before simulation the complete geometry of the casting should be included in the program. After this an enmeshment is accomplished which permits a coarse or a finer discretisation of the casting volume. In the actual casting 250.000 elements have made the enmeshment.

After anodising, the colour of the oxide layer varied over the casting. Where the dark areas are seen in figure 2 (slow solidification time), the oxide layer had a darker colour than in the areas where the solidification time was fast.

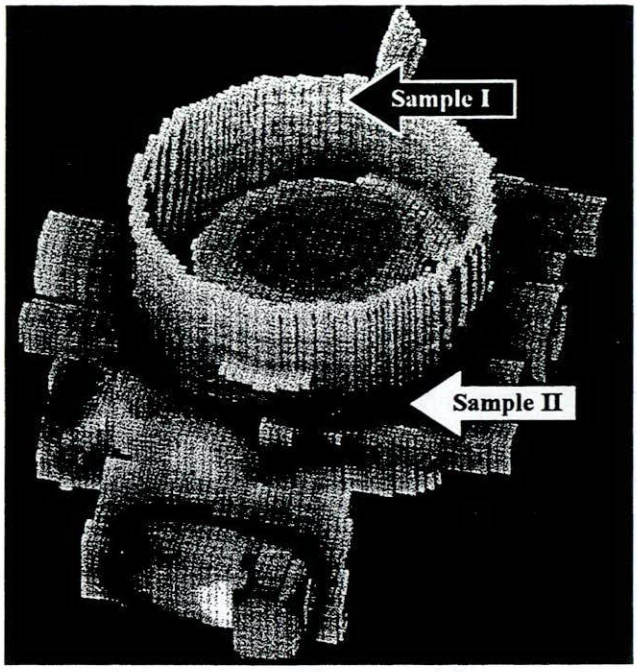

Figure 2, The simulated solidification time for the casting, 100% filled.

In sample I the solidification time was 1.44 seconds after 100% filling of the mould. In sample II the solidification time was 7 - 8 seconds after 100% filled.

The solidification time in sample I was short because of the high solidification (cooling) rate due to the thickness of the part, which is very thin. The solidification has happened immediately, with a large undercooling and by this the microstructure near the

surface is fine. Nucleation rate has been high and the growth rate low.

The cooling rate was lower in sample II. Here the same microstructure was obtained, but the grains should be more coarse. Here it is due to the dimension of sample II, which is expected to make the solidification time longer than in sample I, and, thus allowing the microstructure to grow in size.

Figure 3 shows the micrograph of sample I. The thickness of the layer is approximately 5 μm and the microstructure consists of primary aluminium and a fine eutectic.

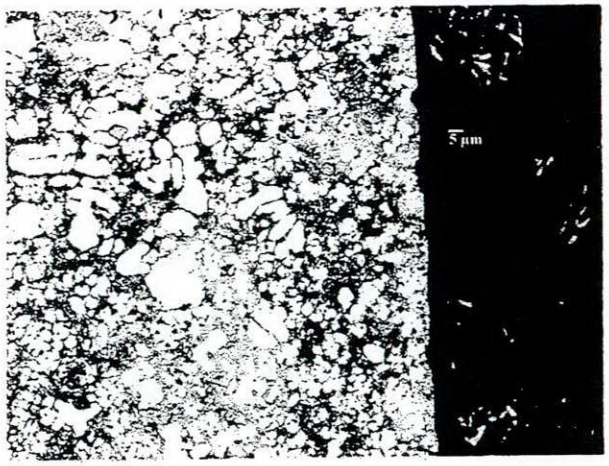

Figure 3, Sample I, Light microscope 250X, thickness of oxide layer is about 5 μm.

Looking at the aluminium - silicium phase diagram under equilibrium conditions, figure 4, the silicium can be found in three ways:

① soluted in aluminium

The white areas in figure 3 are the primary α-crystals formed, when the liquidus/solidus line is reached. The primary α phase represents solid aluminium with up to about 1.65 % Si in solid solution.

② as Si crystals in the eutectic

The eutectic between the primary α-crystals consists of primary α-crystals and silicon crystals, formed when the eutectic temperature is reached.

③ as primary Si-crystals when the alloy is hypereutectic

The alloy used is not hypereutectic, which is why no primary Si crystals are present.

Silicon is found as silicon in solid solution and in the eutectic in this alloy.

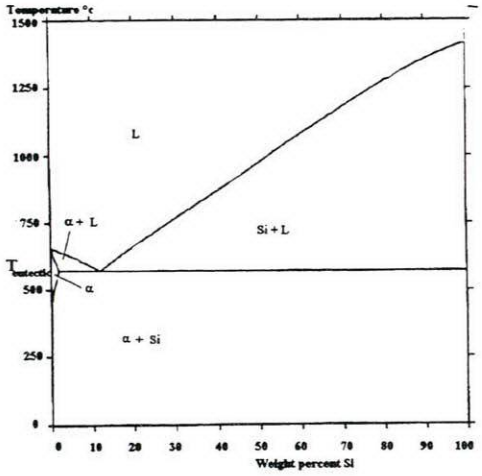

Figure 4, Phasediagram Al-Si.

During solidification segregation of intermetallic compounds is possible. The alloy contains copper, magnesium, manganese, iron and other elements, giving the possibility of many different phases. $CuAl_2$, Mg_2Si, $FeAl_3$, $MnAl_6$ are some of the conceivable phases in the alloy SIS 4250. These phases will also be fine because of the high solidification rate, but they are difficult to see in the figures. In this paper they will not be taken into account, but in future work their influence on the surface finishing will also be estimated.

Figure 5 shows the micrograph of sample II. In this case the thickness of the oxide layer is approximately 25 μm.

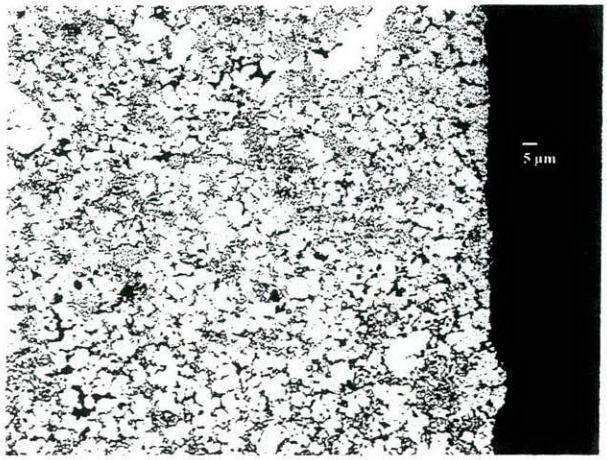

Figure 5, Sample II, Light microscope 250X, thickness of the oxide layer is about 25 µm.

In this preliminary work micrographs from the light microscope have not been subjected to image processing. In general the microstructure is very complex. However, we anticipate that some image colour processing will be possible after refinement of the etching procedure. For the moment we will confine ourselves to a qualitative discussion of our findings.

The silicon crystals in the eutectic are perhaps a bit different in the two samples but it is not easy to see. The structure in sample II looks more fine grained than the one in sample I. This does not agree with the above explanation. At the same time it can be difficult to explain the differences in the thickness of the oxide layer by the difference in the microstructure.

It is also known that the solidification starts already in the cylinder because of the lowering of the temperature when pouring the melt into to the mould. The melt therefore contains a certain amount of nuclei before reaching the final place. This leads to the necessity of a much smaller undercooling because of the growth on the nuclei already formed. This can explain the fine microstructure obtained in sample II in spite of the fact that this microstructure should be coarse because of the low solidification rate.

The aluminium x-ray images were subjected to image processing. Based on the image analysis the phase distribution of the α-crystals and the eutectic were quantified. Normally the results are presented as colour coded images showing the variation in elemental composition across the field of view. In this paper the results are shown as greytone images, figure 6.

The black areas in the metal phase represent the highest amounts of aluminium. The greytone of the oxide layer does not correctly indicate that this part contains the lowest amount of aluminium.

The white edge seen along the oxide layer is due to lack of resolution in the x-ray measurement.

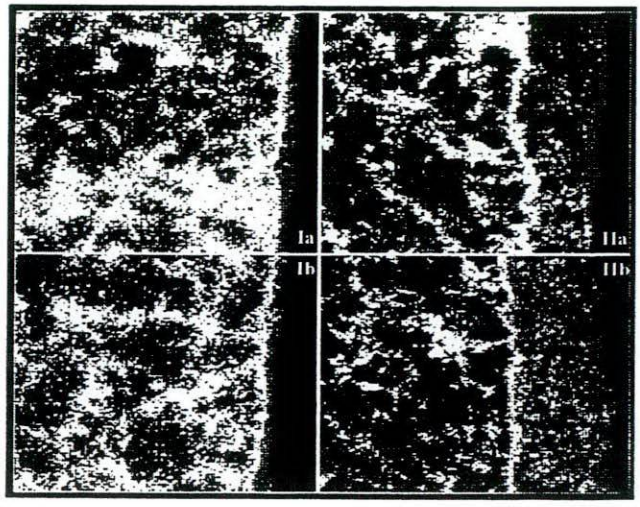

Figure 6, X-ray images for Al as seen in two fields of view (left side sample I; right side sample II)

The images Ia and Ib show sample I. The oxide layer, which appears on the right side of sample I is, as already told, 5 µm. By comparing it with sample II, image IIa and IIb on the right side, where the oxide layer is 25 µm, the difference in the bulk material is obvious. The white phase is the eutectic and the black phase is the primary α-crystals in both samples.

In figure 6 the images of sample Ia and Ib show the difference in the distribution of the eutectic in sample

IIa and IIb. The eutectic is much finer distributed in sample I than in sample II.

This fine and dense distribution of the Si-rich eutectic contributes to a surface in sample I which has a higher potential than sample II. At the same time there will be more silicon in the α-crystals in sample I compared to sample II due to a higher solidification rate.

Due to that the current will flow against sample II instead of sample I. The higher current in sample II will cause the solution of the aluminium to be higher, and, thus the oxide layer will be thicker.

Conclusion

The conclusion of the paper is, that the finishing of a surface is strongly related to the metallurgical development of the casting:

Solidification
↓
Microstructure
↓
Surface finishing
(application/properties)

To obtain a high quality of surface finishing a good surface is necessary. This kind of surface can only be produced if the *surface metallurgy* is known. This leads to the importance of being able to produce an appropriate microstructure. The possibility of controlling the microstructure lies in the casting process.

The MAGMAsoft program, simulate filling and solidification of the casting and gives therefore the possibility to fulfil the necessary conditions. Not only the electrochemical properties (important in anodising) but also other technical properties can be improved by using the casting simulation program to decide the optimal microstructure.

The casting in this investigation is complex. The thickness of the oxide layer varied much over the parts of the casting. The thickness of the oxide layer should have been about 15 μm but it varied from 5 - 40 μm.

A thick oxide layer was expected on sample I because this part was close to the cathode during the anodising process. Sample II was much further away from the cathode, so here it would be expected that the oxide layer was very thin. This is opposite to what was observed for the two samples. This is properly due to the finer distribution of silicon in sample I compared to sample II caused by a higher solidification rate.

A high content of silicon increases the anodising voltage and by this the current will flow more easily to sample II. The dissolution of the matrix metal will, therefore be faster on sample II than on sample I and thus make the oxide layer thicker on sample II.

Our results show that there is a correlation between solidification, microstructure and the result of the surface finishing. Still more work is needed before the CSF method can be used in common practice.

Acknowledgement

The authors wish to express their gratitude for the valuable discussions with E. W. Langer and G. Bech-Nielsen.

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ALLOYS AND TEMPERS IN HARDCOATING

Richard E. Going, CEF
R o G Enterprises, Ashland, MA

Everything that can or will apply to any hardcoating job shall be called out on the work traveller. The most important being Alloy, Temper and Thickness desired.

If you are not satisfied or are suspicious of the Alloy and Temper then call the customer. (Remember: it is your right as a hardcoater to ask for a Certificate of Conformance which will give the metallurgical break-down of that particular alloy.)

Wrought aluminum alloys can be broken into the following, non-heat-treatable and heat treatable alloys.

Non-heat-treatable alloys will depend upon the hardening effects of elements, such as; manganese, silicon, iron and magnesium. Further strengthening is made possible by various degrees of cold working which is denoted by the "H" series of tempers. If you have 3003-H34, the breakdown is as follows:

H3 is strain hardened and stablilzed - the 4 will indicate the degree of strain-hardening remaining after the stabilization treatment.

Heat-treatable alloys receive their initial strength from the addition of copper, magnesium, silicon and zinc. Increasing the temperature plus hot and cold thermal treatments will increase the strength. A good example is 6061-T6 heated @ 350° for 8 hours and then stretched becomes 6061-T6511 which will coat almost twice as fast as T6.

Then there are castings which are very porous and sometimes contain up to 13% silicon. The best castings for hardcoat seem to be 40E, 43, 108, 214, 218, 319 with 355 and 356 being popular.

Metallurgically speaking:

The purpose of any heat treating is to releave internal stress depending on the temper of the alloy.

The rate a part will coat will be determined by the finish before hardcoating, the alloy, temper, electrolyte, the temperature of the electrolyte and how fast you dare to push.

Notes:

Hardcoat plus duplex seal is very good for a marine atmosphere except the fatigue strength may be lower.

To reduce much of the copper that has accumulated during processing, leave a sheet of 3003 in the processing tank overnight.

Because the conductivity of aluminum is about 49-51%; more and more 6063-T6 is being used for cathodes, instead of lead.

Aluminum-copper alloys seem to be more prone than others to galvanic corrosion and also burning.

Zinc has no effect on the coating if the percentage is low, but 7075 and 7178 will have 5.6 - 7%.

If you are doing a 7075-T6 forging, the forging cannot eliminate inclusions or porosity containing gas; stock substantially free of such internal discontinuities is essential.

Aluminum alloys have or may contain silicon, iron, copper, manganese, magnesium, chromium, 2000, 3000, and 4000 some nickel, zinc, titanium, lead, boron, zirconium, beryllium and vanadium to mention a few.

The porosity of hardcoat will vary with the alloy composition.

Aluminum alloys have or may contain:

Silicon	Chromium
Iron	Nickel
Copper	Zinc
Manganese	Titanium
Magnesium	Lead
Boron	Zirconium
Beryllium	Vanadium

Thickness, Hardness, Adhesion and Dimensional change seem to be effected by the following:

Magnesium
Copper
Silicon
Manganese
Zinc
Nickel

PRE-TREATMENT

The Foreplay of Aluminum Finishing

SurFin '94
Indianapolis, Indiana
June 21, 1994

B.W. "Bill" Sharp
Marketing Manager
Novamax Technologies (U.S.) Inc.

PRE-TREATMENT
The Foreplay of Aluminum Finishing

Pre-treatment of Aluminum has been in existence since the beginning of anodize. However, as technology has changed, environment concerns have surfaced and improved quality has been demanded, these treatments have been forced to change. We will address some of these changes.

I. Cleaning

Aluminum may be cleaned with various type cleaners. Vapor degreasing, aqueous cleaners which are solvent based, alkaline or acid cleaners have been used. The type cleaner is based on the soil which is to be removed. The types of soil include:

* Carbonaceous deposit
* Oil-based lubricants
* Solid particles (dust, buffing compounds, etc.)
* Oxide Films

Other considerations are water hardness heat availability, air agitation and etch versus non-etch.

In some operations a two step cleaning operation is ideal. The organics must be removed first, normally with a heavy duty, non-etching, non-silicated, alkaline cleaner followed by the appropriate rinses and an acid clean for the removal of oxide films. Cleaner formulations are constantly changing to utilize new technologies and new wetting agents which are environmentally friendly.

Vapor degreasing is quickly becoming a process of the past due the elimination of fluorcarbons. However, in aluminum finishing, most vapor degreasing may be replaced directly with an aqueous cleaner.

Acid cleaner technologies has grown over the past two years. In the past phosphoric acid based acid products were used almost exclusively in the industry. However, with the need to reduce or eliminate phosphates, other mineral acids have been blended with new technology methods to provide the industry with environmentally friendly acid cleaners.

II. Etching

Etching is a means to give aluminum metal various degrees of a matt finish. Etch considerations include:

- Finish desired
- Amount of metal to be removed (die lines)
- Temperature requirements
- Alloys to be etched
- Foam blanket
- Leveling of finish
- Contaminate levels

Typically, an etch bath consists of 6 to 12% by volume 50% caustic, a complexing agent to hold aluminum in solution, leveling agents, scale inhibitors and spangling preventatives.

Etch baths are categorized as

- Simple etch
- Extended life
- Regenerated

The basic reactions which take place in an etch bath are:

1. Dissolution of Aluminum:

$$2Al + 2NaOH = 2H_2O \rightarrow 2NaAlO_2 + 3H_2 \uparrow$$

2. Precipitation of Aluminum Hydroxide

$$NaAlO_2 + 2H_2O \rightleftharpoons Al(OH)_3 \downarrow + NaOH$$

3. Formation of an insoluble scale

$$2AL(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$

In reaction 1, aluminum dissolves in sodium hydroxide and water to form sodium aluminate and liberate hydrogen gas. In reaction 2, sodium aluminate and water for the reversible reaction to give an aluminum hydroxide precipitate and free caustic soda. In reaction 3, aluminum hydroxide reacts to form alumina (hard precipitation) and water. To prevent the reaction (3) from occurring, the etch bath must be maintained at the proper operating conditions.

Typically 20 to 40 microns (0.8 to 1.6 mils) of aluminum will be removed from the surface. 2.67 gms of aluminum per square meter of surface per micron will be dissolved in the etch solution. Theoretically, 40 gams of caustic soda are required to etch 27 gm of aluminum; however, in actual practice a surplus of free caustic soda is required. Table 1 shows typical compositions of different etch baths.

Regardless of the type of etch bath, dissolved aluminum must eventually be removed. Table 2 shows the quantity of sludge produced from typical etch operations. For every pound of aluminum extrusions etched, about one pound of sludge is produced.

The new generation etch is utilizing a caustic etch recovery system. This system was developed in Japan and is widely used today, across North America. Regeneration of caustic soda etches occur when the sodium aluminate hydrolysis (reaction 2) occurs under controlled

conditions. This system will reduce the caustic soda usages by 65-75%. One draw back to CER has been the surface finish. In a typical CER system the metal will have a shiny appearance, since chelating agents cannot be used with a CER system.

However, development in the area of surface finish enhancement has resulted in an etch formulation that will produce a dull, matte finish (gloss number 4-8). Aluminum trihydrate crystal by-products are produced and can be sold for use in liquid aluminum, refractory bricks, cements, and as fire retardant additive for composite materials and plastics.

Table 2 concludes that sludge waste is reduced by 80-87%.

III. Deoxidizing and Desmutting

After etching in a sodium hydroxide based etch solution, a smut is left on the aluminum. This smut will vary in color from a light grey to a black. The smut tends to be heavier, the lower the purity of the aluminum and particularity heavy on copper based alloys (2024). Smut consists of particles of oxide; intermetallics, silicon, etc., which are insoluble in the alkaline solution.

Smut is removed by immersion in an acid solution. Typical deoxidizer - desmutters are:

1. Nitric Acid - 15 -25% vv removes smut very well but does not deoxidize. Nitric acid over 3% vv passivates the metal.
2. Mineral Acids with chromic acid, basically used in Aerospace but due to the environmental impact of chrome, is being replaced.
3. Mineral acids with ferric sulfate is the most widely used system, however, the ferric sulfate drags out and leaves a reddish deposit on the rise tanks.
4. Mineral acids with peroxide is the most economical, however, peroxide is unstable and requires a lot of bath maintenance.

5. Nitric acid with amoniumbi fluoride is used primarily for castings.

6. New technology deoxidize, desmutters with no chrome, no iron and minimum metal removal. The initial cost to charge a tank is high but use cost are proving to be very economical.

IV. Rinsing

After each process step, rinsing is required. Rinsing will:

* Stop the previous reaction.
* Remove contaminates.
* Prevent contamination of next process bath.
* Lower use cost.

Rinsing can be defined as the removal of a harmful clinging film of process solution from the work piece. Rinses should be air agitated and counter flowed where feasible to reduce water consumption. In order to produce good quality pre-treatment, good rinsing is required.

Pre-treatment, the foreplay for <u>Good</u> Aluminum Finishing

Table 1 - Characteristics of various etch baths

Item	Simple Etch	Extended-Life Etch*	Regenerated Etch
NaOH (total), g/L	114	253	105
NaOH (free), g/L	70	60	67
Al, g/L	30	130	27
Temperature, degrees C	60	60	60
Dragout, l/m^2	0.3	0.6	0.3

* This bath also contains chelating additives such as sodium gluconate.

Table 2 - Sludge Production in Aluminum Etching/Anodizing

Basis: 1000 ft^2 ($93m^2$) of extrusion surface area

Etch thickness (per side)	1.0 mil (25 micron)	1.5 mil (38 micron)
Aluminum dissolved in etching	13.8 lb (6.3 kg)	20.7 lb (9.4 kg)
Aluminum dissolved in anodizing (0.7 mil anodic film)	1.6 lb (0.7 kg)	1.6 lb (0.7/kg)
Waste sludge produced without regeneration	298 lb (135 kg)	431 lb (196)
Waste sludge produced with regeneration	55 lb (25 kg)	55 lb (25 kg)
Waste sludge reduction	81.5%	87%
Crystal byproduct with regeneration	39 lb (17.7 kg)	61 lb (27.7 kg)

Note: 1000 ft^2 of extrusions will typically weigh about 400 lb. Therefore, without regeneration, a pound of waste sludge is generated for every pound of aluminum finished.

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Several Experiments On Aluminum Surface Treatment

By K. Kaminaga and T. Sato

INTRODUCTION

The following experimenta are repoted in this paper. Grey coloring of aluminum by two step anodizing, coloring of anodized aluminum by smoking, deposition of SiO_2 colloids into the pores of anodized aluminum by CVD, electrophoretic deposition of oleic acid into the pores of anodized aluminum, laser marking on anodized aluminum , and other experiments.

Grey coloring of aluminum by two-step anodizing.

Grey oxide filem was formed on aluminum by anodizing aluminum in sulfuric acid bath and by re-anodizing it in low concentration bath of carboxylic acids such as oxalic acid, tartaric acid, citric acid and so on. Fig.1 shows the voltage versus time curve during re-anodizing of sulfuric acid film in a 1.0 g/l tartaric acid bath at galvanostatic anodizing current density of 0.25 A/dm^2. At the start of re-anodizing of sulfuric acid film, the voltage increased to 18 volts suddenly. This vertical voltage rise is due to the barrier layer of sulfuric acid film. The re-anodizing voltage increased gradually to 120 volts after the vertical voltage rise. This voltage rise is due to the thickening of the barrier layer of sulfuric acid film. The gradient of voltage rise became a slightly smaller at higher voltages than at 120 volts. The reason for this is due to the formation of a new oxide film under the sulfuric acid film. When the re-anodizing voltage reaches to the maximum voltage, the current decreased. At this stage, the sulfuric acid film became grey.

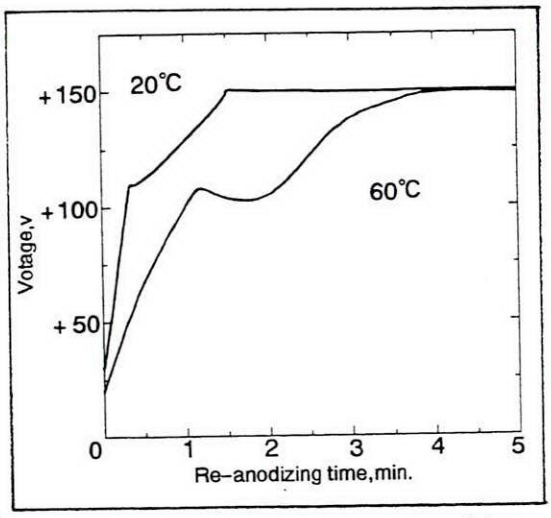


Fig.1–Voltage vs. time curve during re-anodizing

Photo.1 shows the cross section of the grey film through electron microscope. The electron microscope observation shows that the oxide film formed by re-anodizing of sulfuric acid

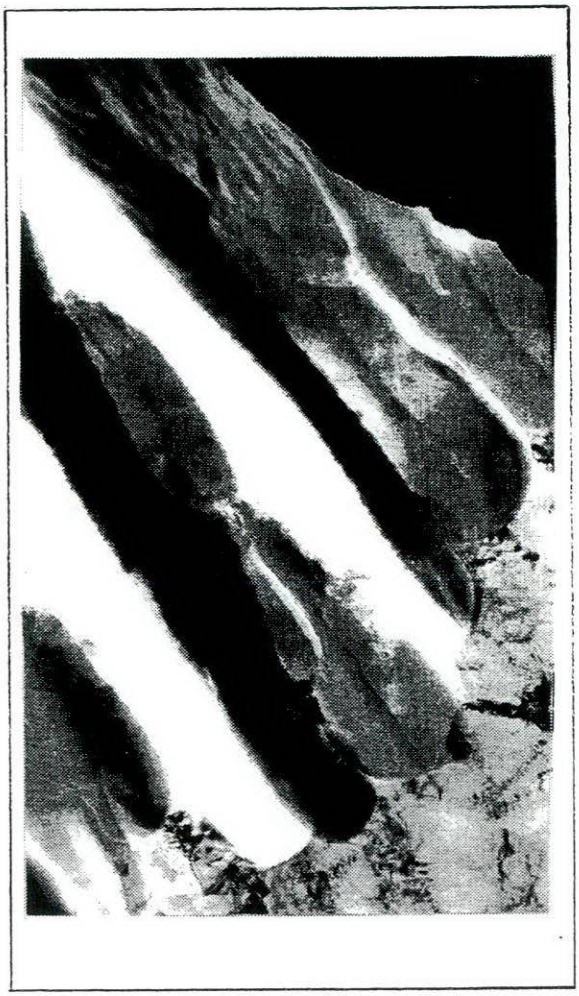


Photo.1-Cross section of grey anodic film.

film is a new-porous oxide film. The sulfuric acid film is not colored and only a uniform and transparent barrier layer is formed even if the sulfuric acid film is re-anodized in the high concentration bath of tartaric acid. The experimental condition "Law concentration" is the most important factor in the grey coloring method. The higher the voltage at the second anodizing, the deeper is the grey color. When the temperature of the second anodizing bath is 20℃, a re-anodizing voltage higher than 150 volts is necessary. When the bath tempareture was about 60℃, a grey film was formed even at 100 volts. The sulfuric acid film does not become grey when the thickness of the sulfuric acid film is less than 10 microns. So, this grey coloring is appliciable only for thick sulfuric acid films.

Coloring of anodized aluminum by smoking.

Meat and fishes are usually treated with smoke by burning wood to enhance taste and to preserve them for a longer time, as shown in Fig.2. This process is called "Smoking".

Anodized aluminum can be colored yellow, brown, or black by smoking. As the pore diameter of anodized aluminum is about 200 angstroms and the pore density of anodized aluminum is 76 billion pores/cm^2, organic compounds in the smoke deposit in the pores coloring the anodized aluminum. The shade of the color depends on the concentration of smoke temperature during smoke treatment and the treatment time. The color of anodized aluminum becomes yellow if smoked for 5 minutes, brown if smoked for 10 minutes and black if smoked for 30 minutes. Black wood tar deposits on anodized aluminum when the smoking time is longer. It is said that wood tar kills bacteria or molds, so anodized aluminum treated with smoke has pasteurization ability.

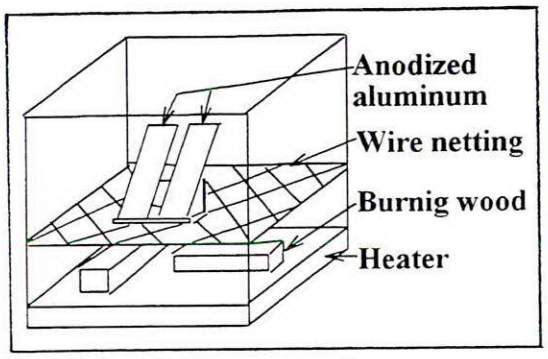


FIg.2-Smoking treatment of anodized aluminum

Deposition of SiO_2 colloids in the pores of anodized aluminum.

Studies of "Sol-gel coating" on metal sheet are popular these days. For example, if ethylsilicate sol is coated on a metal sheet and the coated sheet is heated, SiO_2 film (glassy film) is formed on the metal sheet. The corrosion resistance of this film is very good. However, since ethylsilicate sol in the coating tank is solidified by hydrolysis of ethylsilicate with water after the coating operation, most of the ethylsilicate sol is not used. The authors have investigated the relationship between the proporties of the vapors of ethylsilicate and improvement in the corrosion resistance of snodized aluminum. Small amounts of ethylsilicate and anodized aluminum were taken in a stainless steel vessel, and the vessel was heated in the oven. The heating time was 30 minutes. Fig.3 shows the relationship between the heating temperature of the vessel and corrosion resistance of anodized aluminum.

Deposition of oleic acid in the pores of anodized aluminum.

Oleic acid is deposited in the pores of anodized aluminum, when sulfuric acid film is re-anodized in a solution of sodium oleate. Fig.4 shows the voltage versus time curves and current versus time curves, when sulfuric acid film was re-anodized in a bath containing sodium oleate of 1.0 g/l, at a constant current density of 0.2 A/dm^2. The voltage vs time curve is divided into four parts. The voltage rise of part ① is due to the electric resistance of barrier layer of sulfuric acid film. The voltage rise of part ② indicates the formation of thicker new barrier layer on the bottom of the pores of sulfuric acid film. The volatage rise of part ③ and the maximum voltage of

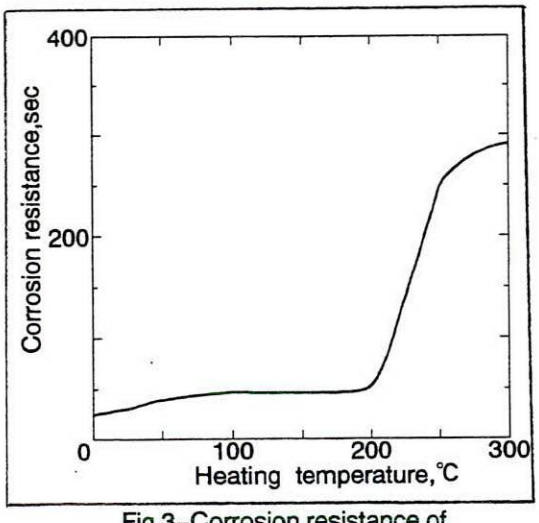


Fig.3-Corrosion resistance of vapor-treated oxide film.

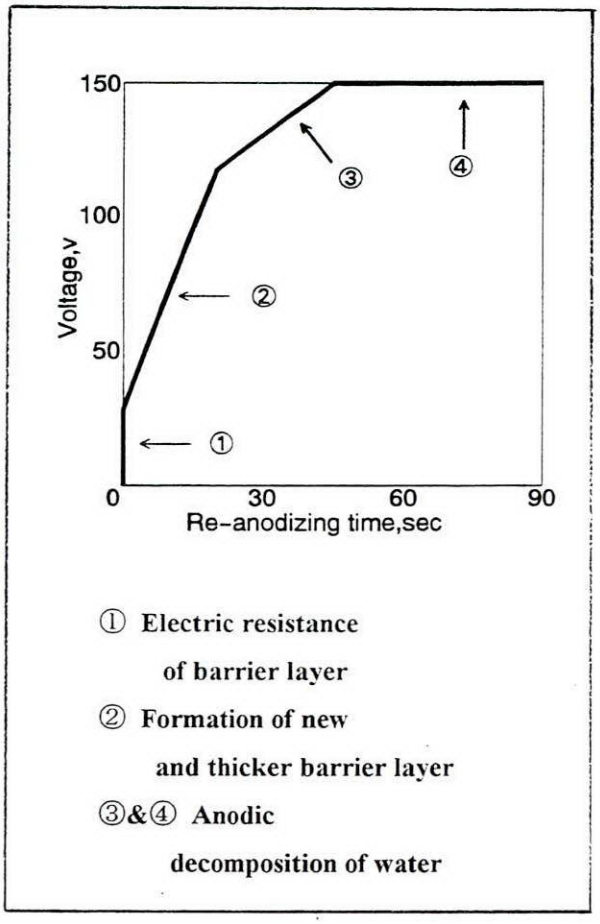


Fig.4 - Voltage vs. time curve during re-anodizing of anodic oxide film.

part ④ are due to the anodic decomposition of water given by equation (1).

$$2H_2O \rightarrow O_2 + 4H^+ + 4e \qquad (1)$$

Then, oleate anions in the pores of sulfuric acid film are neutralized by H^+ ions generated from the bottom of pores and oleic acid is deposited in the pores of the sulfuric acid film. Equation (2) shows the neutralization reaction in the pores.

$$C_{17}H_{35}COO^- + H^+ \rightarrow C_{17}H_{35}COOH \qquad (2)$$

The voltage vs time curves at various experimental conditions are shown in Fig.5 ~ Fig.7. Law concentration bath of sodium oleate is preferable. Sodium sulfate is harmful to the deposition of oleic acid. A thicker oxide film is preferable for deposition of oleic acid.

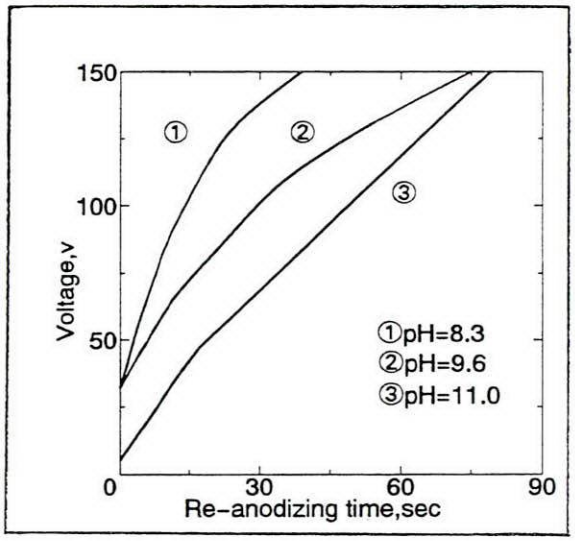


Fig.5-Effect of pH of the oleic acid bath on re-anodizing of oxide film

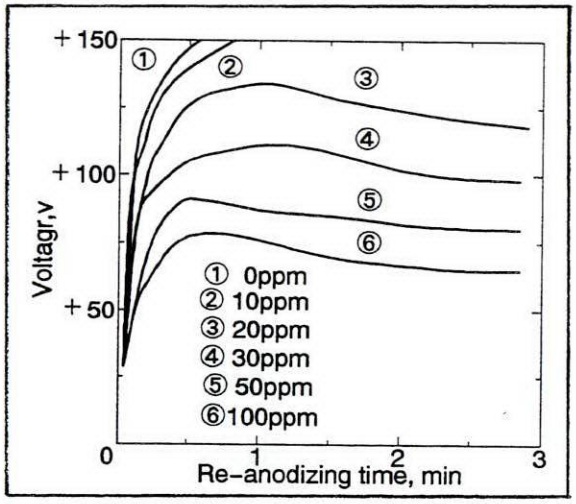


Fig.6-Effect of Na_2SO_4 on re-anodizing of anodic oxide film

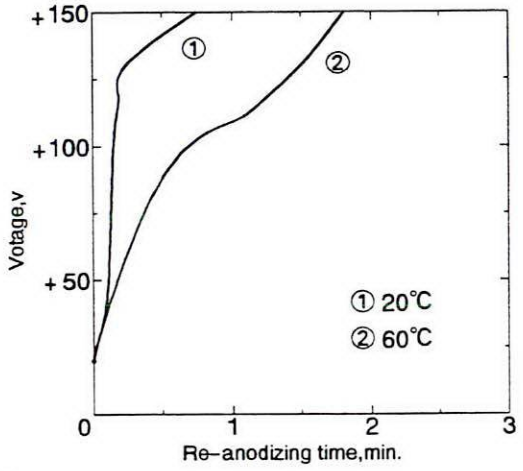


Fig.7-Effect of bath temperature on re-anodizing of oxide film.

Laser marking on anodized aluminum by CO_2 laser.

Letters or figures were drawn on anodized aluminum by scanning with CO2 laser beam.The depth of these marking lines is shallow, because the CO_2 laser is reflected by the aluminum substrate. This marked aluminum was anodically electrolyzed in a solution of sodium chrolide to increase the depth of the marked line. Only laser-marked part of aluminum plate was anodically dissolved. The other part, covered with anodized aluminum did not dissolve. A deep and wide concave-shaped lines could be formed on aluminum in this way. This situation is shown schematically in Fig.8.

Another application of CO_2 laser marking on anodized aluminum is partial electroplating on aluminum. If anodized aluminum is electroplated after CO_2 laser marking, the metal deposits only on the laser-marked part. Metal is not electrodeposited on other parts where the aluminum is covered with anodized film. This process is shown schematically in Fig.9.

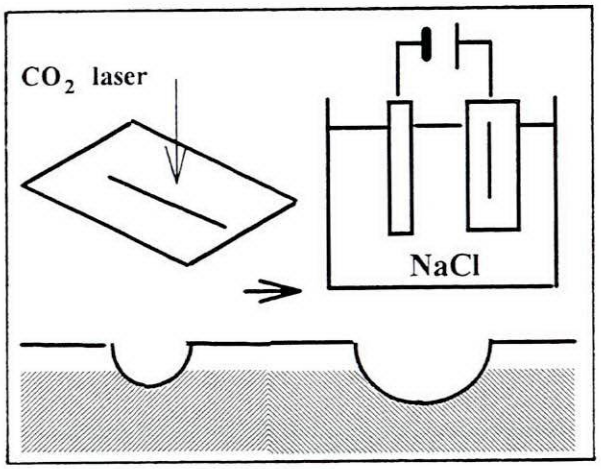


FIg.8-Widening and deepening of the concave formed byCO_2 laser.

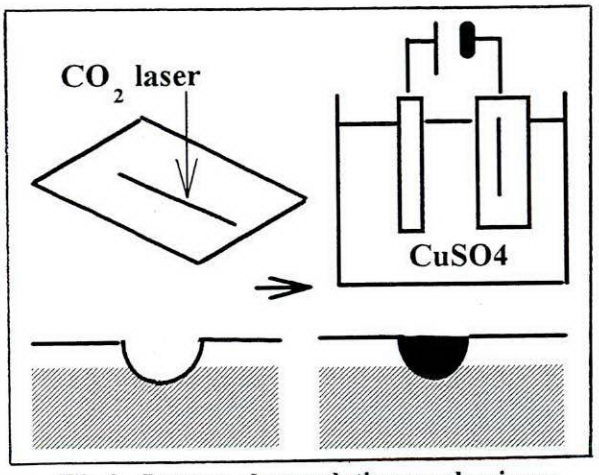


FIg.9 - Pattern electroplating on aluminum whose oxide film is masking pattern.

Other experiments.

Other experiments were also carried out by the authors. These are (1) amorphous electroplating in nickel sulfate bath by pulse plating, (2) multi-layer plating in copper sulfate and nickel sulfate mixed bath by pulse plating, (3) pattern plating without masking by pulse plating, (4) electroplating in the extremely law-concentration bath, (5) metal vapor deposition on transparent materiales by YAG laser, (6) concave pattern formation on the inner surface of glass tube or vessel and (8) anti-copying sheet. Some of these experiments are shown schematically in Fig.10 ~ Fig.13 and photo.2.

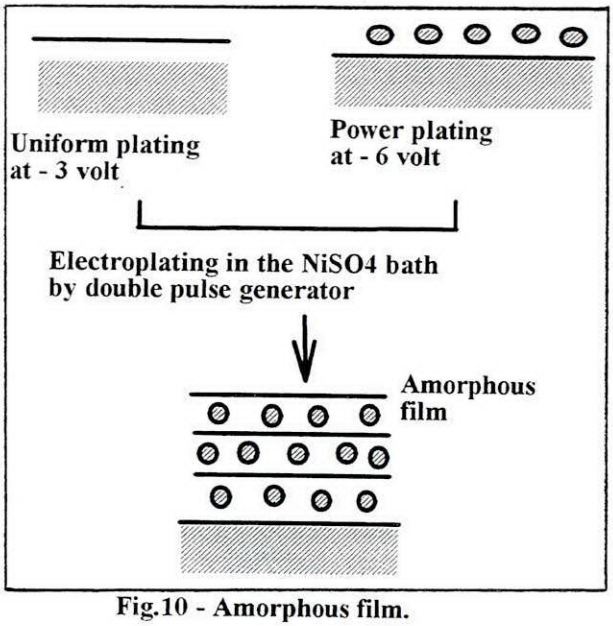


Fig.10 - Amorphous film.

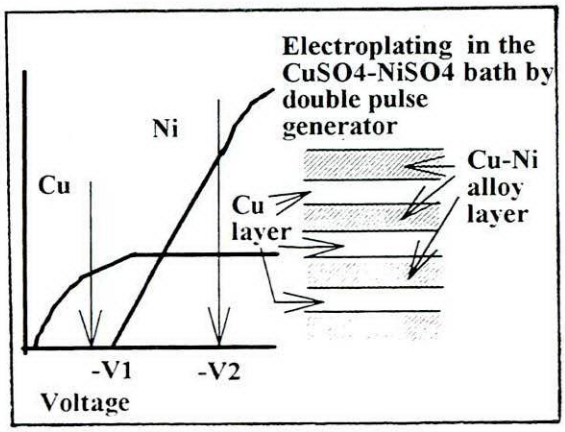


Fig.11 - Multi-layered electroplating

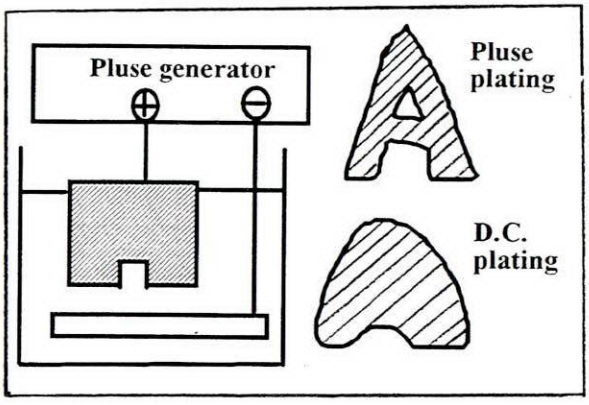


Fig.12 - Patern electroplating
Without masking

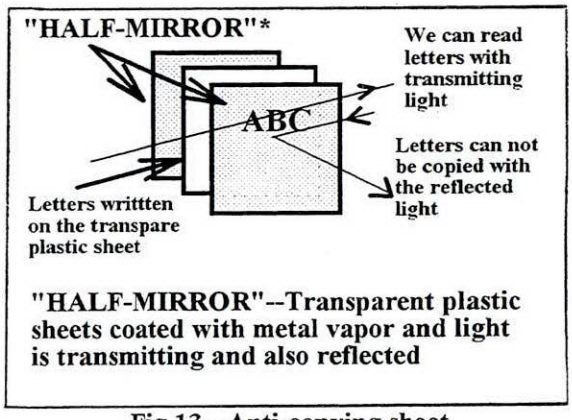


Fig.13 - Anti-copying sheet



photo.2- Surface of film electroplated in the 1.0g/l NiSO4- 1.0g/l Citric acid bath

Conclutions

Several novel methods have been reported here. However, these are preliminary experiments carried out at a small laboratory in the university. The authors will be happy if readers of this report use the basic concepts and ideas of some or all of these preliminary experiments, and develop them to carry out full-fledged and detailed experiments.

Anodizing by Current Density

by Charles A. Grubbs

Sandoz Chemicals, Metals Department

Today, the modern anodizer is faced with challenges never before considered. The quest for Quality and reproducibility has become the by-word of many of their customers. SPC, Quality, Computer Controlled lines, Auto-analyzed process tanks and many other advances have pushed the anodizer into the "high-tech" world of finishing whether he likes it or not. This is not all bad though. Some of the advances, properly implemented, can save the anodizer a lot of time and money.

However, even with these advances, many "old-time" finishers hold on to the old, out-dated methods of doing things. One of these methods is the use of ***CONSTANT VOLTAGE*** *for anodizing. Some anodizers will not consider the many disadvantages of anodizing by constant voltage rather than the more preferred way of using constant current.*

One of the most commonly used excuses is ***"I run a job shop and the parts I receive are too complex to be measured".*** *The reality is that in most job shops, at least 70-80% of the parts received can be measured, but it is easier to "do it the old way";* ***a "cop out".***

There are some anodizing jobs that will not require this type of control. "Commercial" finishes only require evidence of an anodic coating and would not be considered as a quality anodize - only a necessity!

CONSTANT VOLTAGE

Anodizing by constant voltage can be compared to driving your car blindfolded. Because the voltage is only the ***driving force*** *(much like the car's accelerator pedal) in a very dynamic system, other methods of control must be employed. The best method is the use of* ***CONSTANT CURRENT.***

CONSTANT CURRENT

Let us again refer to the above automobile analogy. If we consider the accelerator as the voltage and the current as the Cruise Control, we can see how constant current is a more controllable system of finishing.

As you are aware, when using cruise control on your automobile, you set the desired speed (amperage). You then allow the accelerator pedal (voltage) to accelerate or decelerate as needed to maintain this speed. This is the same thing that happens in an anodizing tank. The voltage will fluctuate according to the

needs of the system being anodized, while maintaining the required amperage. Bath temperature, acid concentration, aluminum content, aluminum alloy, temper and many other variables will change the voltage necessary to give you a good, consistent anodic coating.

THE ANODIC COATING

The anodic coating is an extremely good resistor. As it's thickness increases, the more resistant to passage of electrical current it becomes. Therefore, a constant voltage level, applied in the anodizing bath, will only be able to overcome a certain level of resistance. This means the current density will decay as the anodizing process continues, producing an anodic oxide film that will be less and less abrasion resistant. Conversely, an anodic oxide, formed at a constant current, will be consistent throughout, irregardless of the changing conditions.

SAVINGS

Another advantage to using constant current is the time savings. Because of the current decay when using constant voltage, it takes longer to form the necessary oxide film thickness. With constant current, you can accurately predict the time necessary to

form a given oxide thickness ***(720 Rule - see below)****. This means that the parts being anodized will spend less time in the sulfuric-*

acid bath and will have less outer surface oxide dissolution due to the proximity of the oxide to the acid.

No matter the makeup of the anodizing electrolyte, the sulfuric acid in the bath will dissolve and soften the coating to some extent (a function of time and temperature). The higher the electrolyte temperature, the higher the dissolution rate. If a combination of high temperature and low current density are employed (as might be the case with constant voltage), the resulting oxide will have low abrasion resistance and will most likely offer high resistance to adequate sealing.

Many anodizers who employ constant voltage anodizing would be astounded at the production increases they could realize if they were to control the current instead of the voltage. As stated above, the anodizing time and the oxide thickness can be predicted very accurately when aluminum alloys are anodized at constant current.

The 720 Rule

We know, for instance, that it takes ***720 amp-minutes per square foot to produce 1.0 mil of oxide*** *(except in the case of the 2xxx and some casting alloys). Therefore, if we want to know how long it will take to anodize a part to 0.7 mil oxide thickness (Class I Architectural finish) at 15 asf, we simply plug the*

knowns into the formula and solve for the unknown.

therefore:

720 ÷ 15 x 0.7 = 33.6 minutes.

Many anodizers have to keep the parts in the anodize tank for 50-60 minutes to attain 0.7 mil oxide. This is because they are anodizing at constant voltage and having to allow for current density decay. If, on the other hand, they anodize by constant current, a considerable time savings will be realized (in this case, 16-26 minutes).

Therefore a typical anodizer who anodizes by voltage can, in many instances, double his production and produce a more acceptable part at the same time.

As an example, alloys 5005 and 1100 were anodized under various controlled conditions and the parameters recorded ***(see Table I)****. From these data, you can see the value of anodizing by constant current, namely:*

1. The oxide thickness was well within the predictable range on the parts anodized using constant current, whereas the parts anodized by constant voltage had a wide oxide thickness variance.

2. As the temperature was lowered, the oxide thickness variation was greater.

RAMPING

Another anodizing consideration which must be taken into account is the ramp speed: " How long do I take to reach full current?"

There is no hard & fast rule to follow. If the ramp speed is too fast, burning of the parts can occur; if too slow, soft,mossy coatings will be formed due to the low current densities employed during ramping and the solution effect of the electrolyte because of prolonged anodizing times.

*In the case of **regular anodizing (68-72°F)**, a ramp speed of 15-30 seconds is usually sufficient if the parts are correctly & tightly racked.*

*For "room temperature" hardcoating **(45-55°F with appropriate anodizing additives)**, the ramp speed will be in the range of 45 seconds to 1 1/4 minutes.*

*Low temperature hardcoating **(30-45° F)** requires a somewhat slower ramp, usually 1-2 minutes, to guard against the possibility of burning.*

If the ramp time is extended much beyond these times, the anodic coating quality can be grossly affected. Soft coatings will be formed which will accept dyestuffs readily, but will also allow these same dyes to leach very rapidly during both rinsing and sealing. This type of anodic oxide structure is difficult, if not impossible to seal due to the very "open" pore structure formed. Obviously, the formation of a softer coating will give negative results to any abrasion tests run on the anodized part's surface.

There are a few alloys that will not lend themselves to "fast" ramp speeds. The 2XXX alloys and some casting alloys exhibit a greater tendency toward burning when the current is applied too rapidly. However, even these "problem" alloys will react positively to a moderate ramp speed ***(2-3 min).***

Over the years we have seen ramp times that have ranged from ***10-60 minutes****! In these cases, the anodizer was dismayed that he could not pass a simple seal test, or a salt spray test, or an abrasion test, or understand why his dye leached so badly in his rinse and seal tanks. It was not until he decided to anodize by constant current and to control his ramp speed that these tests were passed & the dye and seal chemical usage was greatly reduced.*

EDUCATION

None of the facts that have been presented in this paper are ***new.*** *Mostly, they are common sense items that have been overlooked or forgotten for some reason. Maybe we did not train new anodizers correctly. The rush to do a "fast" job may have gotten in the way of doing a "quality" job. Competition could have lured us into forgetting our basics and we accepted the "easy" way as the*

" correct" way.

For whatever reason(s), we should look at how we are anodizing and determine if we want to stay in this business or be replaced by other coatings which ***DO*** *use forethought and quality to gain a foothold and market share in our customer base.....****the choice is OURS!!!***

Table I

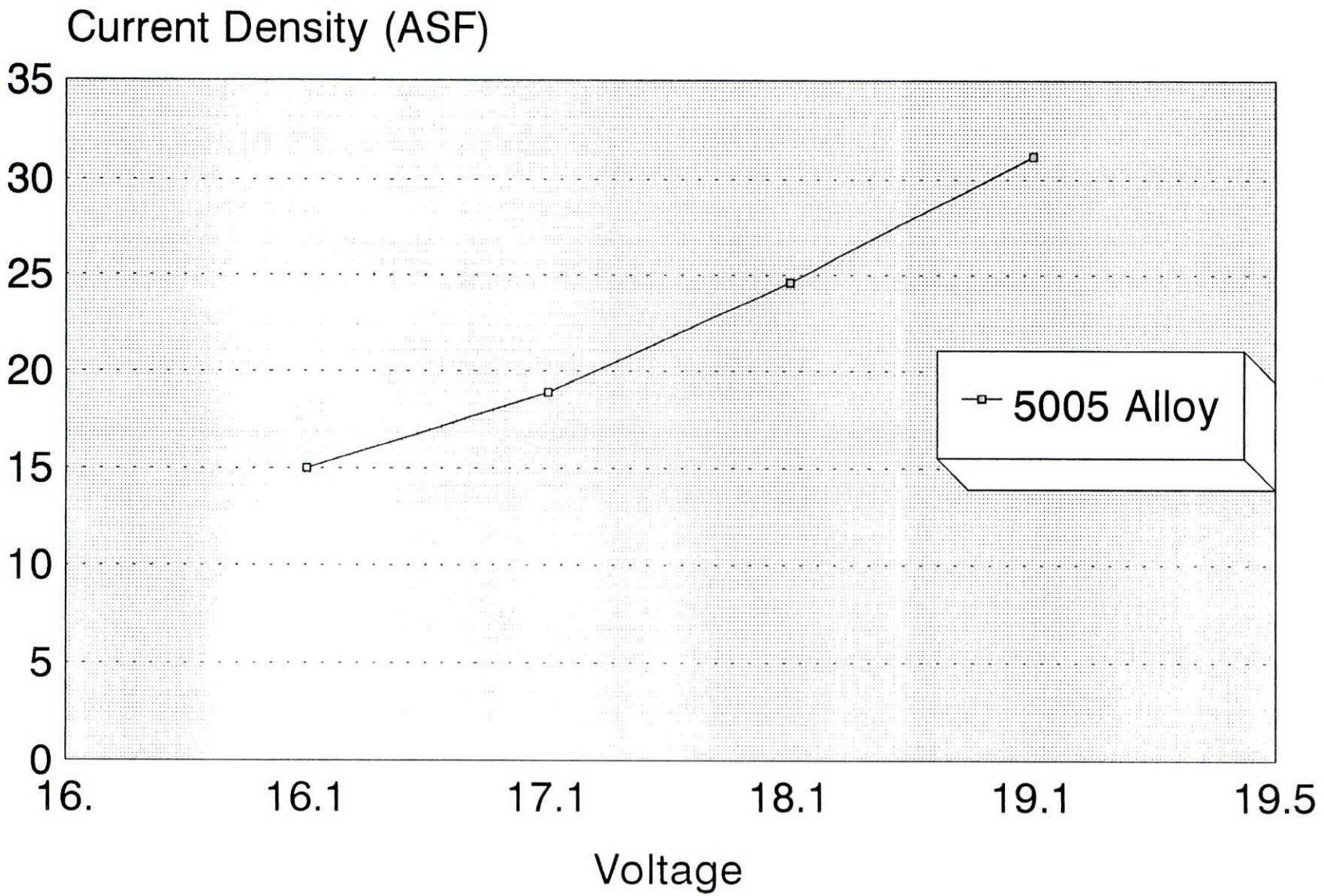
Oxide Thickness Variations

Alloy	*Temp. °F*	*Anod. Conditions*	*Oxide Thickness (mils)*
5005	*70*	*Current Density*	*1.19*
5005	*70*	*Voltage*	*0.96*
5005	*63*	*Current Density*	*1.23*
5005	*63*	*Voltage*	*0.78*
1100	*70*	*Current Density*	*1.22*
1100	*70*	*Voltage*	*0.96*
1100	*63*	*Current Density*	*1.21*
1100	*63*	*Voltage*	*0.78*

Anodizing Conditions: 60 min; 185 g/l sulfuric acid

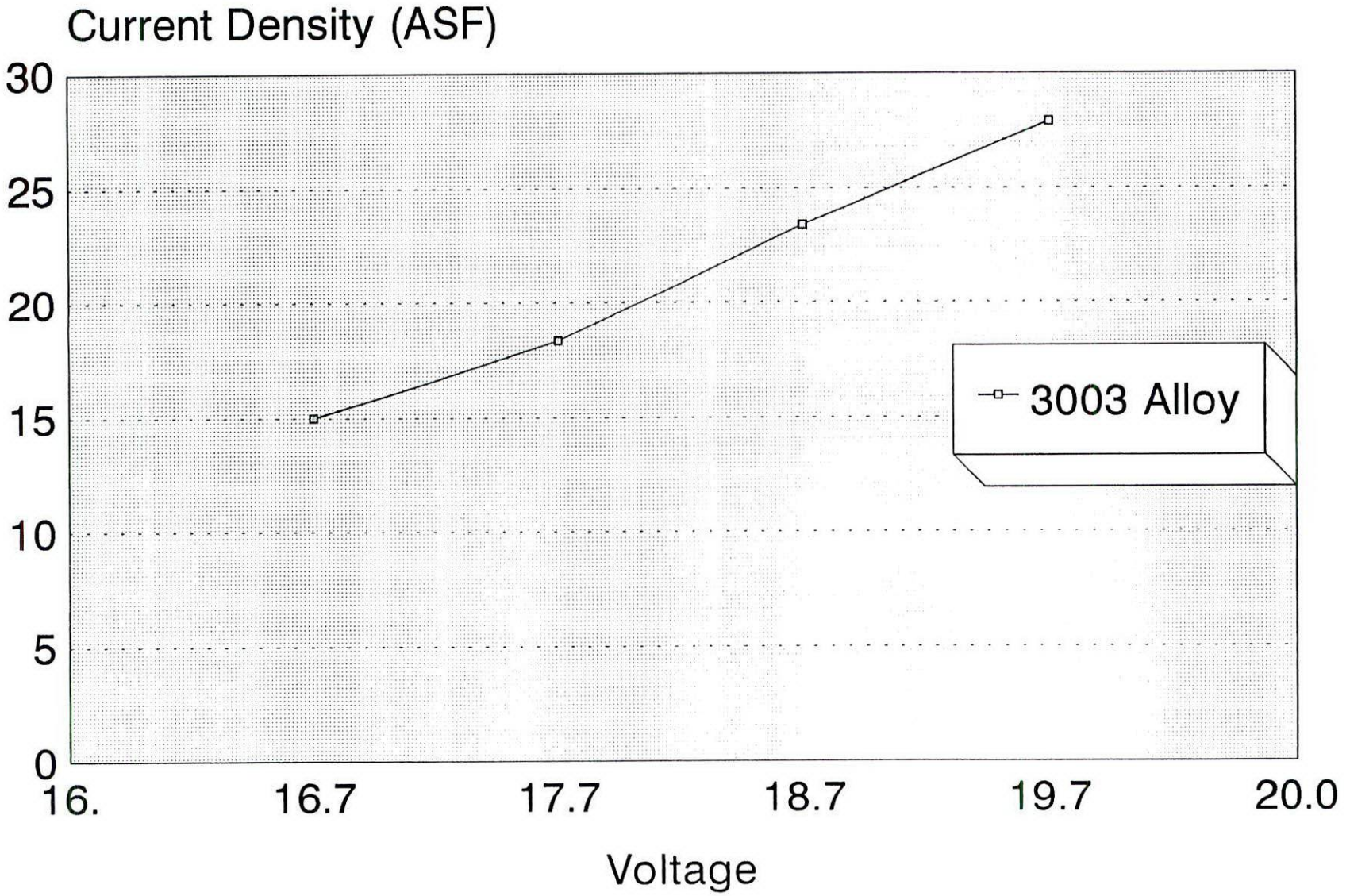
Current Density vs. Voltage Change

70°F Anodize, 185 g/l acid



Current Density vs. Voltage Change

70°F Anodize, 185 g/l acid



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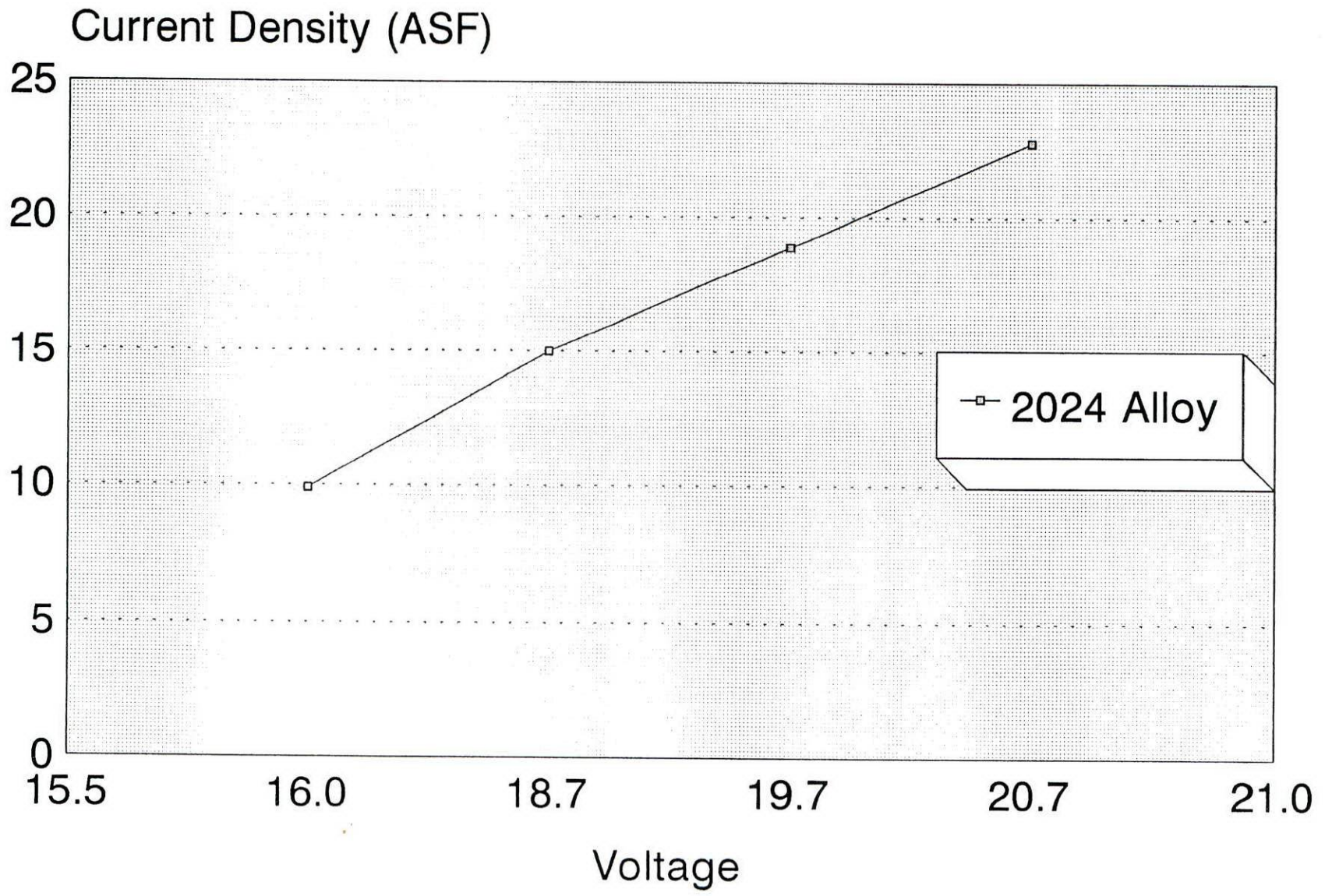

FASTER, HARDER, BETTER

BY
WAYNE D. CHANDLER
SOUTHERN INDUSTRIAL CHEMICALS, INC.

This paper describes methods of producing a higher quality, more uniform anodic film by manipulating the chemical and physical parameters of the anodizing bath.

Quality has become the watchword of american industry. Numerous programs based on Dr. Deemings teachings, also the ISO 9000 program instituted in Europe and rapidly spreading to the United States have been developed and pushed over the past ten (10) years. Today, I am talking about a very small part of these programs, but one very important to all of us involved in anodizing, the improvement in quality of the aluminum anodic coating. The great thing about these improvements is that to achieve them is relatively inexpensive and require very little additional training or procedures to implement.

In order to obtain a higher quality anodic coating the metal has to have the proper chemistry and heat treatment. Contrary to the belief of extrusion foremen the anodizing shop can not make gold from lead or in this case a saleable product from improperly alloyed, extruded or heat treated metal. Once the metal is in the anodizing shop for these recommended changes in chemistry and/or physical conditions of the anodizing tank to have the desired effect, the part coming to the anodizing tank must be clean, free of smut, etched well either with caustic or bright dipped, and the racks need to be in good repair and the contacts uniform. The condition of the racks is one of the most important parts of assuring there is not a cause for burning which cannot be corrected in the anodizing tank.

The reasons for making these changes to the anodizing tank are:

1. Faster Anodize Times
2. Harder Coatings(less scratches.)
3. More uniform coatings (more even coloring)
4. Better Seal Quality
5. Less Critical Temperature Control.
6. Less Critical Chemistry Control
7. Less Chance for Burning.

1. Faster Anodize Time - The methods described will allow higher amps per square foot to be run through the part without burning the coating decreasing the amount of time necessary to get a coating of the desired thickness.(Appendix 1)

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1. Faster Anodize Time - The methods described will allow higher amps per square foot to be run through the part without burning the coating decreasing the amount of time necessary to get a coating of the desired thickness.(Appendix 1)

2. Harder Coating - The attack on the anodic coating by the sulfuric acid in the bath and the temperatures produced at the surface are reduced leaving thicker cell walls hence a harder coating.

3. Uniform Coatings - Reduces the attack on the coating as a whole which gives a more uniform coating which is very important for decorative anodizing since it will have an effect on the reflectance of the light off the coating.

4. Better Seal Quality - Smaller pores mean the seal will act faster which will give an effective longer seal time. Some time true hard coat is not sealed at all.

5. Less Critical Temperature Control - Anodizing temperatures to 95° F (36° C) may be used without burning.

6. Range of acid concentration not as critical since less attack on part.

7. Less chance of burning - (dissolution of coating leaving powder)

Today I will be referring to "normal" hard coating. The hard coating which is achieved by chemical and mechanical means at normal sulfuric acid anodizing temperatures, (70-95 ° F) acid concentrations (140-230 g/l) current densities (10-24 amps/ft^2) and thickness of coating (0.2-1.0 mil.)versus what is referred to as "true" hard coat.Temperatures of (28 - 32 ° F), current (24 - 60 amps/ft ^{2}) acid concentrations (220 - 300 g/l) sulfuric acid and thicknesses (2-5 mils).

There are numerous methods in the literature(1)for achieving a hard coating on aluminum alloys. These include mixed acids, organic solvent additives, metal salts and acid mixtures, organic molecules in acids. Most of these have been developed for "true" hard anodic coating and not "normal" hard anodic coatings. In this paper I am concentrating on the methods which have been used in decorative anodizing or "normal" hard anodic coating. I will also describe one additive which is used in "true" hard coat anodizing because it shows the range of materials which have been investigated for "true" hard coating.

The "true" hard coat additive which I shall describe is from Patent 3,390,063.(2) The two "normal" hard coating processes I am going to describe are the the one covered in Patent 3,524,799 (3) commonly referred to as the Reynolds MAE process

and one based on using microexplosive air in the anodizing bath presented in a paper by Mr. Satoh at the 1990 AES SurFin in Boston.(4)

The additive method for improving "true" hard coatings which I referred to above is a patented method (1) using an extract from Redwood Bark which was originally used as fertilizer.

The quebracho extract is recommended in true hard coat anodizing temperatures 32° F (0° C) and 24 - 60 volts according to the patent 3,390,063. The advantages of this material is quicker coating and a harder coating according to Taber abrasion test. The theory behind this method is that the material chelates metals which keep contaminates from being incorporated in the coating.

The extract also inhibits the incorporation of sulfate ions in the coating which causes a harder coating.

Two methods of producing the "normal" hard coating are using the Reynolds MAE (2) based chemicals which are in widespread use in the United States and a mechanical method based on micro-explosive air agitation of the tank. I will first discuss the practice of the methods and then the theory of each process. The practice of the Reynolds based material will be talked about first followed by the air agitation method.

The origin of the material was due to a Reynolds Aluminum NASA research project to find a tough hard white coating that would be reflective and visible to trackers looking for the space craft as well as being more resistant than paints for coating. As a side benefit it was found that different mixtures of organic acids and sulfuric acid would allow the anodizers to anodize at tempertures, concentrations of acids, and currents which in the past would have produced soft coatings, or no coatings, or what is generally referred to as burned coatings. The percentage used was between 2 and 4% by volume. The temperature range is 32 ° F (0° C) to 95 ° F (35 ° C).

The advantages of the Reynolds based additives over the other baths are as follows:

1. The Reynolds based materials are non-hazardous.

2. The increased coating rate and harder coatings can be achieved with normal rectification.

3. Normal chilling can be used.

4. Temperatures up to 96° F (35° C) can be used in the anodizing bath.

5. The coating produced is more uniform making dyeing more uniform and easy to control.

6. The desired thickness is achieved at 2 to 3 times the normal speed depending upon the size of the load and the amount of the rectification available.

7. The coating produced is indistinguishable from coatings produced without the additive.

8. Burning is greatly reduced due to the removal of heat from the surface.

The disadvantages of the Reynolds are as follows:

1. More expensive than sulfuric acid.

2. The additives organic materials carried into the rinse tanks can lead to algae growth which can cause problems in the waste treatment systems and appearance problems on the parts.

The second method I will be discussing is a mechanical method put forth by Mr. Satoh at the 1990 AES meeting. According to his paper there is widespread use of this method in Japan.

A mechanical method of controlling burning is micro-explosive air agitation (2). The method comprises air agitating the anodizing bath using a diffusion pipe which puts out 30-50 micron air bubbles at 30-80 l/min/meter of pipe when air was sent from one end the maximum length is 1.5 M (5 ft) or 3 M (10 ft) if air is sent from both ends.

The use of this form of agitation has the following advantages.

1. Prevents burning at elevated temperatures and currents.

2. Produces a hard coating.

3. Seal is improved over conventional agitation.

4. Brightness of metal is better.

5. Surface smoothness is better.

6. Dyeing time is unaffected.

The disadvantages of this form of agitation are as follows:

1. Equipment to purchase,tubes which give 30 - 50 micron air.

2. Maintenance of pipes to make sure air is uniformly distributed over the entire length and width of the tank.

3. Racking of parts and configuration of parts which could block air movement.

4. Testing was caried out on small size operations 10 ft maximum length which would limit applicability.

The theory of how each of the processes works will be discussed next.

First, the Reynolds MAE process and second micro-explosive air agitation method.

The theory of Reynolds MAE type additives mechanism for improving the coating is that the polyhydric acid and the organic acid act as thermal regulators dissipating the heat formed by the aluminum oxide coating.

The sulfuric acid acts to oxidize the organic acids which reform the more stable forms when the heat and current are eliminated. Therefore the usage is very low for the hard coat additives in the actual anodizing process. The main usage is due to dragout.

The theory of the micro-explosive air agitation is that the fine bubbles act to physically diffuse the heat generated in anodizing from the surface of the part. Also a more uniform temperature, and even distribution of the acid throughout the anodizing solution reduces uneveness of coating and slows down the attack by the sulfuric acid on the anodic coating.

Conclusion :

Both of the methods claim to produce basically the same effects which are:

1. Harder coating

2. More even coating

3. Easier to dye

4. Faster coating without burning

5. More consistent color from organic and inorganic dyeing and two-step electrolytic coloring.

6. Use of higher temperatures which increase conductivity, speed up coating and reducing strain on the cooling system.

7. Less critical chemistry control

8. No special rectification or chilling requirements.

The advantages of the chemical over the mechanical are that it can be maintained easily and is not affected by part configuration. The main disadvantage is added cost.

No matter which method is used in your operation there are definite advantages to using some method to allow the speed up of coating making your operation more profitable and able to compete.

As the anodizing industry progresses into the 21st century these methods are simple steps which can be taken to give a "Faster, Harder, and Better" anodic coating at a very reasonable cost.

1. S. Wernick, R. Pinner, P.G. Sheasby, "The Surface Treatment and Finishing of Aluminum"; 1987, Vol. II pp 663-684.

2. Working, K. C., U.S. Patent 3,390,063.

3. Dale H. D., U. S. Patent 3,524,799.

4. Satoh, H., AES 77th Annual Technical Conference; Boston, 1990 pp 247-260.

THE EFFECT OF POROSITY TEST ATMOSPHERES ON THE INTEGRITY OF Pd-Ni PLATINGS

by Simeon J. Krumbein, Diane Y. Hanse, and J.D. Kronicz

The usefulness of gas-type pore corrosion tests for assessing the quality of gold finishes on contact surfaces (1-2) had led to attempts to extend these porosity test methods to other types of metallic finishes. Such tests, particularly those that use nitric acid vapor as the oxidizing or corrosive medium, have been the mainstay of porosity testing for the gold platings on electrical contacts and similar small surface-area conductive components.

When properly carried out, the standard nitric acid vapor test (3-4) has been found to meet the minimum criteria for a good pore-corrosion test. These criteria (2,5) or requirements are:

1. A reproducible degree of severity for a particular plating and substrate system.
2. The ability to detect all pores that penetrate the plating or platings.
3. Convenient exposure times.
4. The ability to give good separation of pore-corrosion products at the pore sites,

   and most importantly:

5. The corrosive medium must not attack the metallic coating whose porosity is being determined.

Unfortunately, during the commercial development of palladium and palladium alloys as alternatives to gold on contacts, various workers had continued to use the nitric-acid vapor test method for the porosity assessment of these new plating systems. One early example is shown in Table I.

Such procedures did not take into account fundamental differences in reactivity between palladium and the more noble gold and platinum. The latter metals are normally inert to nitric acid and other strong oxidizing agents, such as chlorine bleach. Palladium, on the other hand, is one of the least noble of the "platinum metals". Both palladium metal and palladium and palladium-nickel platings can undergo significant attack in these chemical environments (7-9), thereby defeating one the major porosity test requirements and leading to spurious and misleadingly low results.

TABLE I

SPURIOUSLY LOW RESULTS FROM THE NITRIC-ACID POROSITY TESTING OF COMMERCIAL PALLADIUM PLATINGS.

PLATING	THICKNESS (μm)	"POROSITY" (pores/cm^2)
Hard Gold	0.8	150
Pd-Ni Alloy	0.8	1.6
Pd-Ni Alloy with Gold Flash	0.8	0.6

Preliminary Experiments and Results

Since chemical attack on the plating metal may not be visually obvious during the relatively brief time interval of the test, a number of short experimental programs had been carried out in our laboratory over the years in order to determine the characteristics and extent of these corrosive attacks. A number of these are described below in abbreviated form,. They are roughly in chronological order and involve palladium foil and platings of palladium and palladium-nickel alloy, as well as plating systems incorporating a gold flash over the palladium-based coating.

A. Acid Immersion Tests

1. Acid Immersion -- Palladium Foil

The method used was to degrease a piece of "pure" palladium foil and suspend it halfway into the acid or solution of interest, at room temperature (21-23°C), for 30 minutes. It was then washed down with deionized water into the liquid until a 1:1 dilution had been made. The foil was then examined under the microscope, and the solution analyzed for palladium by atomic absorption with the following results (Table II), in parts per million (ppm).

TABLE II

DISSOLVED PALLADIUM FROM VARIOUS REAGENTS

REAGENT	(PALLADIUM CONCN (ppm)
Concentrated Nitric Acid (HNO_3)	7.8
Concentrated Sulfuric Acid (H_2SO_4)	1.2
Concentrated Hydrochloric Acid (HCl)	1.3
Chlorine Bleach (5.25% NaOC1)	1.3

Note that the data are for a 30 minute reaction, and that the limit of resolution of the analytical technique is 0.3 ppm (i.e., only one-fourth of the smallest amount detected). Also note that the bleach is an alkaline solution, with pH = 12.6.

Optical examination of the foil (with a 10-70X steromicroscope) showed that the nitric acid had etched the palladium at and above the liquid level, while leaving it smooth and bright below the meniscus. The former was probably due to the NO_2 that was evolved by the nitric acid at the palladium surface (and identified by its brown color). With the other three reagents, however, we did not see any changes in the appearance of the palladium surface.

2. Acid Immersion -- Palladium Platings

Some very early work with porous and micro-cracked palladium platings (1.8 μm over phosphor bronze) involved suspending the samples in concentrated nitric acid for 40 minutes. Much palladium was dissolved, as determined by a measured concentration of 198 parts per million in the (1:1) diluted acid. In addition, examination of the coupons showed that the acid had etched all the cracks in the plating and "developed" them into fairly-wide coppery lines, as well as producing a few individual holes down to copper.

3. Acid Immersion -- Palladium-Nickel Platings

Two one-inch square phosphor-bronze flats had been plated with 80:20 palladium-nickel alloy (1.9 μm over a 1.2 μm sulfamate-nickel underplate) by the commercial plating-bath vendor. Each of these was immersed about three-quarters of the way into separate beakers of concentrated nitric acid, at room temperature and without stirring. The first sample was immersed for 5 minutes and the second for only two minutes in order to minimize physical (i.e., noncorrosive) removal of the palladium-nickel plating. The latter had occurred with the first sample when the acid attacked the underlying bronze, and subsequently undercut the platings.

Upon removal from the acid, each sample was washed down with deionized water into its beaker until a 1:1 dilution of the acid had been made (and the liquid volume doubled). The resulting solutions were then analyzed separately by atomic absorption for palladium, nickel, copper, and tin, the latter being the main alloying additive in the phosphor bronze.

1. The concentrations of the various metals removed by oxidative acid attack are listed in Table III. Note that the palladium concentrations are approximately the same for both immersion times, indicating that the outer palladium-nickel platings had been almost completely dissolved away by the acid. In contrast, both the nickel and copper concentrations are significantly greater for the longer immersion time.

TABLE III

PALLADIUM-NICKEL ALLOY PLATED SQUARES
IN CONCENTRATED NITRIC-ACID

(80-20 Pd-Ni Alloy; 1.9 μm over 1.2 μ Nickel Underplate, over Phosphor Bronze).

IMMERSION TIME (MINUTES)	Ni (ppm)	Cu (ppm)	Pd (ppm)	Sn(1) (ppm)
5	358	342	448	<10
2	134	18	428	<10

(1) Note: The detection limit for tin was 10 ppm for this analysis.

2. Almost complete removal of the palladium-nickel plating was confirmed by scanning electron microscopy (SEM) analysis of the dull gray (nickel underplate) surfaces that remained on portions of the samples after the acid immersion. Only trace amounts of palladium were detected, although these were widely, though non-uniformly, distributed over both sample surfaces.

B. Porosity Test Conditions

1. Nitric Acid Vapor--Palladium-Nickel

Phosphor bronze test strips, comprising both flat and curved surfaces, and plated (by the same commercial plating bath vendor as in the previous program) with 80:20 palladium-nickel alloy, were exposed for 60 minutes to the standard nitric-acid vapor test conditions that are used for determining porosity in gold platings.*

All of the exposed pieces were attacked to some degree by the nitric-acid vapor. In the first run, which comprised test-strip shapes plated with 0.8 μm of palladium-nickel, the most common mode of attack was by pore corrosion, as determined by optical microscopy. However, indications of direct attack on the palladium-nickel were also observed, as well as examples of blistering and exfoliation that may have involved both mechanisms. In practically all cases, however, the pore-corrosion indications tended to have a "wet" appearance and to be surrounded by wet-looking haloes -- indicating dissolution of the palladium-alloy coating.

The corrosive attack on the palladium-nickel alloy was confirmed by washing down a flat (square) sample and a pair of hemispherical samples with hot, essentially-neutral deionized water, and analyzing this wash water for copper, nickel, and palladium (Table IV-A). The results of Table IV-A also showed that the predominant corrosion reaction was at the nickel underplate, since the concentration of soluble nickel was much greater than that of palladium.

**As specified originally in Western Electric Manufacturing Standard 17000, Section 1097, Issue 11 (January, 1983) Method C, and since revised and incorporated into ASTM Standard Test Method B-735-92.*

TABLE IV

TEST STRIP SAMPLES OF 80-20 PALLADIUM-NICKEL

Elemental Analysis of Soluble Corrosion Products After Nitric Acid Vapor Testing

A.	**RUN #1** (all 0.8 μm)	**Ni (ppm)**	**Cu (ppm)**	**Pd (ppm)**	**pH**
	Flats	18.5	0.43	0.66	6.8
	Hemispheres	11.2	0.50	0.35	6.9
	(Hemispheres corrected for area difference)	(44.8)	(2.0)	(1.4)	

B.	**Run #2** (Cylinders)	**Ni (ppm)**	**Cu (ppm)**	**Pd (ppm)**	**pH**
	1.9 μm Pd-Ni	4.73	1.46	2.15	6.4
	0.8 μm Pd-Ni	5.31	1.70	1.13	6.5
	(0.8 μm corrected for different number of samples)	(2.65)	(0.85)	(0.56)	

For the second run, the half-cylinder test-strip shape was used, and samples with 0.8 and 1.9 μm thicknesses of the 80-20 palladium-nickel were chosen for testing.

Again, the primary mode of attack was by pore corrosion, with brownish haloes being observed on all the parts. In addition, on the inside of the cylinders, especially with the 0.8 μm plating, the brown coloration was seen to cover most of the surface.

One of the 1.9 μm samples and two 0.8 μm samples were then soaked in hot deionized water for 30 minutes to dissolve away the corrosion products. The resulting solutions, upon analysis (Table IVB), again showed that the palladium-nickel alloy plating was attacked by the nitric-acid vapor. An additional indication of direct chemical attack on this plating can also be seen by noting in the table that considerably more palladium was dissolved from the thicker 1.9 μm sample than from the 0.8 μm platings.

2. NITRIC-ACID VAPOR -- GOLD-FLASHED PALLADIUM-NICKEL CONTACTS

In a later program, 30 minute nitric-acid vapor porosity test exposures were carried out on contact posts or springs from three different connector manufacturers. All of the contacts had been plated with a gold flash over the palladium or palladium-nickel coatings and had been fabricated into electronic connectors (mostly headers). All the posts were similar in size and design, with square cross-sections and pyramidal tips. In addition, one of the manufacturers was also represented by leaf contacts (No. A-2 in Table V, with the same plating system and similar dimensions as the posts.

After the porosity test had been concluded, three posts of each type were soaked in boiling deionized water. Subsequent elemental analysis of the soak water showed that a considerable amount of palladium had been oxidized to water-soluble species. Although the gold was not chemically attacked, a significant amount had been removed by physical (non-corrosive) means, such as by undercutting or exfoliation.

Table V lists the concentrations of the oxidized palladium, nickel, and copper in terms of total micrograms of dissolved metal (per cm^2) for each 3-post sample.

TABLES V

ANALYSIS OF SOAK SOLUTION AFTER 30 MINUTE HNO_3 TEST
(Connector Contact Posts With Gold Flash Over Pd or Pd-Ni)

Product and Code	Pd Type	Elemental Analysis (micrograms/cm^2)			
		Ni	Pd	Cu	Au
Company A; Posts	80Pd-20Ni	11.4	12.9	16.4	N.D.
Company A; Leaf Contacts	80Pd-20Ni	21.4	27.1	21.4	N.D.
Company B; Posts	Pd (with Ni underplate)	14.3	28.6	37.9	N.D.
Company C; Posts	80Pd-20Ni	32.1	42.9	85.7	N.D.

N.D. = None detected. The detection limit for gold was equivalent to 2.4 micrograms/cm^2.

Current Program

Introduction

Since the completion of these early projects, much progress has been made (by the plating industry) in the development of improved commercial plating baths and plating processes for palladium-nickel coatings. In addition, there has been wide acceptance of the practice of applying a thin gold flash as the topmost layer for palladium-nickel contact platings (10-12), although there are still disagreements concerning the choice of soft or hardened gold for the flash plating.

It was therefore decided to organize a new investigation into the effects of pore-corrosion test atmospheres on the integrity of palladium-nickel finish systems. Our main purpose was to determine the relative susceptibility of palladium-nickel coatings from different commercial plating baths to the attack of those gaseous reagents that are emitted during porosity tests. In addition, we would also investigate the relative ability of hard and soft gold-flash coatings to protect the palladium alloy from this chemical attack.

Experimental

All of the platings were applied to paddle-shaped copper samples, whose circular portion was 26mm in diameter. The plating was carried out by Ed Garver of our Plating Research Department. Separate sets of samples were beaker-plated with palladium-nickel from three different commercially-available plating baths by following the instructions of the manufacturers of that particular bath. For each type of palladium-nickel the samples were given the following basic variations:

1. No gold-flash overplating.
2. With a cobalt-hardened gold-flash overplating, and
3. With a soft ("pure") gold-flash overplating.

The palladium-nickel compositions were all 80:20, with a 5% maximum variation. The nominal palladium-alloy thickness was 1.5 μm and the gold-flash thicknesses were in the 0.08-0.12 μm range. All in all, nine separate sets of plating variations were made, and given the designations listed in Table VI.

TABLE VI

DESIGNATION OF PALLADIUM-NICKEL COATING VARIATIONS

Pd-Ni Bath Supplier	Gold-Flash Overplating		
	None	Hard Gold	Soft Gold
Company A	A	AH	AS
Company B	B	BH	BS
Company C	C	CH	CS

Each experimental run consisted of running a porosity test on all nine plating types at the same time, by exposing one sample of each in the same 10-liter vessel during the test run. At the completion of the test exposure (60 minutes duration) and the subsequent 125°C, 30 minute oven drying step (3), each sample was immersed in a small quantity of near-boiling (85-95°C) deionized water for 30 minutes, and the resulting solution, after filtration was made up to 100 ml. Each solution was then analyzed separately for dissolved palladium, nickel, copper, and gold by atomic absorption spectroscopy, similar to that carried out in our earlier programs.

Results

When the samples were examined momentarily after removal from the nitric acid test vessel, but before being placed in the drying oven, wet looking areas, reddish in color, were observed on all the bare Pd-Ni (i.e., without gold flash) surfaces. In particular, a red liquid, indicating dissolved palladium, could be seen as a puddle or bead along the bottom edge of these samples.

The atomic absorption analyses for the first set of samples are given in Table VII. Note that significant amounts of palladium and nickel (both limited to the Pd-Ni alloy, since there was no nickel underplate) were attacked and dissolved by the nitric acid vapor even when a gold flash was present.

TABLE VII

NITRIC ACID VAPOR ATTACK ON Pd-Ni PLATING SYSTEMS
(AFTER 60 MINUTE POROSITY TEST EXPOSURE)

Pd-Ni Type (See Table VI)	Gold Flash	Elemental Analysis ($\mu g/cm^2$) Ni	Pd	Cu	Au
A	None	284.	63.9	82.5	---
AS	Soft	8.3	4.7	17.3	ND
AH	Hard	35.	15.1	63.5	ND
B	None	265.	157.	209.	---
BS	Soft	22.3	3.0	65.5	ND
BH	Hard	15.2	8.1	51.0	ND
C	None	352.	593.	184.	---
CS	Soft	77.9	10.3	140.	ND
CH	Hard	28.9	4.4	77.5	ND

ND = None Detected. The detection limit for gold in this experiment was 0.14 micrograms/cm^2.

CONCLUSION

The many experiments that were outlined in this report show that the nitric-acid vapor porosity-test atmosphere will attack palladium and palladium-nickel alloy finishes, even when "protected" with a gold flash. In the near future, we hope to report on similar determinations with the moist sulfur vapor ("flowers-of-sulfur") and sulfurous acid/SO_2 porosity tests.

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APPLICATION OF IRREVERSIBLE THERMODYNAMICS TO TRANSPORT PROCESSES IN SULFURIC ACID BASED AQUEOUS ANODIZING SOLUTIONS

S. K. JALOTA
OLIN CORPORATION
METALS RESEARCH LABORATORIES
NEW HAVEN, CT 06511

Theory of irreversible thermodynamics has been applied to transport processes in sulfuric acid based aqueous solutions for the anodizing of aluminum and its alloys. The electrochemical processes which occur during anodizing are explained in terms of transport of charge and mass, affinity of chemical reactions and the existence of ionic charge on the substrate contrary to the prior theory of migration of aluminum ions at the aluminum-oxide boundary zone. Specific conductivity and other transport properties of anodizing solutions are described in terms of more fundamental linear intrinsic mobility coefficients of individual ionic species and their interionic interactions.

It is further shown that although, in the external circuit, the applied voltages, currents and overall system resistance are inter-related, in the solution their effects are independent of each. At constant voltage anodizing in dilute sulfuric acid solutions, the current drops exponentially which limits the anodizing time and achievable thickness. This phenomenon allows hard anodic films to be produced at substantially higher voltages but at moderate current densities. The benefit is that the anodic film stresses, cracks and voids normally experienced while hard anodizing at lower voltages and high current densities in strong sulfuric acid solutions are significantly reduced.

Parameters which favor the rates of formation and dissolution of aluminum oxide are provided so that by a meticulous control and application of such parameters, anodic films of highest and consistently repeatable quality can be produced. Benefits and applications of anodic films, obtained at higher voltages, in the electronics field are discussed.

Anodizing of aluminum and its alloys is commonly performed in aqueous solutions of sulfuric acid. For decorative applications a 15 to 20% by weight solutions and temperature of 18 to 22°C are employed. For hard anodizing where a product has to meet severe impact and wear, and perform dielectric functions, much lower solution temperature is necessary. Variations in solution composition, temperature, current, voltage and the aluminum alloys being anodized all affect the film strength, porosity and its functional properties.

Considerable effort has been put in perfecting the process of anodizing over the last twenty to forty years[1,2]. Advent of proprietary additives[3] has led to the use of somewhat higher temperatures than near 0°C and voltages up to 20V. In addition to the use of chemical additives[3], employment of straight DC voltages and currents have been replaced with superimposed AC over DC and pulsed DC voltages and currents[4] to produce hard anodic films for functional applications such as in the anodizing of electronics printing rollers[5] where wear resistance and dielectric (electronic charge holding) capacity of the outer anodic film surfaces are of paramount importance.

The aluminum alloy chosen for a functional application has an impact on the anodizing voltages and currents because each requires a different voltage-current density relationship. Alloys containing copper-magnesium require a higher voltage than those containing silicon-magnesium, manganese or pure aluminum. Reference 6 classifies excellent to unsuitable aluminum alloys for decorative to functional applications.

Little attention has been paid to the application of irreversible thermodynamics[7,8,9,10] to the electrochemical reaction mechanisms which govern the anodizing processes. The process of anodizing

is thermodynamically irreversible in nature. The chemical reactions which take place during anodizing are governed by the second law of thermodynamics. There is simultaneous transport of charge and mass, existence of thermal gradient and affinity for chemical reactions in the system. It is important therefore to look into the whole domain of anodizing from this view point and have a better understanding of the reaction mechanisms in order to produce anodic films of consistent and repeatable qualities for any intended decorative or functional applications.

Provided in this article is the prior theory[11,12] of ionic diffusion and reliance on specific conductivity of dilute sulfuric acid solutions vs an alternate concept of the affinity of chemical reactions, the transport of charge and mass and the existence of ionic charge on the substrate, of the theory of irreversible thermodynamics[13,14]. Benefits of anodizing in dilute solutions at higher voltages for applications in electronics field are discussed in terms of the properties of the anodic films thus produced. It is further demonstrated that such properties are repeatable and consistently achievable.

PRIOR THEORY OF IONIC DIFFUSION AND RELIANCE ON SPECIFIC CONDUCTIVITY

Csoken[11,12] studied in the early sixties the process of anodizing in terms of ionic diffusion and specific conductivity of sulfuric acid and determined the effects of applied external voltage and current in very dilute solutions. His discussion was based on diffusion and material constant of ions, physico-chemical characteristics of the oxide-electrolyte interface and specific conductivity of the electrolyte. The specific conductivity, k, of sulfuric acid (Fig.1) was considered to be the fundamental parameter which was affected by the relationship, E-1:

Specific conductivity,

$$k = f(C[H_2SO_4] \times \alpha \times f\lambda \times \Lambda o) \qquad (E\text{-}1)$$

where

C = Electrolyte concentration in gm equivalents/l
α = Degree of dissociation of the electrolyte
$f\lambda$ = Coefficient of electrostatic interaction of ion mobilities
Λo = Equivalent conductivity at infinite dilution

Csoken concluded that except the soluti concentration, $C(H_2SO_4)$, other parameters equation (E-1) do not considerably change t specific conductivity of the electrolyte so that t latter can be considerably decreased by lowering t solution concentration. At small to medium curre densities, it is possible to increase the cell volta several times to cause conversion of aluminum aluminum oxide at the metal-oxide boundary zo according to equation (E-2) and obtain faster rate aluminum oxide formation and a reduction in t degree of dissolution of aluminum oxide. T concentration of ionic aluminum, c (Al^{3+}), migratir at the aluminum-oxide boundary zone ar converting into aluminum oxide is given by:

$$c(Al^{3+}) = f(D, V) \qquad (E\text{-}$$

where

D = Diffusion coefficient of aluminu ions
V = Applied external voltage

Based on this theory, Csoken was able to obtai maximum rate of formation of aluminum oxide whi its rate of dissolution remained at a minimum in 1% sulfuric acid at a temperature of about 0°C ar applied voltage of 40-60V. The porosity of th anodic film thus formed was 4-6%. Microhardnes was VHN 450 to 620 Kg/mm² in comparison wit microhardness of VHN 40-80 Kg/mm² for porou oxide coatings. No additives were reported to hav been utilized in the 1% sulfuric acid experiments[11 Modern integral color anodizing processes[15,16,17] ar performed at even lower H_2SO_4 concentrations (0.1 1% range) with the addition of organic dibasic acid and the employment of higher voltages (>60V) an temperatures (15-20°C). By keeping th concentration of sulfuric acid near 1% in thes solutions, higher thicknesses, in the range of 50-7 microns (2-3 mils) have been obtained[18].

APPLICATION OF THE THEORY OF IRREVERSIBL THERMODYNAMICS TO TRANSPORT PROCESSE IN SULFURIC ACID ANODIZING SOLUTIONS

Unlike Csoken's theory[11,12] in which migratio of aluminum ions at the aluminum - oxide boundar zone, the diffusion coefficient of aluminum ions applied voltage and specific conductivity of th

electrolyte are considered to be the principle parameters controlling the process of anodizing, the theory of irreversible thermodynamics provides explanation in terms of (a) the existence of an ionic charge on the substrate as a consequence of applied external voltage, (b) the transport of charge and mass, and (c) the affinity of chemical reaction between positively charged substrate and the negatively charged ionic species present in the solution in the formation of anodic film.

According to the theory of irreversible thermodynamics[13,14] following reactions take place concurrently during anodizing:

1. Transport of heat due to thermal gradient
2. Transport of charge and mass
3. Chemical reaction due to affinity between oppositely charged species

These processes are thermodynamically irreversible in nature and must obey the second law of thermodynamics which states that in an irreversible reaction, Entropy, is not conserved, where Entropy of a system is a measure of its degree of disorder. There is net positive production of Entropy and the rate of production of Entropy, is expressed as the sum of the products of flows and their conjugate forces which exist in the system as explained in Eq. (E-3). For a system in which three reactions take place, the following relationship holds[13,14]:

$$E = T\sigma = Js\ \mathrm{grad}(-T) + \sum_{i=o}^{n} Ji\ \mathrm{grad}(-\mu i) + Jch\ (Aj) > 0 \qquad \text{(E-3)}$$

E is the entropy, σ is the dissipation function, and T is the absolute temperature, $\sum_{i=o}^{n}$ is the summation of ionic species, 0 to n in the system, Js, Ji and Jch are the flow of heat, flow of matter and chemical reaction, all multiplied by their conjugate forces defined by temperature gradient (-T), electrochemical potential ($-\mu i$) and the affinity for chemical reaction, Aj, respectively. In a thermostatically maintained temperature bath, the following equations are applicable:

$$E = T\sigma = Ji\ \mathrm{grad}(-\mu i) + Jch\ (Aj) > 0 \qquad \text{(E-4)}$$

As shown in Eq. (E-4), anodizing process may be considered to be taking place in a two component system in which the theory of irreversible thermodynamics is applicable. There are two principle forces and two principle flows respectively involved in the reaction mechanism.

Relationships between flows and forces in a multicomponent system are well defined by the theory of irreversible thermodynamics in terms of linear transport and inverse frictional coefficients, L and R, respectively[13,14]. Vectorial transport properties such as specific conductivity, diffusion coefficients, activity coefficients and transport numbers of ionic species in an electrolyte are also defined in terms of the coefficients L and R of the theory of irreversible thermodynamics. For example, specific conductivity, k, is defined as:

$$k = F^2 X (Z_1^2 L_{11} + Z_1 Z_2 (L_{12} + L_{21}) + Z_2^2 L_{22}) \qquad \text{(E-5)}$$

where F = Faraday constant, Z = ionic charge on species, 1 and 2, L_{11} and L_{22} are the mobility coefficients of cations and anions respectively, $L_{12} = L_{21}$, is the coefficient of interionic interactions between the cations and the anions.

Relations also exist in terms of inverse frictional coefficients, R_{11}, $R_{12} = R_{21}$ and R_{22} in terms of specific or equivalent conductivity, diffusion and activity coefficients and transport numbers[13,14,19].

PRACTICAL CONSIDERATIONS OF THE THEORY OF IRREVERSIBLE THERMODYNAMICS

Consideration of Transport Phenomena

It is shown in Eq. (E-5A) that the specific conductivity, k, is a function of the mobility coefficients of the individual ionic species and their interionic interactions coefficients, i.e.

$$k = f(L_{11}, L_{12}, L_{21}, L_{22}) \qquad \text{(E-5A)}$$

The coefficients, L_{11} and L_{22} are the intrinsic mobility coefficients of cations and anions, i.e. the mobilities these ions will have in the absence of interactions from other species, and $L_{12} = L_{21}$ are the coefficients of interionic interactions. These

TABLE 1
TRANSPORT DATA ON SULFURIC ACID IN AQUEOUS SOLUTIONS AT 25°C

#	Concentration Moles/ℓ	Sq. Root % wt/vol	% wt/vol	Specific Conductivity	$L_{11}/N \times 10^{12}$	$L_{12}/N \times 10^{12}$	$L_{22}/N \times 10^{12}$
1	0.00	0.0	0.00	0.000	37.564	0.000	2.148
2	0.05	0.7	0.49	0.029	28.527	1.509	2.164
3	0.10	1.0	0.98	0.051	26.052	1.811	2.145
4	0.50	2.2	4.90	0.214	22.278	1.750	1.923
5	1.00	3.1	9.80	0.400	20.387	1.535	1.803
6	2.00	4.4	19.60	0.664	16.363	1.130	1.497
7	3.00	5.4	29.40	0.792	12.829	0.923	1.282

TABLE 2

CURRENT, TIME, AND THICKNESS DATA AT CONSTANT VOLTAGE INTEGRAL COLOR PRODUCTION ANODIZING

Power Cycle	Current I A/dm^2	Time t(min.)	Total Amp-Min. Consumed $/dm^2$	Thickness S μm	Change in Thickness $dS(\mu m)$	Log I $I = (A/dm^2)$	I/S $I/\mu m$
Ramp Time	8.0	5	24.35	7.90	7.9	.907	.126
Moderate Current Density Range	4.34	8	36.98	12.0	4.1	.646	.083
	2.70	11	45.50	14.8	2.8	.431	.068
	2.25	14	51.75	16.8	2.1	.352	.060
	1.80	17	57.63	18.7	1.9	.255	.053
Low Current Density Range	1.64	20	62.56	20.3	1.6	.215	.049
	1.52	23	67.10	21.8	1.5	.182	.046
	1.46	26	71.50	23.2	1.4	.164	.043
Extrapolated Data	1.42	29	73.29	23.8	0.6	.152	.042
	1.39	32	74.62	24.2	0.4	.143	.041
	1.36	35	75.60	24.5	0.3	1.34	.040

TABLE-3
Factors Controlling the Rates of Film Formation and Dissolution in Anodizing

#	Factors Affecting, Rf	#	Factors Affecting Rd
1.	Higher voltages and currents	1.	Lower voltages and currents
2.	Strong electrolyte but lower concentration & temperature	2.	Strong electrolyte and higher concentration & temperature
3.	Weak electrolyte but higher concentration	3.	Prolonged anodizing at very low current densities
4.	Combination of strong electrolyte with lower concentration and weak electrolyte with higher concentration	4.	High voltage and very low current density & substrate polarization
5.	Faster heat dissipation with good agitation	5.	Poor heat dissipation and localized heating
6.	Inert or anodizable intermetallics such as Si, Mg	6.	Reactive or dissolving intermetallics such as Cu, Zn
7.	Controlled substrate surface finish	7.	Uncontrolled substrate surface finish
8.	Annealed substrate after heat treat	8.	Unannealed substrate after heat treat

coefficients are more fundamental than the kinetic properties such as equivalent or specific conductivity or the diffusion coefficients. A knowledge of these mobility coefficients provides a better understanding of the mechanism of transport processes in electrolyte solutions.

In order to understand the significance of the transport parameters, experimental data was obtained from literature[19] and numerical values of L_{11}, $L_{12} = L_{21}$ and L_{22} were derived for sulfuric acid solutions in the concentration range, 0 to 30% weight by volume. These are presented in Table-1 and graphically shown in Figures 2 to 4.

It may be seen that mobility of hydrogen ions drops sharply (Fig. 2) and interionic interaction increases initially then drops (Fig. 3) with increase in concentration while mobility of sulfate ions remains constant (Fig. 4) in the concentration range of 0 to 1% and then starts dropping. Unchanging mobility of sulfate ions, L_{22}, in the concentration range of 0 to 1% is of great significance in the anodizing process since it denotes that the anodic reactions, in which sulfate ions participate, should be highly efficient.

In addition field assisted dissolution of anodic film in dilute solutions is also minimal. This is one reason why the anodic films formed in such dilute solutions of sulfuric acid are found to have the least porosity, high microhardness and superior break-down voltage values[11,12].

Consideration of Electrochemical Phenomena

Electrochemical potential, grad ($-\mu i$), causes two effects:

(a) Removal of electrons from the Al atoms from the substrate surface, i.e.

$$2\,Al - 6e^- = 2Al^{3+} \qquad \text{(E-6)}$$

This renders the substrate positively charged.

(b) Flow of ionic current, I, through the solution, causes water to hydrolyze into hydrogen ions and hydroxide ions, and result in the formation of aluminum oxide, i.e.

$$6H_2O = 6H^+ + 6OH^- \qquad \text{(E-7)}$$

$$6H^+ + 6e^- = 3H_2\ (gas) \qquad \text{(E-8)}$$

$$2\,Al^{3+} + 6OH^- = 2Al(OH)_3 \qquad \text{(E-9)}$$

$$2Al^{3+} + 3SO_4^{2-} = Al_2(SO_4)_3 \qquad \text{(E-10)}$$

$$2Al(OH)_3 = Al_2O_3 + 3H_2O \qquad \text{(E-11)}$$

(c) The reactions, E-9, E-10 and E-11 take place due the existence of secondary force, Aj, of Eq. E-4, which comes into play as a natural consequence of the affinity of chemical reactions between Al^{3+} ions, OH^- ions and SO_4^{2-} ions at the anode/solution interface. (If this secondary force did not exist, there will not be a chemical reaction, aluminum will simply dissolve in the electrolyte and O^{2-} will either cause polarization of the substrate surface or dissipate into O_2 gas).

The formation of alumina incorporating sulfate ions is a consequence of relative affinities between Al^{3+} ions and the hydroxide OH^- ions as well as between Al^{3+} ions and the sulfate, SO_4^{2-} ions to react. This is why the anodizing process is exothermic, i.e. there is release of energy (in the form of heat) due to the existence of natural instability in the system.

Consideration of Electrochemical Modulations in Production

Ji grad($-\mu i$) component of Eq. E-4 represents the current-voltage, I-V, relationship as applicable in anodizing solutions. I, the ionic current in solution, is not directly proportional to the applied voltage, V, but it has rather been shown[20] to follow the exponential function (E-12):

$$I = Ae^{BV/S} \qquad \text{(E-12)}$$

where A and B are the constants, and S is the thickness of the coating. Taking logarithms, Eq. E-12 becomes:

$$\text{Log } I = \text{Log } A + BV/S \qquad \text{(E-13)}$$

Eqs. 12 & 13 show that at constant voltage anodizing, current, I, must decrease exponentially

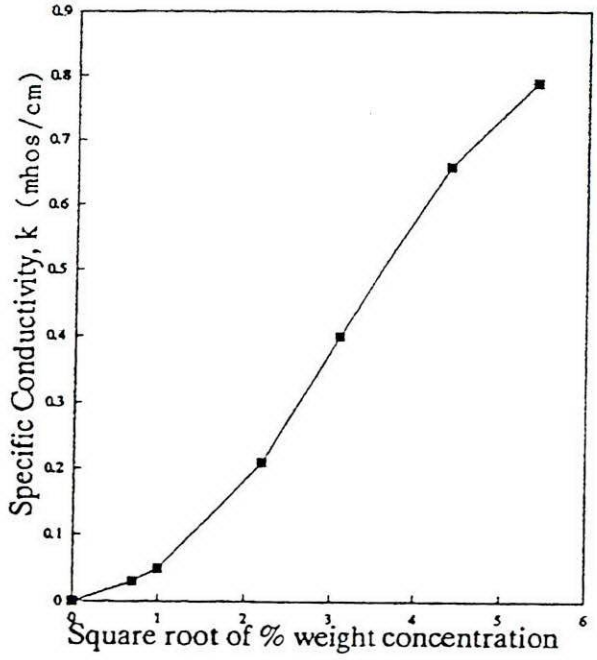

Fig. 1 – Specific conductivity versus square root of percent weight concentration of sulfuric acid.

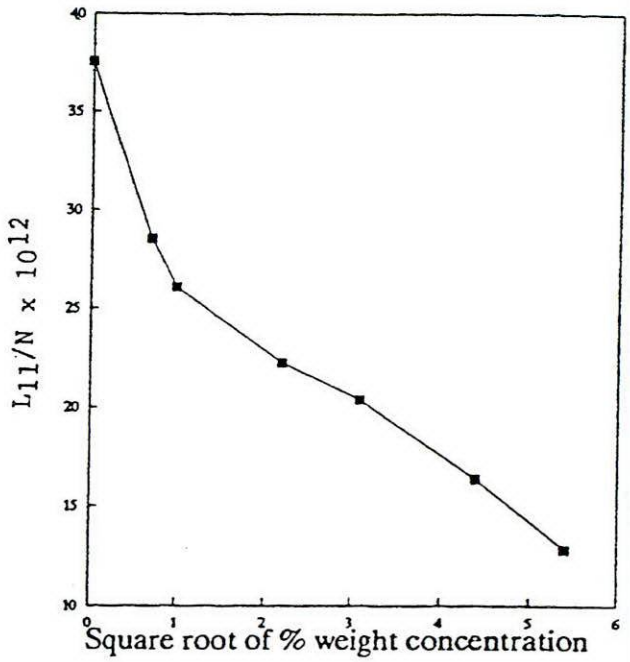

Fig. 2 – Variation in mobility of hydrogen ions with sulfuric acid concentration.

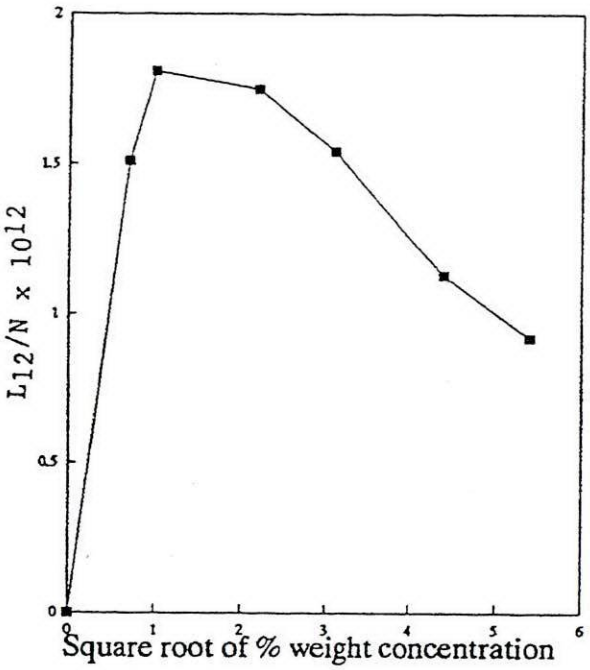

Fig. 3 – Inter–ionic interaction coefficient versus sulfuric acid concentration.

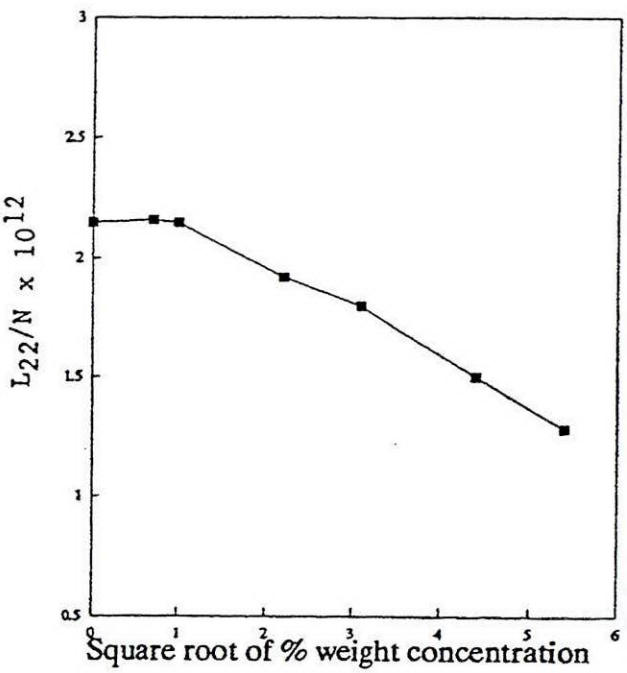

Fig. 4 – Variation in mobility of sulfate ions with sulfuric acid concentration.

with increase in thickness, S, so that Log I is inversely proportional to thickness, S. This relationship is very much applicable in production integral color anodizing as shown in Figs. 5 and 6 in which I is plotted vs time and log I is plotted vs 1/S respectively from data presented in Table-2.

Plotted in Figs. 7a and 7b are the thickness, S, vs time, t, and change in thickness, dS, per 3 minutes, respectively, for anodizing performed up to 26 minutes at 8 A/dm^2.

In Figs. 5 to 7b the graphs have been extrapolated to 35 minutes to show that, if the trends of the curves are followed, there will be minimal thickness increase at about the 35th minute with the set of bath parameters and operating conditions employed in collecting the data (Table-2).

At the 35th minute, if S is maximum, BV/S is a minimum because both B and V are constants. Eq. E-13 becomes:

$$\text{Log I} = A' + B' = \text{Constant} \qquad \text{(E-14)}$$

where $A' = \log A$ and $B' = BV/S$

Although there is no increase in thickness, Current, I, flowing through the system at 35th minute is:

$$\text{I (from Table-2)} = 1.36 \text{ A/dm}^2 \qquad \text{(E-15)}$$

Fig. 7a shows that a thickness of 16-18 microns is achieved in approximately 15 minutes of anodizing averaging a thickness growth of 3-4 microns per 3 minutes at moderate current densities of 2-8 A/dm^2.

The rate of film growth slows down and averages 1-2 microns per 3 minutes from 16 to 26th minute at current densities of 1.5-2 A/dm^2 and becomes minimal at about the 35th minute as shown in Figure 7b.

When thickness increase is minimal, there is still a continuous flow of current through the system. This current is basically dissipated as heat into the solution through the racks and the parts. In addition chemical attack on the parts and field assisted dissolution of the anodic film continue. Prolonged retention in the anodizing bath weakens the sound anodic film previously developed.

For functional applications, it is preferable to anodize at moderate current densities, > 2 A/dm^2 which is also the preferred range for hard anodizing in concentrated sulfuric acid solutions. To continue anodizing in the low current density range, <2 dm^2 is a matter of choice which depends upon the end applications in which superior hardness and dielectric properties of the anodic films are not so important.

Consideration of Chemical Phenomena

Typically, aluminum oxide coatings, produced in 15-20% sulfuric acid at lower voltages (15-25), incorporate 13-18% sulfate[22,25]. The sulfate incorporation in the anodic film produced in dilute sulfuric acid integral color anodizing process was found to be 18%[18]. As such it appears that the inclusion of 'sulfate' in the aluminum-oxide matrix [26] is not as much dependent on sulfuric acid concentration of the anodizing bath as it is on the chemical affinity as explained by the theory of irreversible thermodynamics.

There are several references[15,21,22,23,24,25] which cover the mechanism of anodic film growth. By skillful manipulation of the effects of voltage and current, the electrolyte composition and temperature, the rate of anodic film dissolution,Rd, can be minimized and the rate of film formation, Rf, can be controlled in such a way that undue cracks, voids, and stresses in it are minimized, its microhardness is increased and porosity reduced. Some of the factors affecting rates of film formation and dissolution are provided in Table-3.

Shown in Figs. 8, 9 & 10 are the AEM (Analytical Electron Microscope) micrographs taken using SED (Secondary Electron Detector) of the x-section of anodic film produced in dilute sulfuric acid integral color anodizing process[18]. The effect of anodizing solution concentration and voltage on the barrier layer thickness, cell diameter and pore diameter is shown in Table-4[18]. It may be seen that pore diameter of 50 nm (2μ inch), barrier layer thickness of 140 nm (5.6μ inch) and cell diameter of 240 nm (9.6μ inch) have been obtained.

The anodic film cells are shown in Fig. 9. The barrier layer and the pores in the anodic film are

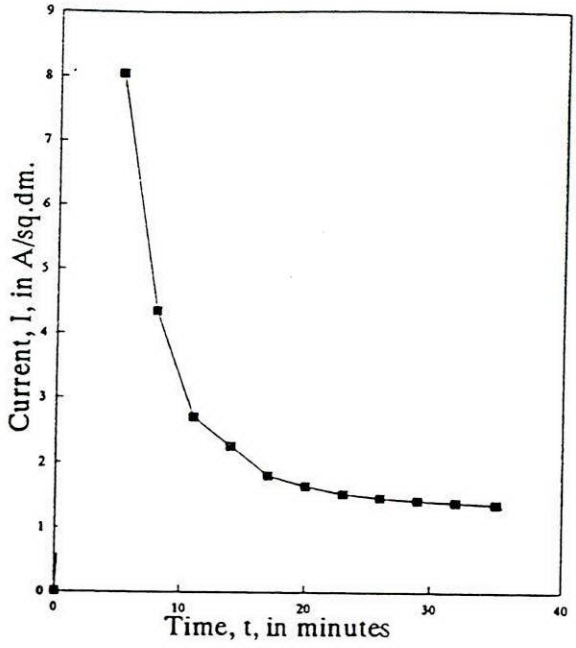

Fig. 5 – Current – Time curve for anodizing in 0.4 – 0.5 % integral color bath.

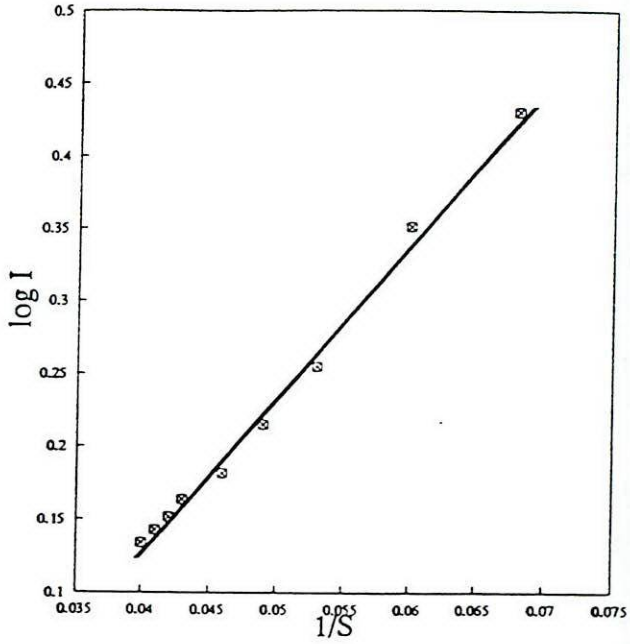

Fig. 6 – Straight line relation between log I and 1/S.

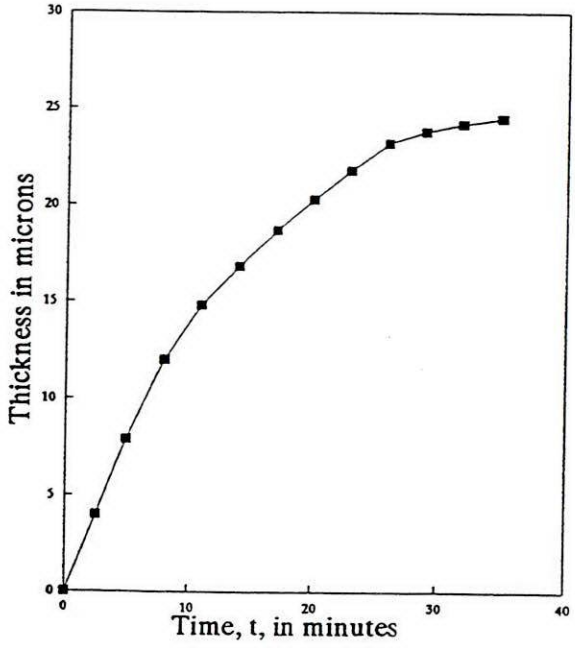

Fig. 7a – Increase in thickness, S, with time, t, in minutes.

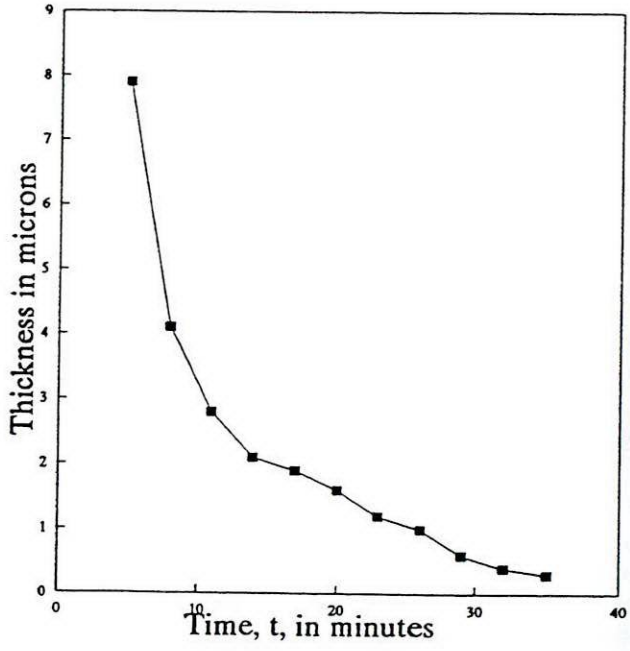

Fig 7b – Change in thickness, dS, at 3 min. intervals

visible at 50,000X as shown in Fig. 10. This figure also shows that the nature of anodic film produced in dilute solutions is not different than that produced in strong solutions, shown in Fig. 11 which represents the anodic film produced in 16.5% sulfuric acid at 1.5 A/dm^2[15]. Both films have very similar structure except that much enhanced barrier layer thicknesses, cell size and lower porosities (4-5%, Table-4) are achievable while anodizing in dilute solutions at higher voltages. Similarity in Figs. 10 and 11 further shows that there is a more fundamental mechanism, controlling the anodizing process, which is independent of the electrolyte concentration. The theory of irreversible thermodynamics does provide that mechanism.

MERITS OF ANODIZING AT CONSTANT HIGHER VOLTAGES

There are many processes[3,4,26] which provide attainment of hard anodic films at voltages of 20-25V. Such processes are useful when overall wear resistant property of the anodic film is of importance. Anodic films produced at low voltages from strong electrolytes are still highly porous so that these can be electrolytically or otherwise (such as with organic dyes) colored. Because the barrier layer thicknesses are low, approximately 0.02 microns (200 Angstroms) at 20 volts[27], these films are not universally applicable when thicker barrier layers and higher break down voltages of anodic films are required[17,28].

For functional applications, anodizing at elevated voltages has many merits. Firstly, the barrier layer thickness, is tremendously increased since it is 12-15 times the applied voltage. Secondly, performing anodizing at 40, 60, 80, 100 etc. volts, barrier layers of thicknesses up to 0.15 micron (1500 Angstroms or 6 microinches) can be achieved. Hard or integral color anodized films incorporating barrier layer thicknesses of this magnitude along with sufficiently built up alumina thicknesses have found excellent applications in the electronics IC-packages for their high breakdown voltages and superior thermal conductivity[17,28].

DISCUSSION AND CONCLUSIONS

Theory of irreversible thermodynamics elucidates fundamental mechanism which, not only explains how the anodic film formation occurs at the substrate surface, it also provides guidelines for controlling the process. This is demonstrated by the application of relationships, E-12 to E-15, to production integral color anodizing data shown in table 2 and Figs 5 to 7. It allows us to decide when to prolong or terminate the process depending upon the properties desired in the end product.

For electronics applications, the anodic films have to be hard but not brittle; must be electrically insulating but thermally conducting; must not absorb humidity or warp in heat; should also have aesthetic appearance and be smooth to touch. To incorporate all these properties in the anodic film and expect 100% yield is to subject the anodizer and the anodizing chemist to a great challenge. The reason being the mechanism of anodizing has yet not unfolded itself as has been the case in the electroplating industry.

There are so many variables, starting with aluminum alloy selection, its heat treat condition, whether cast or extruded, machined or stamped, surface roughness, deburring, pre-cleaning, etching, deoxidation, anodizing and post anodizing treatments, all these collectively affect the anodic film quality. Unless their inter-effects are understood there will still be a question mark on the final anodic film whether it can meet the qualities desired of it in the electronics industry. Miniaturization of electronics devices and expectation of compliance to very tight dimensional tolerances create further challenges.

Advances in metallurgy and manufacturing methodologies have provided anodizable quality of aluminum alloys for applications such as in aircraft, aerospace, architectural and light engineering industries. Applications of anodized devices in electronics industry are still emerging and so are the needs to improve upon anodizable alloys and their inter-metallic particle size control, surface roughness control, pre-anodize preparation and anodizing methodologies.

The purpose of this article is to present a mechanism with which anodic films on aluminum alloys are produced at higher voltages and moderate current densities and support it with practical data. There is no doubt that several other theories have been proposed and treatises exist in literature[1,2,15,22,23,24] but as the applications of

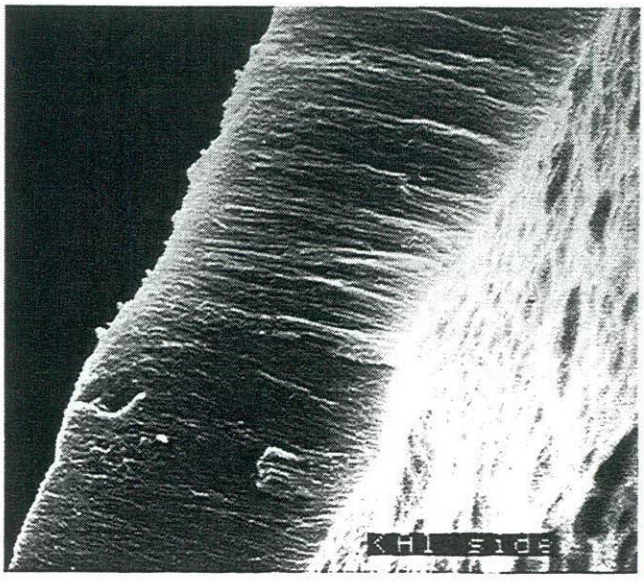

Fig. 8- TEM micrograph of x-section of anodic film produced in dilute sulfuric acid integral color anodizing bath. 3,000x.

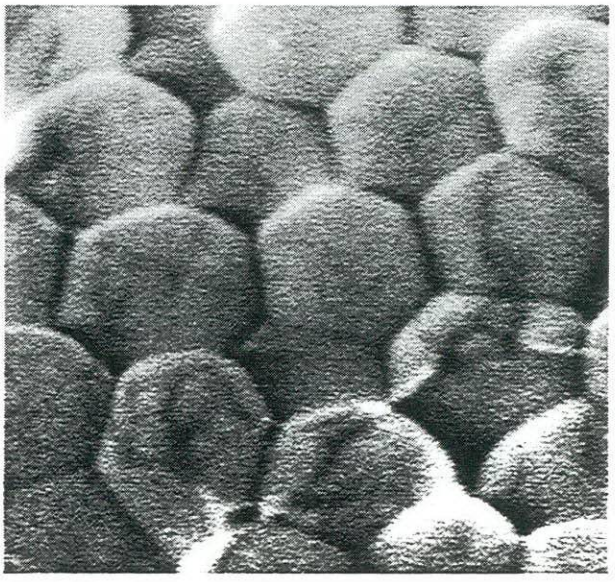

Fig. 9- TEM micrograph of x-section of anodic film cells produced in dilute sulfuric acid integral color anodizing bath. 100,000x.

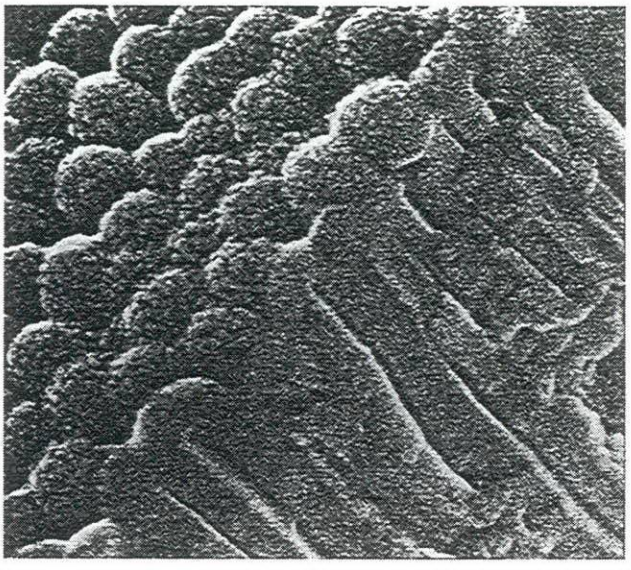

Fig. 10- Same as Fig. 8. 50,000x.

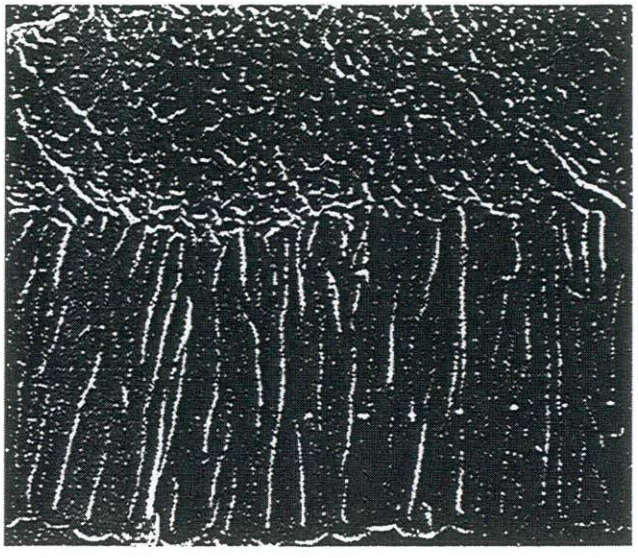

Fig. 11- SEM micrograph of x-section of anodic film produced in strong (16.5%) sulfuric acid. (Reference 15, page 357) 50,000x.

TABLE- 4: Effect of reducing sulfuric acid concentration on anodic film parameters [18]

Concentration	Forming Voltage	Pore Dia. Pd	Barrier Layer Thickness	Cell Dia. Cd	Porosity $100x\ Pd^2/Cd^2$
0.1-1.0% [18]	80V	50nm	140nm	240nm	4-5%
14.5% [15] (15) p. 343, 347	14.3V	18.5nm	14.9nm	39.6nm	22%

anodizing are advancing so are the needs to seek remedies to the problems associated with those applications. It is hoped that this article will be useful to those anodizers, the chemists and the chemical engineers who are still seeking remedies in perfecting their anodizing processes for their intended final applications.

ACKNOWLEDGMENTS

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Plating of 60/40 Tin/Lead Solder For Head Termination Metallurgy

By Saad K. Doss
IBM Corp., San Jose, CA

The current head termination metallurgy consists of plated copper studs followed by plated gold pads. Then the gold wires are ultrasonically bonded to the gold pads. In this presentation the author shows the feasibility of plating tin/lead (60/40) as a replacement for the gold. This solder alloy can be lasersonically bonded to the wires. The thickness uniformity of the plated studs as a function of applied current is determined from the alpha step (Tencor profiles) measurements. The maximum uniformity and smoothness of these studs are obtained at current densities between 60 and 80 ma/cm2. The SEM micrographs of various studs are also shown. The changes in thickness, uniformity, profile, and roughness of films deposited with direct and pulse current are consistent with the expectations for a pulse plating to overcome the mass transport.

I. Introduction

The magnetic thin film heads used in the recording disk files are connected to the read-write electronics by twisted wires. These wires have a copper core, which is plated with gold which is insulated by a polymer sheath. The head terminations are made of gold plated studs. The gold wires are connected to these studs by stripping a wire zone then ultrasonically bonding it to the stud.

This paper describes a new process for the head termination metallurgy. In this process, tin/lead (60/40) solder alloy (commercially purchased) is plated as a replacement for the gold plated studs. This alloy is widely used in the electronic industry for interconnections and masking purposes. The effects of current density and solution composition on the deposit characteristics had been previously investigated (1 & 2). In this paper the author studied the effect of direct and pulse current on the uniformity and composition of the tin/lead plated studs. Also the bath agitation and the anode/cathode design and their location in the plating cell were examined. Furthermore, lasersonic soldering was also introduced for stripping the wire insulation and terminating the wire all in one process step (3). A special lasersonic tip was internally heated by a laser and ultrasonically vibrated. The lasersonic tip burns through the wire insulation and reflows the solder without the need for flux. This forms the electrical connection with the tin/lead plated studs.

II. Experimental

A commercial bath was used in this study. The bath was a fluoborate-free, tin/lead solution. The bath make-up consisted of the following:

tin concentrate (12 g/l),
lead concentrate (8 g/l),
alkanesulfonic acid and
a starter (propanol (6 ml/l),
formaldehyde (3 ml/l), and
hydroquinone (0.2 ml/l).

The starter acts as brightener, wetting agent and grain refiner. The 47mm square samples were made in a 4-liters glass jar with a magnetic stirrer. The larger samples (5 inches) were plated in 60 liters bath with adequate circulation (7 G/M) and a specially designed plating cell. In this cell both cathode and anode were placed horizontal and a specially designed paddle was used between the anode and the cathode during plating.

Sample Preparation

47 mm square and 5″ round non-metallic substrate were used in this investigation. These substrates were deposited with thin film Cu seed. Photoresist was then applied, exposed and developed. A positive imaging rectangular studs resist was produced. The thickness of the resist varied between 7 and 30 microns. The stud dimensions were 230 x 200 microns. These studs were plated with tin/lead solder alloy. The thickness of these studs varied between 5 and 30 microns.

Bath operating conditions

Various current densities both direct and pulse were studied namely; 20, 40, 60 & 80 ma/cm^2. The anode material was made of tin/lead (60/40). The cathode holder was made of stainless steel and plastic. The bath was operated at room temperature. The tin/lead thickness was measured by Alpha step (Tencore P1). The tin/lead composition was determined from the differential scanning calorimetry (DSC) measurements.

The lasersonic bonding was done by using a laser tool with an optical fiber beam delivery, an ultrasonic bonder and a lasersonic soldering tip.

III. Results and Discussion

A linear relationship was obtained from the tin/lead rate of deposition as a function of current density, as shown in Figure 1. This Figure indicates that the rate of deposition increases by a factor of 7 as the current density increases from 20 to 80 ma/cm^2

The SEM photomicrographs of tin/lead plated studs at 20 and 80 ma/cm^2. are shown in Figures 2 and 3 respectively. The increase in current density greatly reduces the grain size of these plated studs.

The effect of direct and pulse current on the thickness uniformity and smoothness are shown in Figures 4 and 5 respectively. The pulse plating is more uniform and smooth as compared with the direct current. These observations suggest that the mass transfer of tin and lead is limiting the rate of deposition in this range of direct current densities. This is clearly demonstrated from the Alpha step measurements (Figures 6 and 7) where a non-uniform stud thickness that varied between 24 microns and 38 microns were obtained from the direct current (Figure 6). The pulse plating Figure 7 gave very uniform thickness with variation only between 32 and 35 microns. Furthermore, the surface roughness measurements by Sloan DEKTAK 3030 of the direct and pulse current plating were 2 microns (p/v) and 0.6 microns (p/v) respectively (Figures 8 and 9). Comparison of Figures (8 & 9) and Figures (4 & 5) shows that the diameter of the nodular growths is approximately equal to the peak to valley roughness. Pulse plating is expected to produce films with finer surface texture than the films deposited with direct current at the range of current densities in which mass transport is rate limiting. Comparison of Figures (4 and 5) shows that the pulse plated films are significantly smoother than the DC films. Low surface roughness enhances lasersonic bonding because it promotes intimate contact between the pad and the wire and it reduces interfacial contamination.

The tin/lead compositions were calculated from the differential scanning calorimetry (DSC) measurements. The melting temperature of the 60/40 (tin/lead) anode was calculated from the DSC (Figure 10). The melting temperature C of the direct and pulse currents terminations (Figures 11 and 12) were similar, 184° C and 185° C respectively. These 2 Figures (11 and 12) clearly indicated that the compositions of the direct and pulse current are similar to the standard anode (Figure 10) and equal 60/40 (tin/lead).

The hardness measurements (knoop) was conducted on as-plated tin/lead, reflowed

plated tin/lead, and plated gold studs using a 10 gram load. The results are summarized in Table 1.

Table 1. Hardness Measurements (kg/mm^2) of Sn/Pb and Au.

Description	Hardness (kg/mm^2)	Depth (microns)
As-plated Sn/Pb	12.3	3.5
Reflowed plated Sn/Pb	21.7	2.7
Plated Au	57.6	1.7

Table 1 showed that the hardness of the tin/lead is only 20% of the gold. The reflow almost doubled the tin/lead hardness but it was still much softer that the plated gold. A typical lasersonic soldering joint which passed the wire pull strength test, is shown in Figure 13.

IV. Conclusion

1- Pulse plating of tin/lead (60/40) solder alloy is superior in thickness uniformity and smoothness as compared with direct current in which mass transport is rate limiting.

2- A linear relationship is obtained from the rate of tin/lead deposition as a function of current density.

3- Finer tin/lead grains are obtained with higher current densities.

4- The diameter of the nodular growths is approximately equal to the peak to valley roughness.

5- The tin/lead composition remains constant as the current changed from direct to pulse.

6- Plated tin/lead was much softer as compared with plated gold.

7- Lasersonic soldering of wire to solder plated stud is successfully demonstrated without the need to strip the wire insulation.

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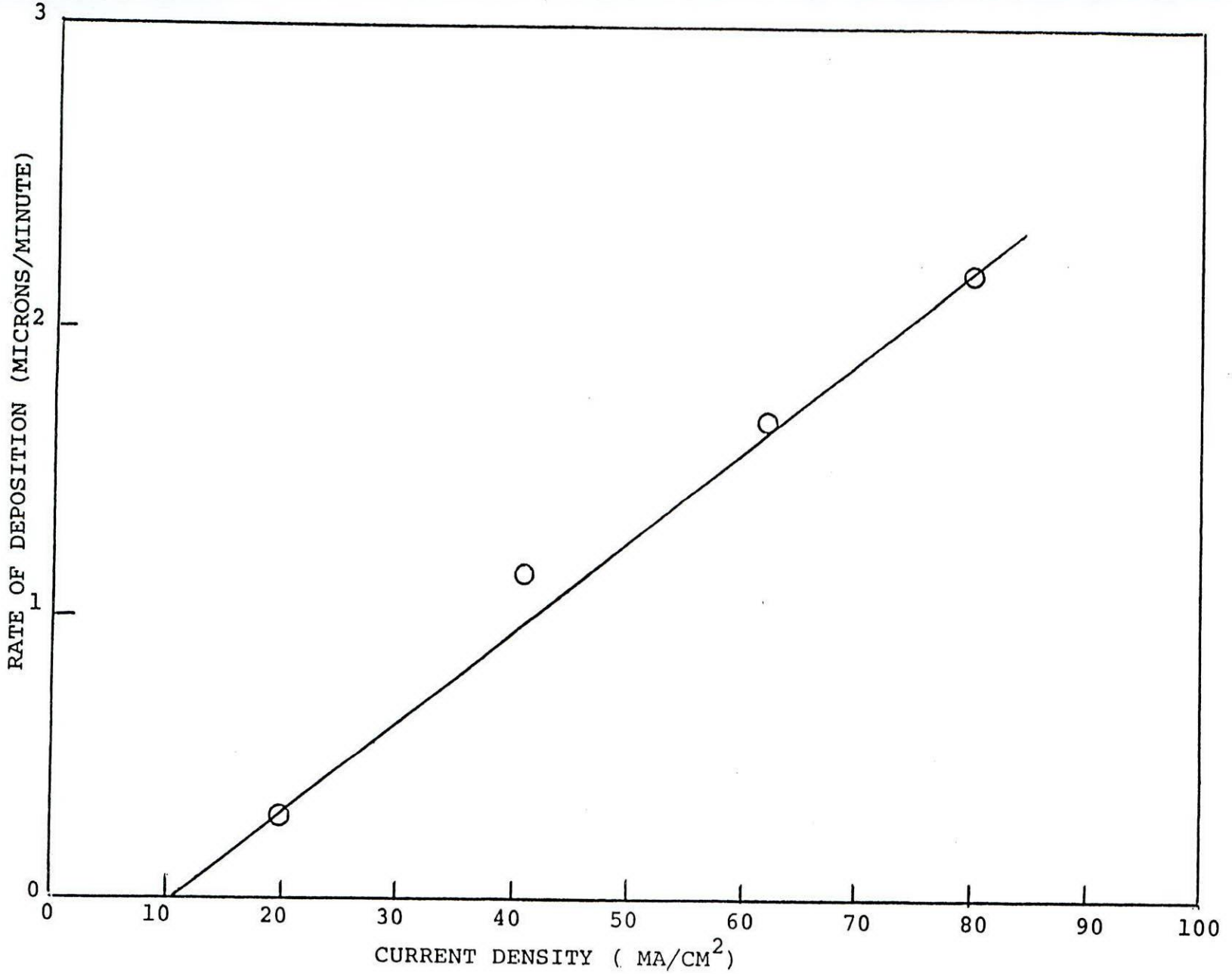

Fig. 1-The rate of deposition of tin/lead (60/40) as a function of current density

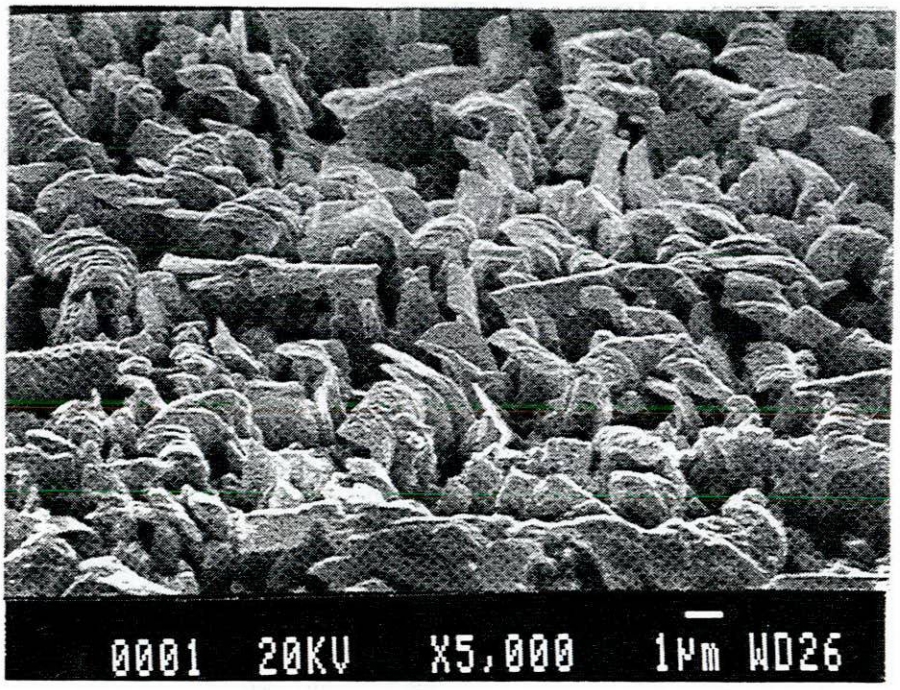

Fig. 2-Tin/lead (60/40) plated stud at 20 ma/cm^2

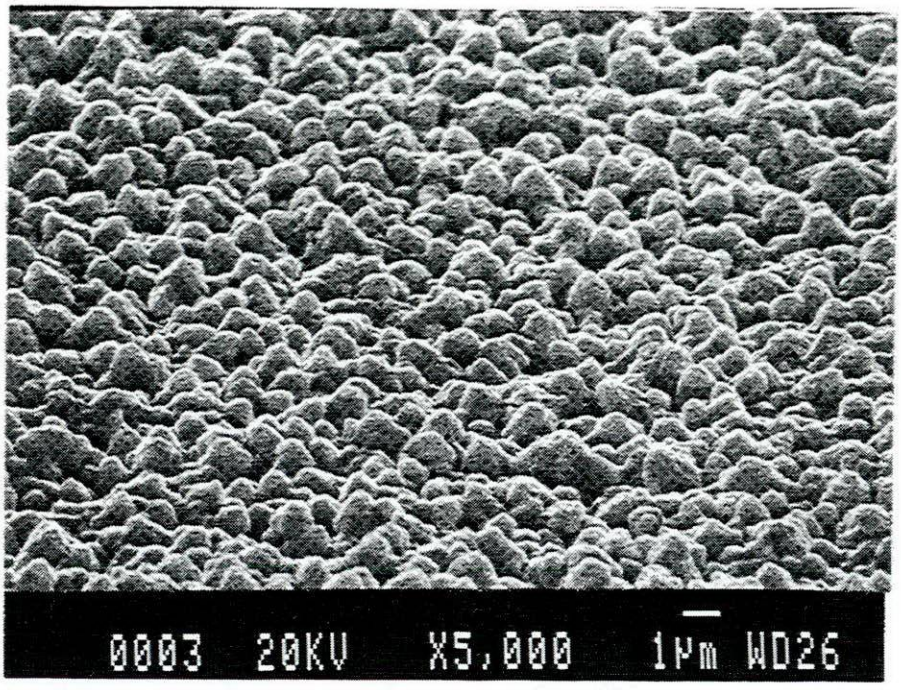

Fig. 3-Tin/lead (60/40) plated stud at 80 ma/cm^2

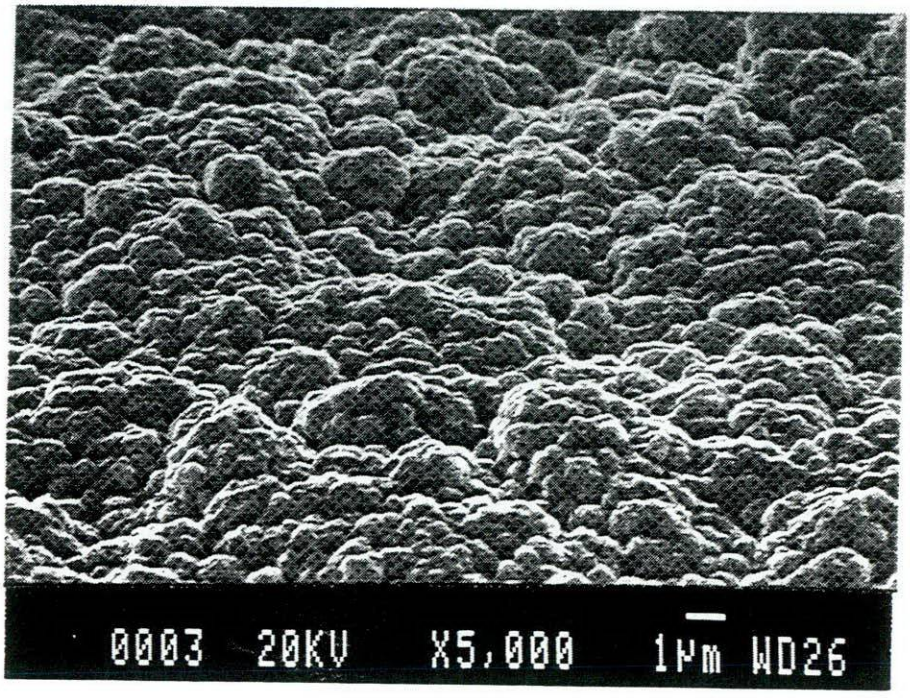

Fig. 4-Tin/lead (60/40) plated stud at 62 ma/cm^2, direct current

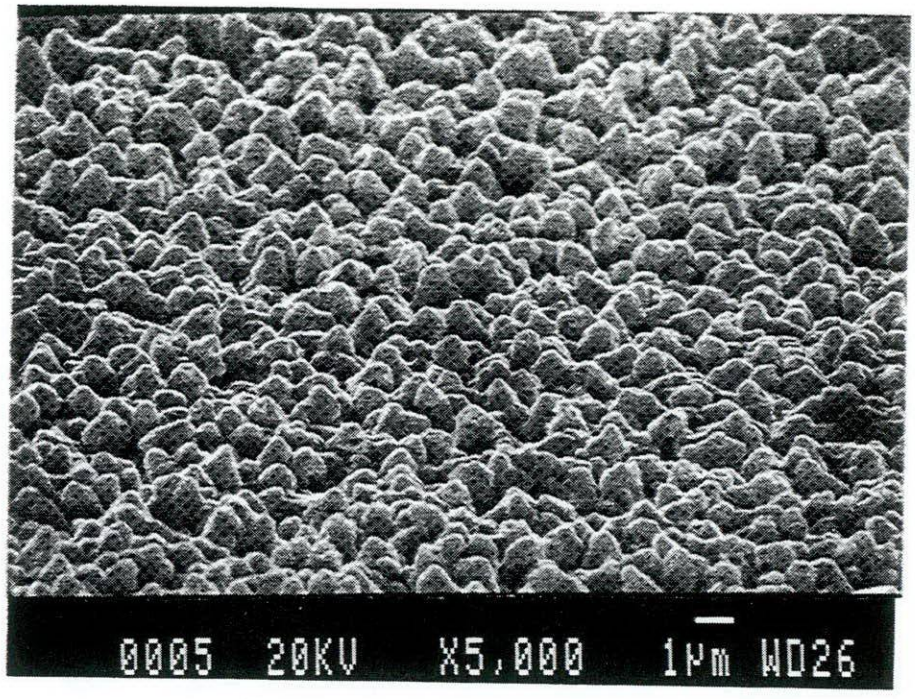

Fig. 5-Tin/lead (60/40) plated stud at 62 ma/cm^2, pulse current

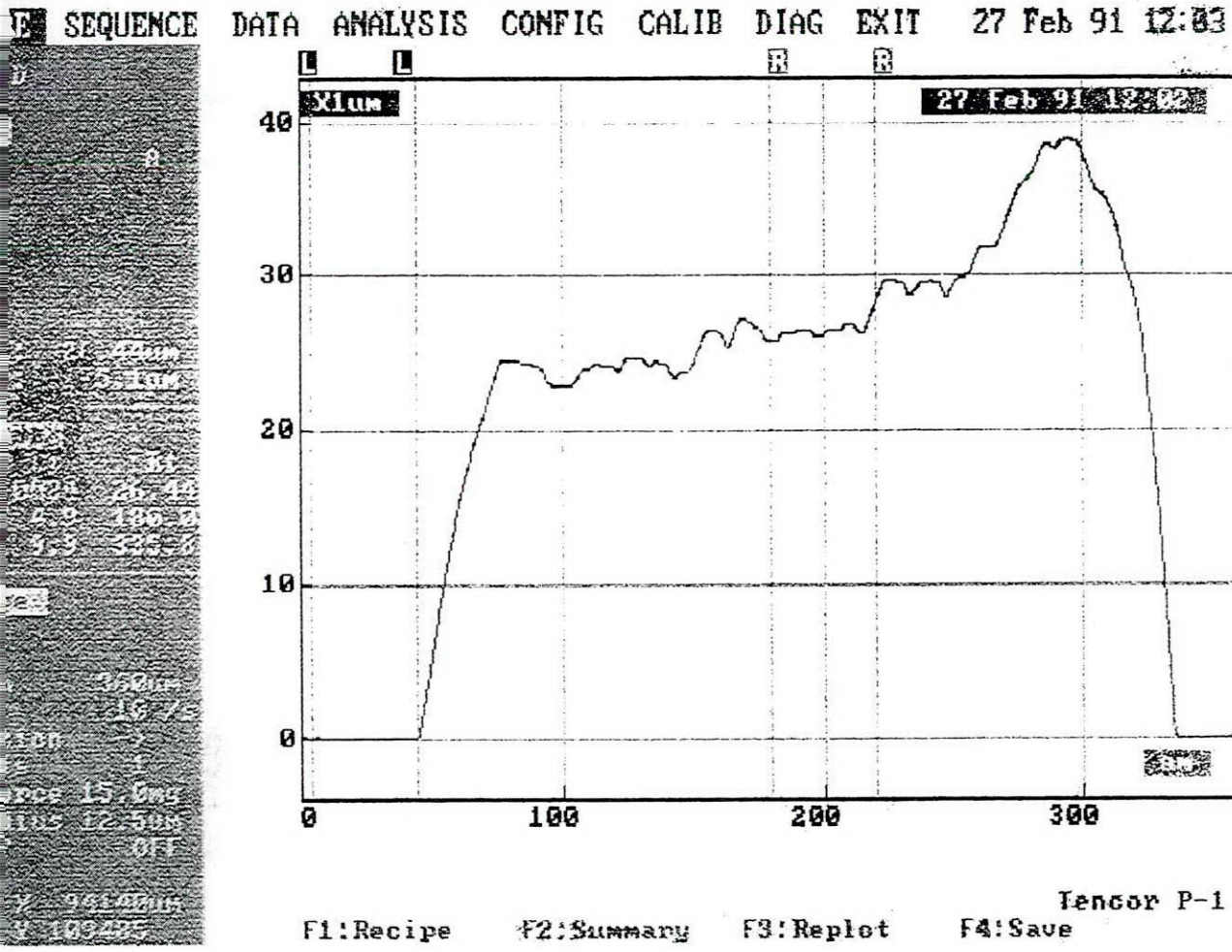

Fig. 6-The profile trace of plated tin/lead (60/40) stud at 60 ma/cm^2 (direct current)

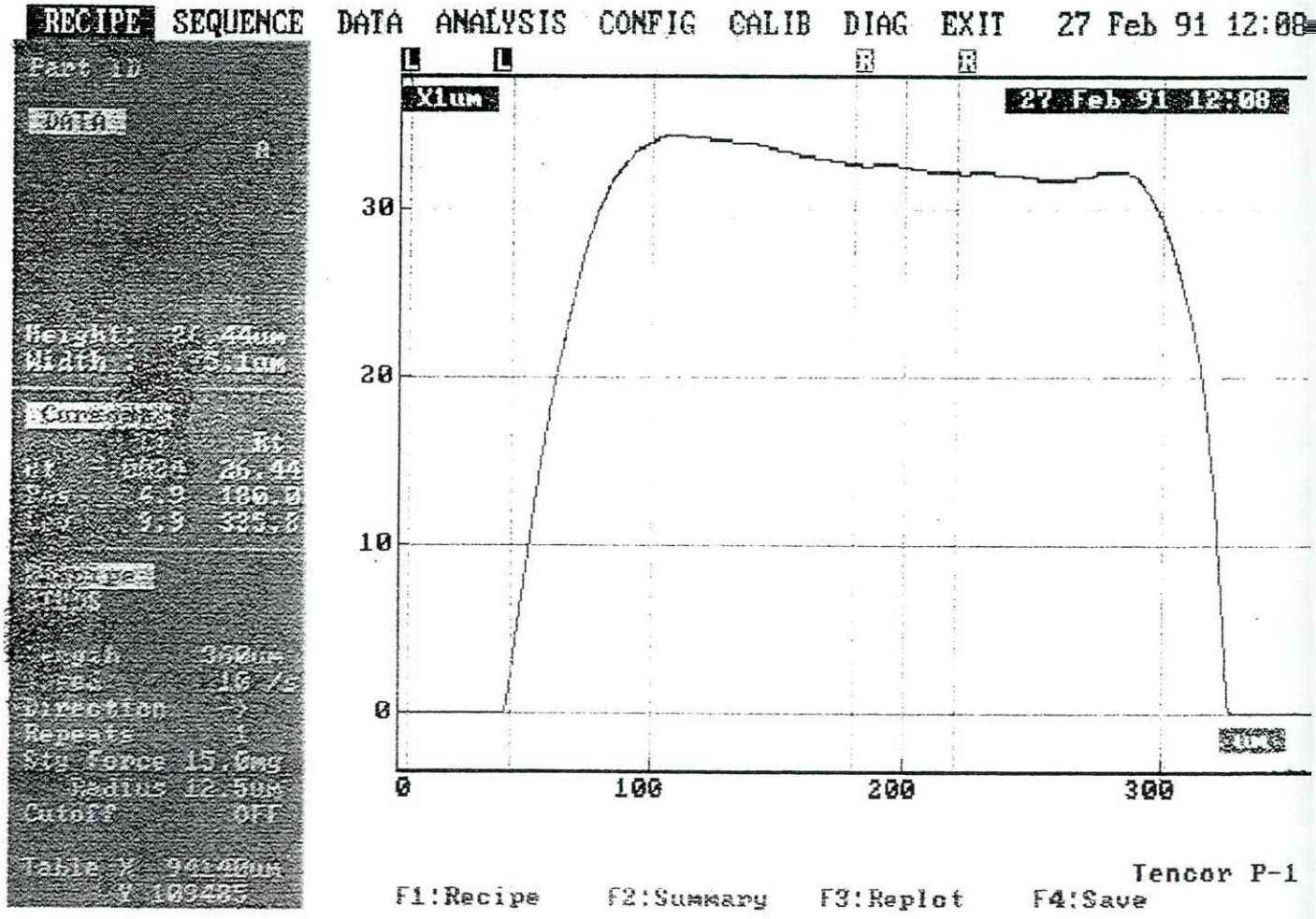

Fig. 7-The profile trace of plated tin/lead (60/40) stud at 60 ma/cm^2 (pulse current)

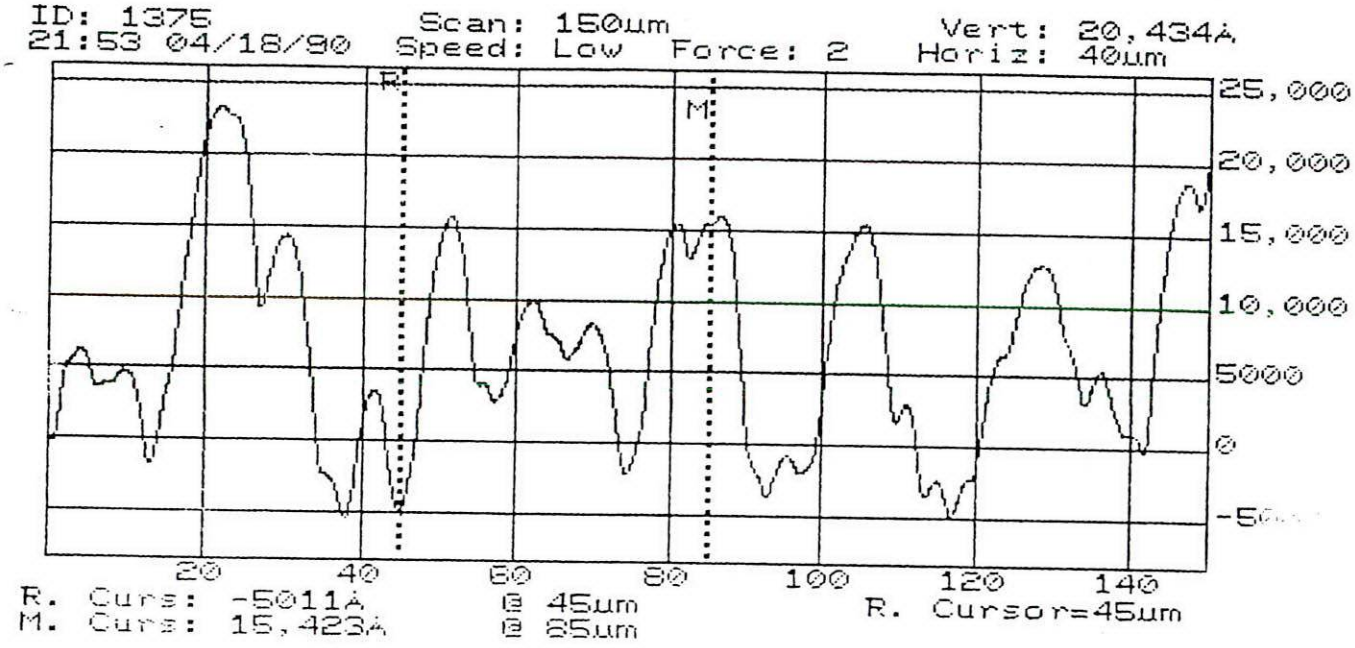

Fig. 8-The surface roughness (P/V) measurements of plated tin/lead (60/40), direct current (60 ma/cm^2)

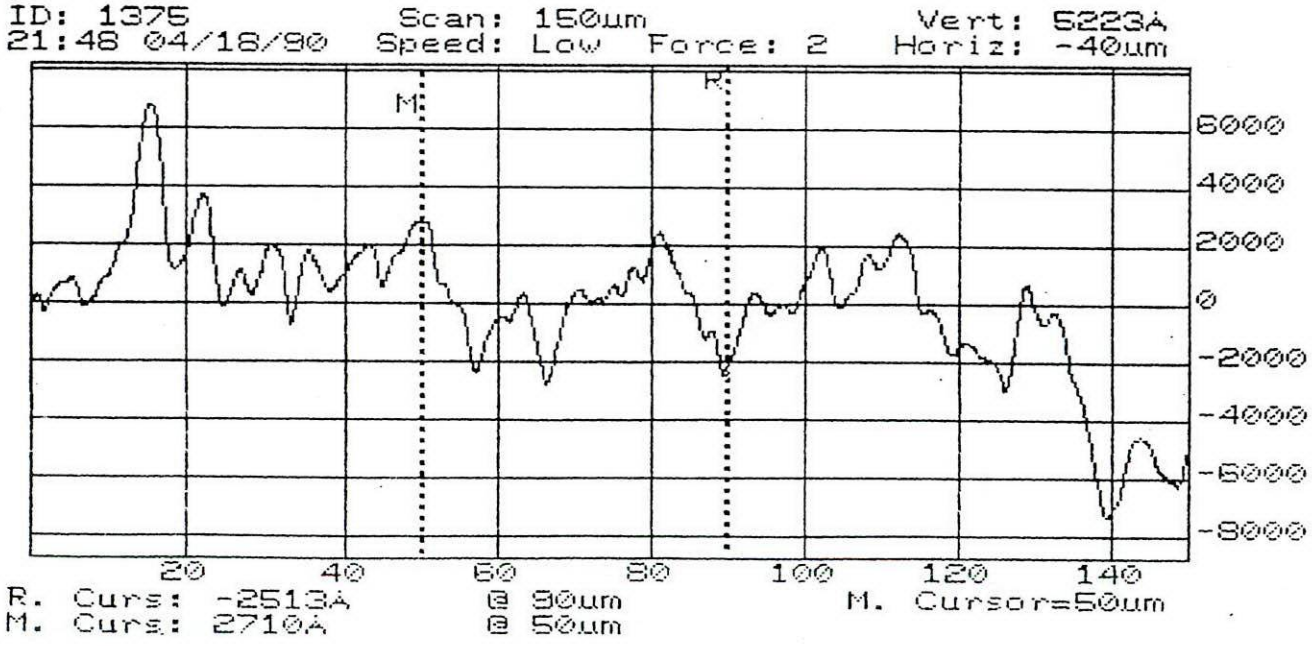

Fig. 9-The surface roughness (P/V) measurements of plated tin/lead (60/40), pulse current (60 ma/cm^2)

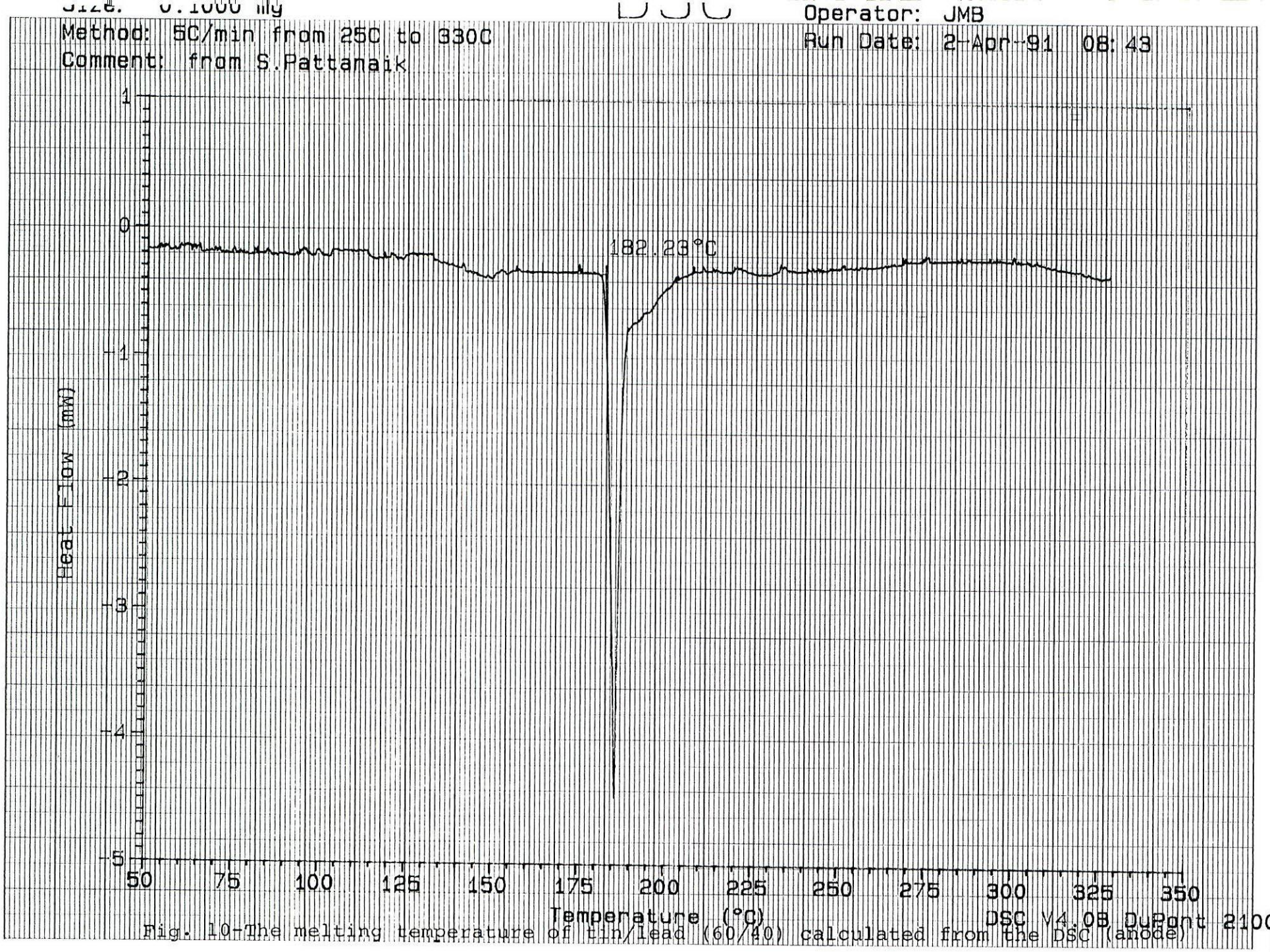

Fig. 10-The melting temperature of tin/lead (60/40) calculated from the DSC (anode)

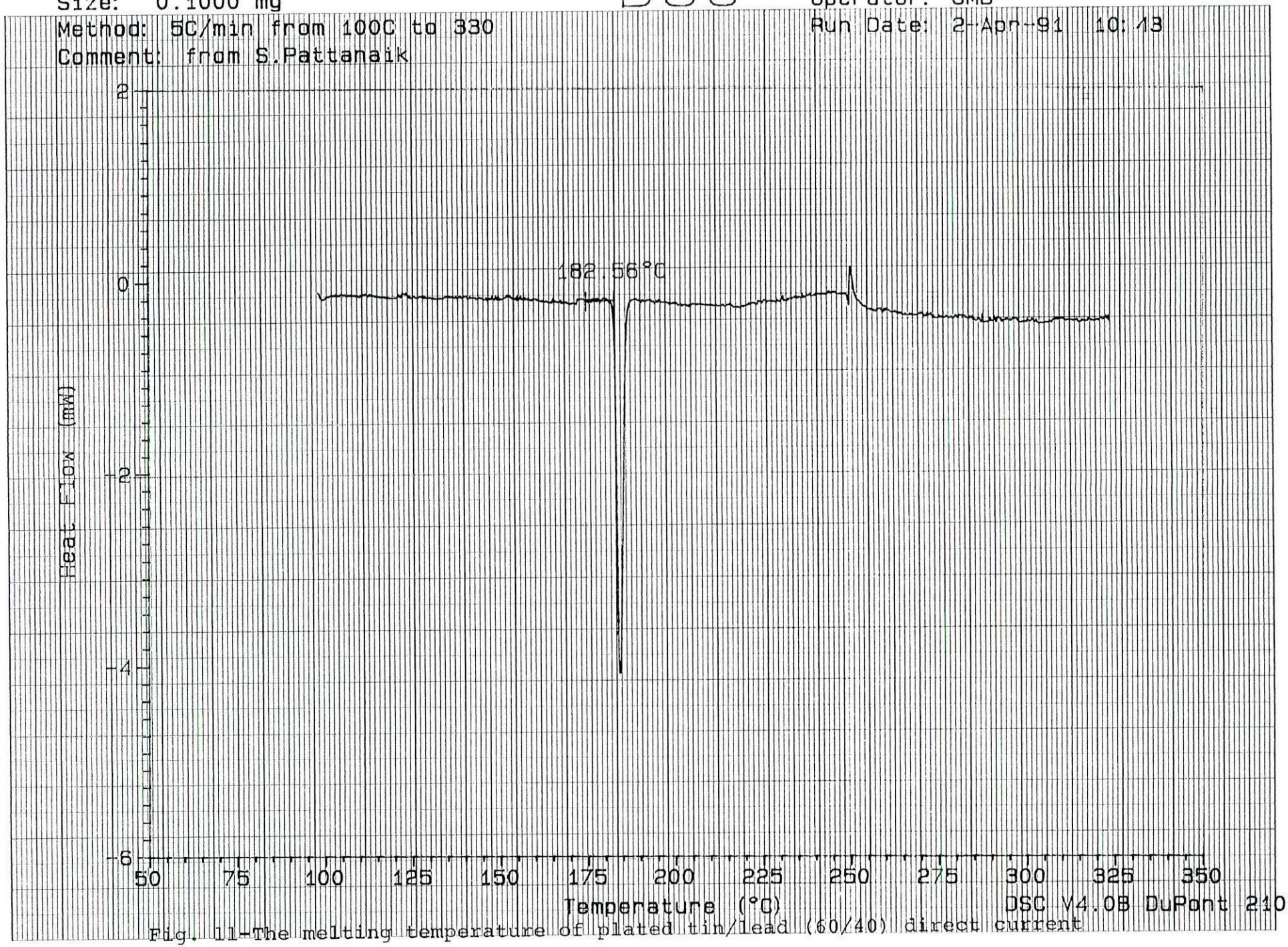

Fig. 11-The melting temperature of plated tin/lead (60/40) direct current

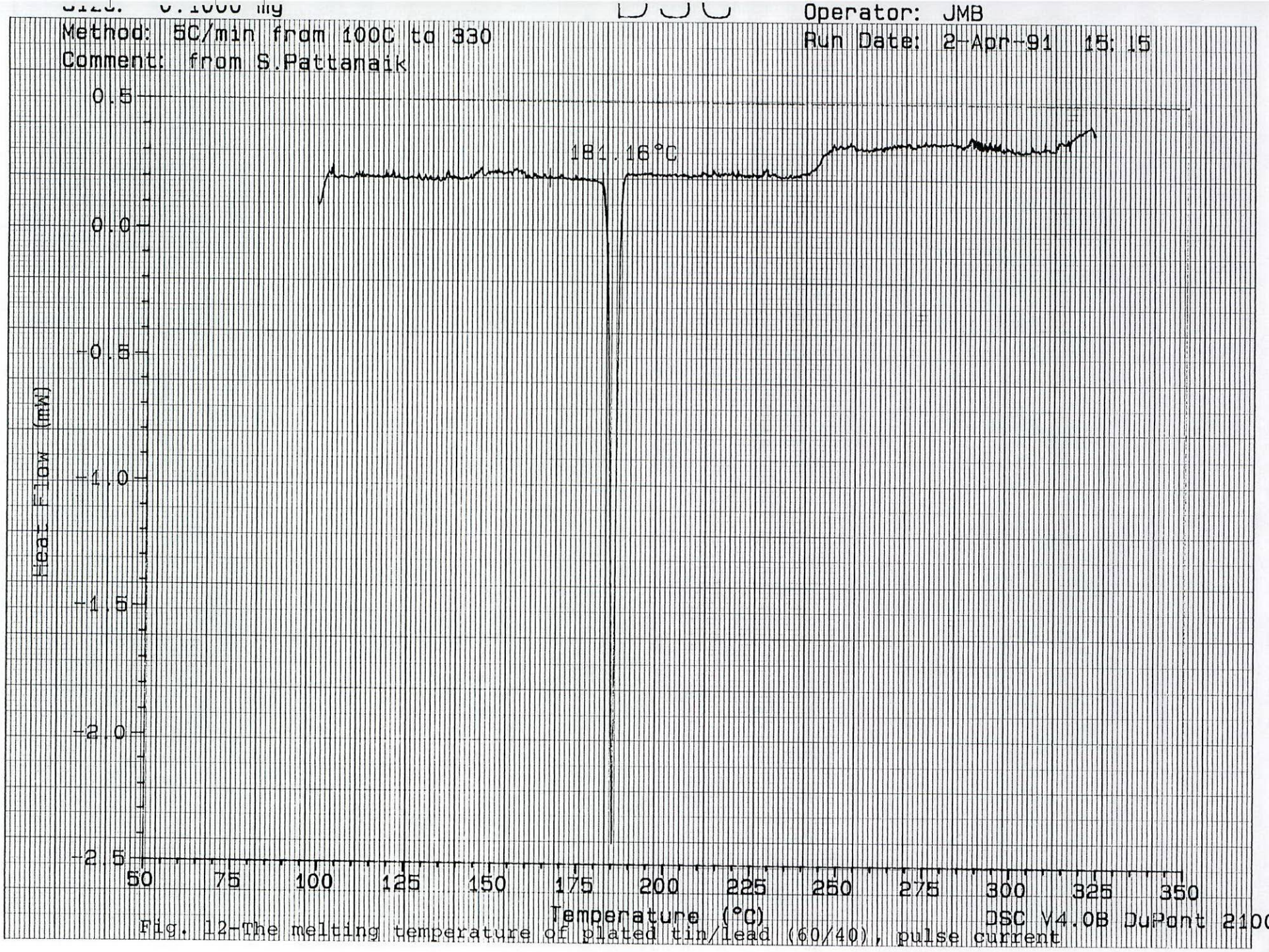

Fig. 12-The melting temperature of plated tin/lead (60/40), pulse current

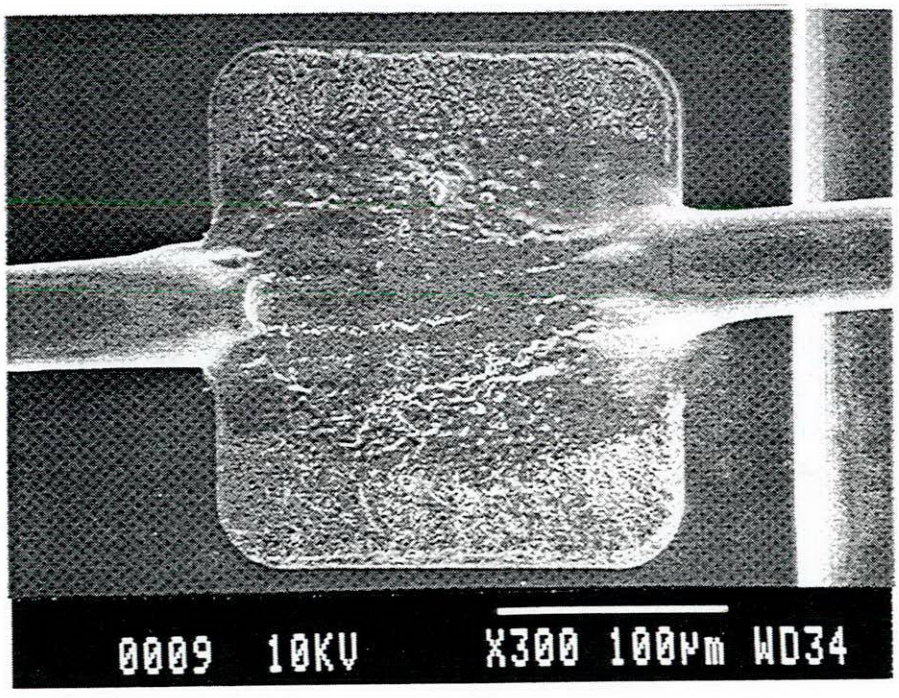

Fig. 13-A typical lasersonic soldering joint

THIN MULTILAYER PALLADIUM COATINGS FOR SOLDERABILITY AND WIREBONDING APPLICATIONS IN ELECTRONIC PACKAGING

I.V. Kadija
J.A. Abys
J.M. Maisano
E.J. Kudrak

AT&T Bell Laboratories
600 Mountain Avenue
Murray Hill, New Jersey 07974

S. Shimada

Dowa Mining Co., Ltd.
8-2, Marunouchi 1-Chome
Chiyoda-ku, Tokyo 100
Japan

Abstract

A detailed study of physical and chemical characteristics of electroplated palladium has led to an understanding of its performance as a solderable and wirebondable material. Furthermore, our understanding of the phenomena and interactions of porosity, interdiffusion, oxidation and dissolution rates of various metals in solder has led to the design of various multilayered palladium coatings useful for advanced electronic packaging applications. Combinations of palladium or palladium alloy with an ultra-thin gold flash exhibit good solderability and wirebonding performance and meet the stringent requirements of MIL-STD-883, Methods 2003 and 2022.

The advantages of this newly developed system which are discussed in detail in this paper.

I. Introduction

Packaging is a critical operation in electronic device fabrication. Compact devices, such as multi-chip-modules, MCMs, are being produced with greater functionality and contact density which has increased process complexity, quality, yield requirements and cost. [1,2,3]. The yield and thus the cost of packaging operations is dependent on the performance of processes such as soldering, wirebonding, and encapsulation which in turn is highly dependent on the type and quality of the surface finish. Conventional processes utilize multi-step, selective plating operations as outlined in Figure 1. This requires the use of expensive "step & repeat" plating equipment and in the case of the pre-plated SnPb finish may suffer from one or more of the following [4,5]:

Pre-Plating Process:

- Silver migration
- Solder bridging (Especially for fine pitch packages)
- Incompatibility with packaging operations (Figure 2)
- Shortened shelf life
- Lack of control of solder thickness (hot solder dip process)

Alternatively, a post-plating SnPb process may suffer from one or more of the following:

Post-Plating Process

- Silver migration
- Solder bridging
- Exposure of IC package to corrosive plating chemicals
- Incompatibility of final packaging operation with SnPb

D. C. Abbott et. al.[5] developed a palladium plated leadframe process and demonstrated its positive impact on component reliability and quality. The focus of this development was a process which reduced process complexity, increased yields and presumably lowered the overall cost for IC packaging operations.

The packaging industry would like to utilize a universal finish which will be solderable and wire bondable regardless of process exposure [4,5]. Figure 2, which shows a typical advanced packaging process sequence, explains why the finish must withstand contamination, oxidation, inter-diffusion and mechanical stress. The focus of this work has been to develop a pre-plated lead frame process which is compatible with other packaging operations and reduces the process complexity, increases yield and lowers the overall cost. Our specific aim was to meet the stringent solderability requirements of MIL STD 883, Methods 2003, 2022, thermal aging criteria which are specific to individual packaging operations, and the AT&T wirebonding specification A-87AL1917.

II. Experimental

IIA. Surface Finish Sample Matrix

In our preceding publication [4] we established that gold-flashed palladium (GFPd) gave excellent solderability and wirebondability. However, due to the thickness of the precious metal layers [4], the cost was considered prohibitive especially by low end manufacturers of integrated circuits. For this purpose specific multilayer finishes (MLS) were investigated as shown in Table 1.

Table 1
Substrates by Layer Configuration and Thickness (Microinches)

Process	Sample	Ni	Pd Total	Au
MLS Finish	Ia	3	(22)*	0
MLS Finish	Ib	3	(18)	0
MLS Finish	Ic	40	(22)	0
MLS Finish	Id	40	(20)	0
MLS Finish	IIa	20	(10.5)	1
MLS Finish	IIb	20	(10)	1
MLS Finish	IIc	20	(10.5)	1
MLS Finish	IId	20	(9.5)	2
MLS Finish	III	20	(12)	0
MLS Finish	IVa	20	(12)	0.3
MLS Finish	IVb	20	(12)	0.4
MLS Finish	IVc	20	(12)	0.7
MLS Finish	IVd	20	(12)	1
MLS Finish	IVe	20	(12)	4
Commercial Finish	V	40	3-5	0

*2-3 layer deposits containing Pd.

The matrix of standardized tests undertaken to evaluate the solderability and wirebondability of the above MLS finishes is shown in Table 2 and described below in Sections IIB-IIC.

Table 2
Matrix of Tests

	Solderability		Wirebonding
	Solder Coverage	Wetting Times	
As Plated	X	X	X
Steam Age	X	X	
Thermal age	X	X	X
Steam Age & Thermal Age	X	X	
Specifications	TM2003	TM-2022	AT&T STD A87L1917

IIB. Solderability Standard Test

The selected standard test for solder coverage was MIL STD 883-TM 2003 which entails exposure of the plated finish to 95°C and 95° RH followed by a "dip & look" for non-wetted or de-wetted areas and/or surface irregularities. Furthermore, it is also critical that soldering is achieved within a one second time frame to be compatible with the line speed of current packaging operations. Thus, the rate of solder wetting as described in TM 2002, is a critical parameter which must be established in the development of novel solderable finishes.

Thermal aging is also a test utilized to evaluate leadframe finishes. A review of Figure 2 demonstrates the necessity for this test. We selected 150°C, 200°C and 250°C for 1, 2, and 5 hours exposure.

IIC. Wirebondability Standard Test Conditions

Wirebonding is typically performed using two techniques: thermosonic and thermocompressive wirebonding. Thermosonic bonding is used more frequently. In thermosonic wirebonding, an apparatus equipped with a hollow metallic tip provides ultrasonic vibrations and pressure needed to bond thin gold or aluminum wires to the chip and leadframe. In thermocompressive bonding, high compressive force and heat are used. Figure 3 shows a diagram of a typical wirebond as described in AT&T standard A-87AL1917. A ball bond is usually made on the chip-side and a wedge bond on the leadframe-side of the connection. The bond quality is determined by performing a pull test using specialized equipment. For statistical purposes we have evaluated our coatings by performing 100 double-bond pulls for each finished test panel.

In the pull test, the force applied when the connection breaks is recorded. Figure 3 lists various types of breaks obtained. Failures may be caused by detachment at the wire/substrate interface, such as breaking at the wire and surface finish or poor adhesion between coating and substrate. A break in the wire itself indicates a strong wirebond.

Several palladium and palladium alloy surface finishes, including an MLS finish, were evaluated for wirebonding. The finishes that were tested are listed in Table 3. In addition, thermocompressive wirebonding tests were performed with Pd coating at 10 microinches thickness only. Twenty microinches of nickel underplate was used for all finishes.

Table 3
Thermosonic Wirebonding Test Matrix

Metal Finish	Thickness (microinches)	Metal Finish	Thickness (microinches)
Pd	5	**PdNi**	5
Pd	10	**PdNi**	10
Pd	15	**Soft Au**	10
		IVd (MLS)	13

IID. Porosity, Diffusivity and Oxidation

Porosity of the layered finish was studied and correlated with solderability. The standard porosity test utilized was ASTM B 799-88.

Thermal aging causes diffusion which changes the surface layer composition. These changes can adversely affect finish solderability. Auger surface analysis and depth profiling were implemented in the investigation of changes in the surface layer composition.

Top surface oxidation can also adversely effect solderability. Auger spectra and thermodynamic reference information must be considered when attempting to explain the rate and extent of surface oxidation on solderability.

III. Results

IIIA. Solder Coverage

One of the objectives of this development was to evaluate the commercially available finish (See Table 1 Group V) and determine the effectiveness of its performance relative to the proprietary multilayer finish system. The performance of the commercial finish is shown in Figures 5-8 and is summarized in Table 4. Our experience with this system is that it does not meet the criteria of MIL STD 883-2003/2022. Furthermore, its performance deteriorates catastrophically under thermal aging conditions.

Our rationalization of the observed phenomena is that the palladium layer thicknesses are too thin and too porous to protect the nickel substrate from oxidation and diffusion phenomena. The presence of nickel oxide at the surface deteriorates the solderability and wirebonding performance. This is clearly demonstrated in Figures 4-7 where porosity is shown to be excessive and the presence of nickel oxidation has been detected on the surface via Auger analysis.

Table 4
Solderability Results

			Thermally Aged				
	As Plated	Steam-aged 8 hr.	150 C for 1, 2 & 5 hr.	200 C for 1, 2 & 5 hr.	250 C for 1, 2 & 5 hr.	200 C for 1, 2 & 5 hr. plus steam-aged 8 hr	250 C for 1, 2 5 hr. plus stea- aged 8 hr
III	Pass	Pass	Pass	Pass	Fail	Fail	Fail
IVa	Pass	Pass	Pass	Pass	Fail	Fail	Fail
IVb	Pass	Pass	Pass	Pass	Fail	Fail	Fail
IVc	Pass	Pass	Pass	Pass	Pass	Pass	Pass
IVd	Pass	Pass	Pass	Pass	Pass	Pass	Pass
IVe	Pass	Pass	Pass	Pass	Pass	Pass	Pass
V	Pass	Fail	Fail	Fail	Fail	Fail	Fail

With the exception of sample IIb (see Table 1), all MLS processes pass Method 2003 test as plated and steam aged. Furthermore, samples III, IVe and IVb pass thermal aging up to 200°C for 5 hours. MLS finishes IVc, IVd and IVe pass thermal aging up to 250°C for 5 hours and the combined steam aging and thermal aging test.

The results clearly demonstrate the superior performance of the MLS finishes. The relationship between porosity and metal diffusion and the performance of the finishes is discussed in sections IIIB-IIID

IIIB. Porosity vs. Solderability Performance.

Porosity to the substrate or base metal contributes to surface finish degradation. This is a well studied phenomena in connector reliability where the migration and oxidation of substrate metals and other contaminants leads to surface passivation and an increase in contact resistance [6,7] We suspected, as touched upon in Section IIIA, that this phenomena would also significantly contribute to poor solderability performance. A schematic representation of this phenomena is seen in Figure 8. Figure 9 and Table 4 clearly demonstrate, as did Figures 4-7, that gross porosity cause poor solderability.

We prepared a series of samples with with varying degres of porosity, by manipulating the plating conditions, to investigate the possible correlation between porosity and solder coverage. Figure 10 shows the results of this investigation which demonstrates with some degree of certainty that this correlation exists. As can be seen, if the porosity level is on the order of 25 pores/cm^2 or less, the solderability is acceptable; if the porosity is on the order of 100 pores/cm^2 or greater, it is unacceptable. The results of these tests are summarized in Table 5.

Table 5
Porosity vs Solderability

	Percent Coverage		
	As Plated	Steam-Aged	Porosity Count(Pores/cm^2)
Ia	99	97	27
Ib	98	97	22
Ic	99	98	28
Id	99	96	28
IIa	98	97	23
IIb	99	92	> 100
IIc	99	97	13
IId	99	98	11
V (Commercial Finish)	99	85	> 100

IIIC. Interdiffusion of Metals vs Solderability

The interdiffusion of metals is a phenomenon which must be considered when developing a finish for leadframe applications due to the high processing temperatures (>150°C) and exposure times experienced in packaging. The presence of non-noble metals diffused from the layers below the layer or leadframe substrate material will adversely affect the solderability of the leadframe finish. The specific rate of diffusion and extent of interdiffusion are functions of the metals employed, the nature of the electrodeposited structure, the layering and thickness of the metal, temperature and exposure times [8,9]. Obviously, interdiffusion will be more pronounced at higher processing temperatures and prolonged exposure times. Furthermore, the thicker the noble metal layer, the better the barrier.

An Auger analysis of the commercially available finish, as discussed in Section IIIA, reveals the presence of nickel on the surface. By analogy to the arguments presented in Section IIIB, we believe that diffusion causes poor solderability because the top layer is too thin, permitting nickel diffusion.

Figure 11 demonstrates the relative abilities of gold and palladium to inhibit diffusion of nickel to the surface. These results demonstrate that the diffusion of nickel from the substrate adversely affects the solderability performance. Within one hour of aging at 250°C the soft gold loses its solderability whereas the palladium barrier survived five hours of aging under these conditions. In this case, it is the diffusion and subsequent oxidation of the non-noble metals which is the cause of poor solderability. Figures 11A and 11B are Auger surface scans of the 250°C thermal aged palladium after 5 and 10 hours. The 10 hour sample (Figure 11B) had nickel diffusion to its surface while no nickel was detected on the 5 hour sample. These findings support the role of nickel diffusion in poor solderability.

To further optimize the proprietary multilayer finish, we have applied the principle of alloying layers for enhanced barrier performance. Figure 12 shows this in an Auger depth profile of two finishes, process III and IVd. By introducing 1 microinch of gold flash on top of palladium we have eliminated nickel diffusion to the surface as observable by the absence of the nickel at the finish surface interface. This modification greatly improved finish performance.

IIID. Intrinsic Oxides & Dissolution Rates of Surface Layers-Effect on Solderability

Although noble metals are considered nonoxidizing, it has been established that thin layers of oxide or chemisorbed oxygen form on their surface[11,12]. The tenacity of these surface oxides varies among the noble metals. Table 6 shows the standard molal enthalpys of formation of oxides of gold, platinum, palladium, nickel and tin along with the solderability of these metals.

Table 6
Oxide Formation Thermodynamics Versus Solderability

	Solderability			
Metal	**As Plated**	**Steam Aged**	**Molal Enthalpy**	**Dissolution Rate in 60/ Solder, 450 C**
Au	Good	Good	Au_2O_3, +80.8	2.95 μm/s
Pd	Good	Marginal	PdO, -20.4	0.035
Pt	Not good	Not good	PtO_2, +41.O; Pt_3O_4, -39	1 x 10^{-9}
Ni	Not good	Not good	NiO, -57.3; Ni_2O_3, -117.0	1 x 10^{-8}
Sn	Good	Marginal	SnO, -68.3; SnO_2, -138.8	NA

Gold promptly forms oxygen monolayers in air, but its oxides are unstable and a positive molal enthalpy indicates that its natural state is oxide-free[12]. This explains why on the surface of the gold finished leadframes there is a favorable condition for solderability.

If one examines Table 6, one may find inconsistencies which indicate that knowledge of the oxidation thermodynamics and the oxidation kinetics of the surface layer cannot be used to predict solderability performance, even though a highly oxidited surface is known to be not solderable. For example, there are other noble metals which are almost oxide free in their natural state. Yet, for example, platinum which has a positive enthalpy for one oxide, PtO_2, and a small negative enthalpy for Pt_3O_4 is entirely non-wettable with solder. Here the formation of intermetallic bond is probably inhibited with the extremely slow dissolution of platinum in solder. Bader[9] shows that the platinum dissolution rate is over 10^8 times slower than that of gold. Furthermore, nickel oxide is less stable than tin oxide. Yet, tin oxide, which is ubiquitous in Sn/Pb commercial processes, does not inhibit solderability because the oxide layer breaks off during the melting stage. This phenomenon cannot occur with nickel because the melting points of nickel and its oxide are so high.

Palladium forms a weak oxide in the air, as indicated by the enthalpy. This, coupled with an acceptable dissolution rate, shows good to marginal solderability.

IIIE. Wetting Time

Table 7 shows solder wetting times measured as per MIL STD 803, Method 2022. These measurements were performed with finishes that had passed coverage tests, Section IIIA.

Table 7
Wetting Time vs Aging

Process	As Plated	Steam Aged 8 Hrs.	150°C 5 Hrs.	200°C 5 Hrs.	250°C 5 Hrs.
III	0.83	1.11	0.73	1.33	1.56
IVd	0.50	0.83	0.85	0.83	0.85
IVe	0.51	0.65	0.62	0.82	0.83
V	0.85	2.30	4.32	8.32	11.55

The commercial finish was included for comparison only. As established in the surface coverage tests in Section IIIA, the commercial finish is inferior and it does not meet the one second requirement. With the exception of the "As Plated" sample (Process V, Table 7), all aging conditions cause the commercial finish to fail. The MLS finish, Process III,shows only marginal delay in wetting following steam aging and at higher temperatures i.e. 200°C and 250°C. This is to be expected as indicated in Sections IIIc and IIId. A remarkable improvement in wetting speed is achieved with the addition of a super thin gold flash. Samples IVd and IVe show wetting times below one second for the entire range of aging conditions.

IIIF. Wirebonding Results and Evaluation

Identical parameters were used for thermosonic bonding of gold-to-gold and gold-to-palladium coatings. This suggests that no significant change to existing operations are needed for wirebonding to palladium. For thermocompressive bonding, the temperature used was at the upper limit of the gold-to-gold bonding parameters. The wirebonding parameters are shown below.

Table 8
Thermosonic Conditions for Wirebonding

Parameter	Range	Au Range
Gold Wire (mils)	1.0-1.5	1.0-1.5
Force (g)	25-60	25-60
Power (Watts)	1.0-5.0	1.0-5.0
Temperature (C)	150	150
Time (mS)	55	55

Table 9
Thermocompressive Conditions for Wirebonding

Parameter	Range	Au Range
Gold Wire (mils)	1.0-1.5	1.0-1.5
Ball Bond Force (g)	40-50	40-50
Wdge Bond Force (g)	80-100	80-100
Temperature (C)	200	150-200
Time (nS)	10	10

The results are presented in Table 10. Only PdNi TD failed, which may be attributed to surface oxidation.

Table 10
Thermosonic and Thermocompressive Wirebonding Test Results

Process	As Plated	Thermal Age 150°C/5 Hrs.
Pd 5	100%	100%
Pd 10	100%	100%
Pd 15	100%	100%
PdNi 5	96%	91%
PdNi 10	100%	95%
Au Soft 10	100%	100%
IVd	100%	100%

The palladium and soft gold finishes show good wirebonding. The palladium-nickel alloy shows marginal performance as plated, and it fails after thermal aging. The failure was caused by the formation of nickel oxide. The multilayer finish (MLS), IVd, shows exceptional performance in wirebonding applications.

The process of wirebonding is performed using an extremely high concentration of power for a short time. Approximately 500,000 Watts per square inch are applied in 55 milliseconds. SEM microscopy (Figure 13) revealed that an integral bond is formed between the wire and the substrate. In order to study the composition of the interface, a gold wirebond was made to a 10 microinch palladium plate and subsequently polished up to the bond interface. An Auger profile, shown in Figure 14, was performed to identify the degree of interdiffusion of the metals present at the interface. The presence of nickel, palladium, copper and gold at the site of the original interface indicates a high degree of interdiffusion.

Conclusion

Palladium and palladium alloy electrodeposits can be effectively utilized in metal finishing for electronic packaging applications. By combining layers designed to preserve the surface finish integrity we discovered multiple layer structures which meet the most stringent soldering requirements. We were able to solder to substrates which had undergone severe thermal and steam aging with only 13 microinches of finishing layer. A correlation of porosity, interdiffusion and surface oxidation was developed which will be expanded upon in the future. Wirebonding can also be performed quite successfully with palladium substrates in both thermosonic and thermocompressive modes of operation.

Figure Captions

1. Selective Plating, "Step & Repeat Process"

2. Effect of Surface Finish on Selected Steps in Advanced Packaging Process

3. Wirebonding Specifications and Failure Mode Description

4. Solderability of Commercial Palladium Finish - Steam Age Effect

5. Solderability of Commercial Palladium Finish - Steam Age Effect - 200°C

6. Solderability of Commercial Palladium Finish - Steam Age Effect - 250°C

7. Solderability of Commercial Palladium Finish - Steam Age Effect - 250°C for 5 Hrs and Steam Age Effect

8. Substrate/Solder Interface Schematic Presentation; Physico-chemical Effects of Surface Aging

9. Thin Palladium Over Nickel Porosity Effect on Solderability

10. Gold Flashed Palladium Porosity Effect on Solderability; 110 Pores per Centimeter Indicate Inadequate Substrate

11. Solderability Comparison; Soft Gold Top Layer vs. Palladium Top Layer Over Nickel. Palladium is a Superior Diffusion Barrier for Nickel

11A. Surface Survey by Auger, Figure 11 - Pd, 5 Hrs; No Nickel on Surface, Good Solderability

11B. Surface Survey by Auger, Figure 11 - Pd, 10 Hrs.; Nickel Oxide Detectable, Non-Solderable Surface

12. Gold Flashed Palladium as an Optimized Diffusion Barrier for Nickel. Nickel Diffuses through a 12 Microinch Multilayer Structure at 250°C. It Does Not Diffuse in Presence of 1 Microinch Soft Gold Top Coating

13. Ball-Bond Cross Section

14. Wirebond Auger Profile - Interdiffusion of Metals

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9. W.G. Bader: Soldering to Palladium and Palladium Coatings, Proc. Conference of American Electroplaters & Surface Finishers Society Symposium, Danvers, MA , September 16-17, 1980, also, Dissolution of Au, Ag, Pd, Pt, Cu and Ni in a Molten Tin-Lead Solder, Welding Journal, December 1969.

10. M. Tandy and F. Bozon-Verduraz, Compt. Rend. C 280 (1975) 317-20.

11. Lange's Handbook of Chemistry, McGraw-Hill Book Company, also, Gmelins Handbuch Der Anorganishen Chemie, Gold, Volume 62.

12. J.E. Brady and G.E. Humiston, General Chemistry, J. Wiley & Sons, New York, NY, 1978

Package Processing Choices

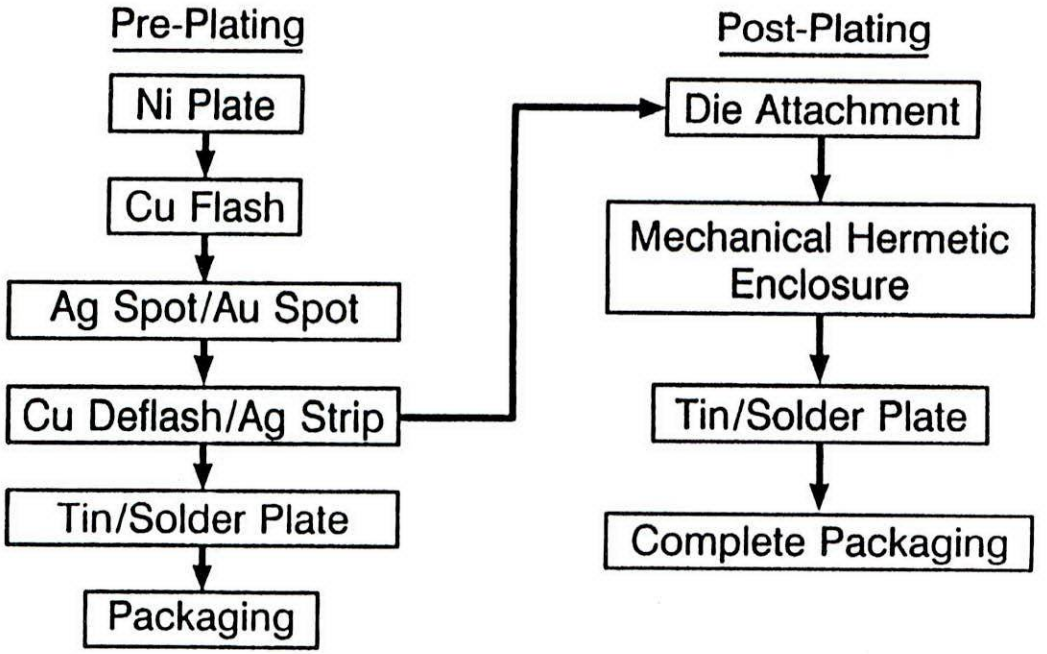


Figure 1

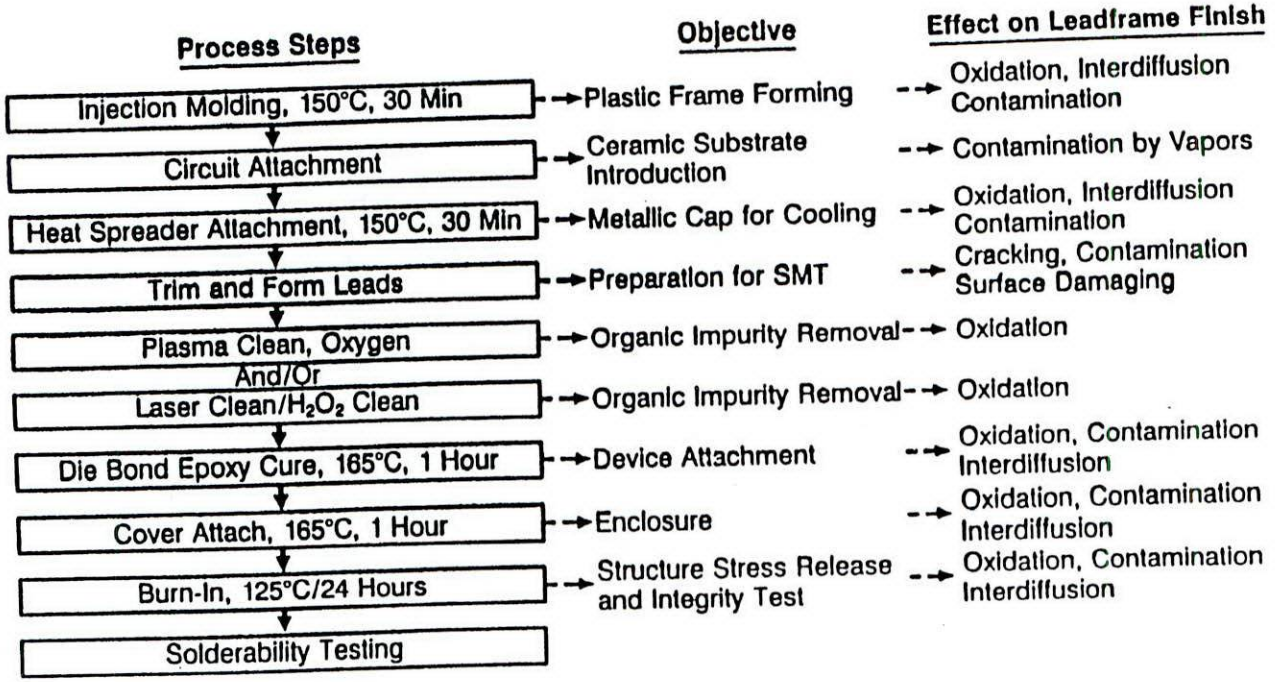
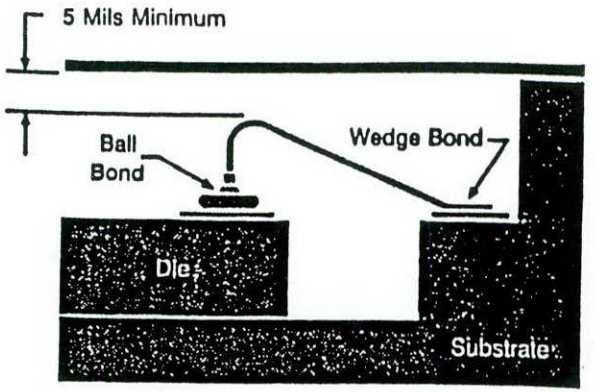

Process Steps
Objective
Effect on Leadframe Finish
Injection Molding, 150°C, 30 Min
Plastic Frame Forming
Oxidation, Interdiffusion Contamination
Circuit Attachment
Ceramic Substrate Introduction
Contamination by Vapors
Heat Spreader Attachment, 150°C, 30 Min
Metallic Cap for Cooling
Oxidation, Interdiffusion Contamination
Trim and Form Leads
Preparation for SMT
Cracking, Contamination Surface Damaging
Plasma Clean, Oxygen
And/Or
Laser Clean/H_2O_2 Clean
Organic Impurity Removal
Oxidation
Organic Impurity Removal
Oxidation
Die Bond Epoxy Cure, 165°C, 1 Hour
Device Attachment
Oxidation, Contamination Interdiffusion
Cover Attach, 165°C, 1 Hour
Enclosure
Oxidation, Contamination Interdiffusion
Burn-In, 125°C/24 Hours
Structure Stress Release and Integrity Test
Oxidation, Contamination Interdiffusion
Solderability Testing

Figure 2



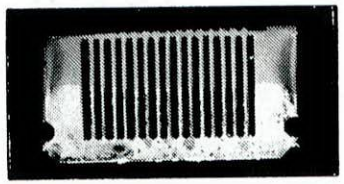
Package Cross Section

Mode	Description	
1	Wire break at least 5 wire diameters above the ball	Pass
2	Wire break above the ball	Pass
3	Failure in bond interface between wire and die metallization	No
4	Wire break at the wedge bond heel	Pass
5	Failure in bond interface between wire and substraste or lead frame metallization	No
6	Lifted metallization from die	No
7	Lifted metallization from substrate or lead frame	No
8	Fracture of die or cratering in die	No
9	Abort test code	

Figure 3

MIL-SPEC-STD 883-TM-2003

Sample



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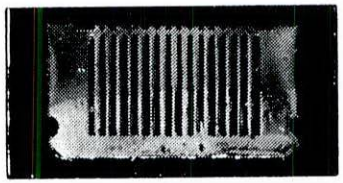
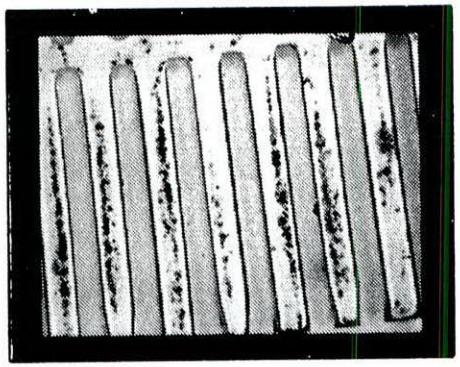


Fail

SEM



Porosity



93BLM129.05

Figure 4

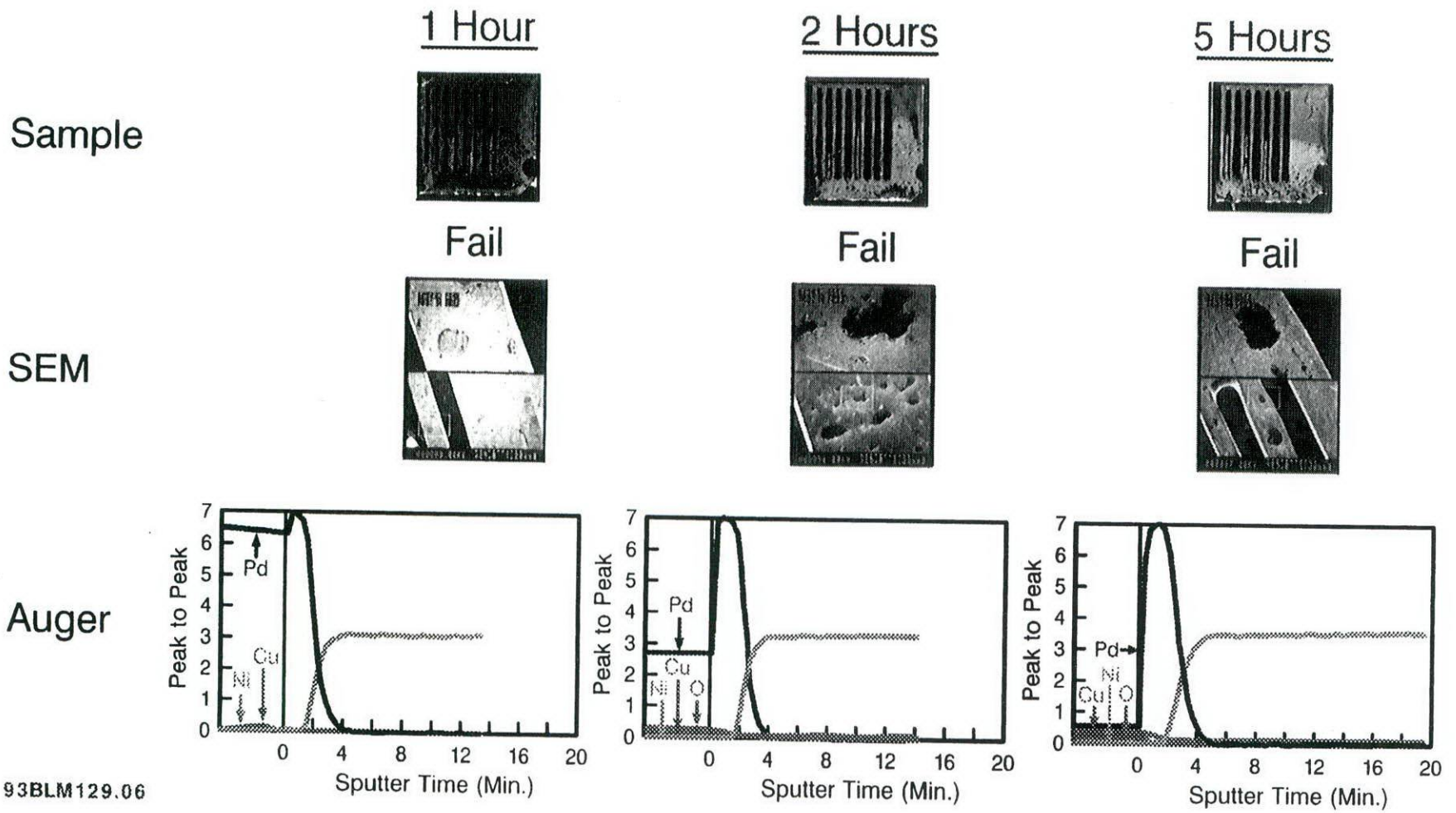

1 Hour
2 Hours
5 Hours
Sample
Fail
Fail
Fail
SEM
Auger
Peak to Peak
Pd
Cu
Ni
O
Sputter Time (Min.)
93BLM129.06

Figure 5

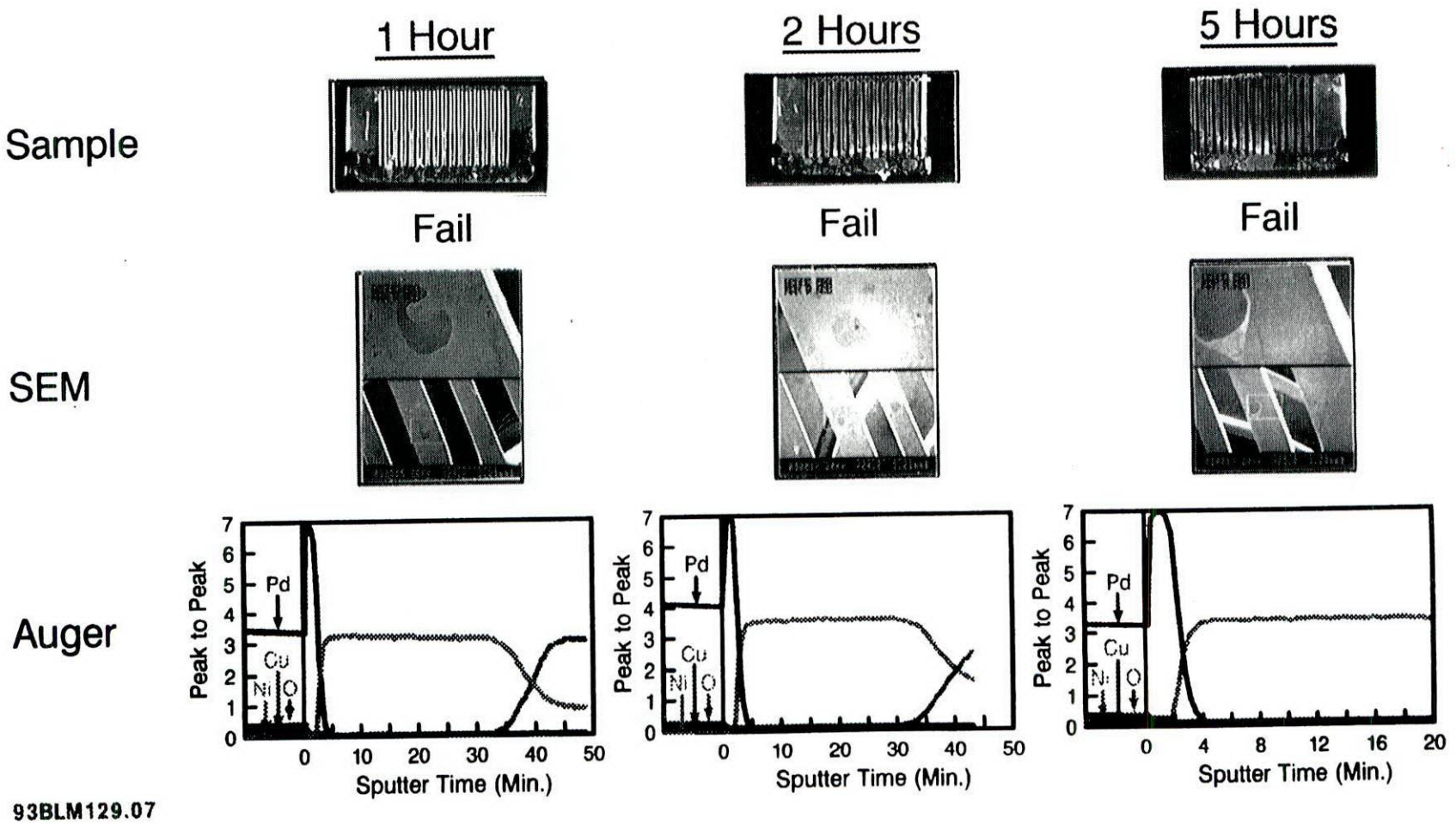
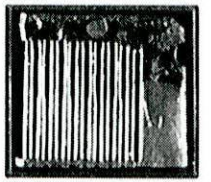

1 Hour
2 Hours
5 Hours
Sample
Fail
Fail
Fail
SEM
Auger
Peak to Peak
Pd
Cu
Ni
O
Sputter Time (Min.)
93BLM129.07

Figure 6

250°C, 5 Hours and 95°C/95% RH, 8 Hours

Sample



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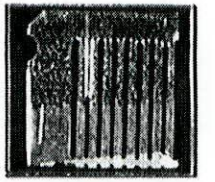
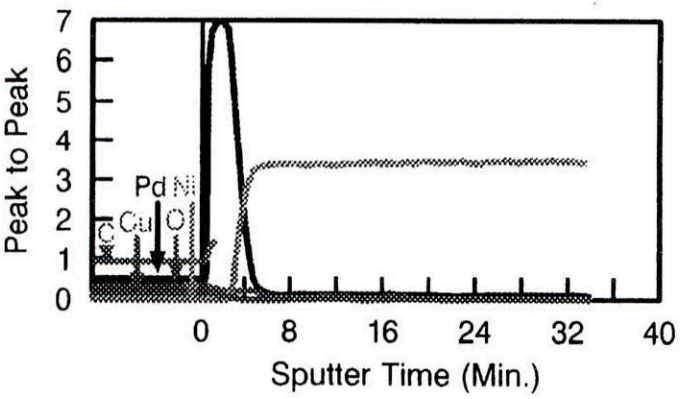


Fail

SEM



Auger



93BLM129.08

Figure 7

Substrate/Solder Interface

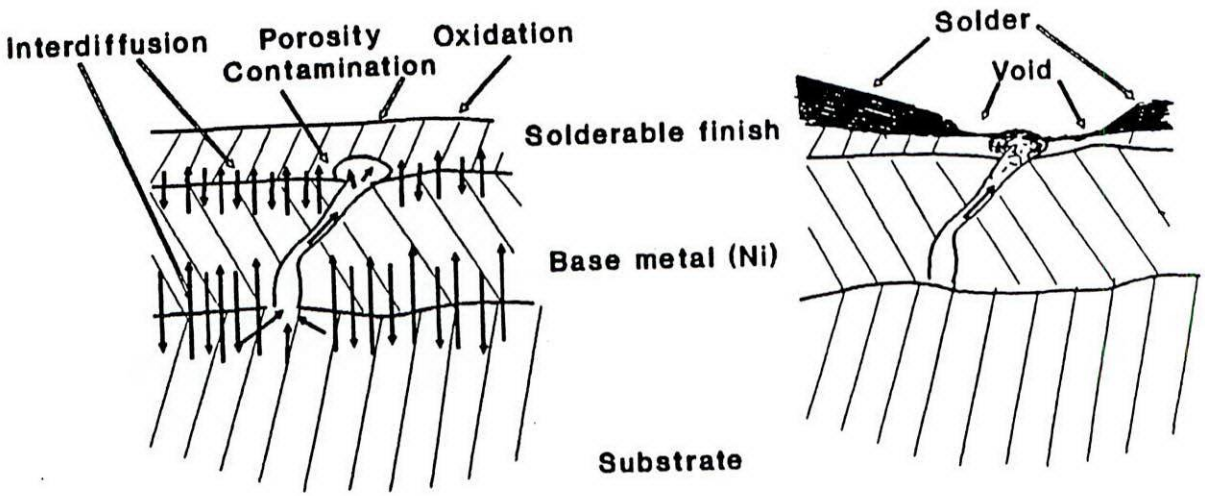
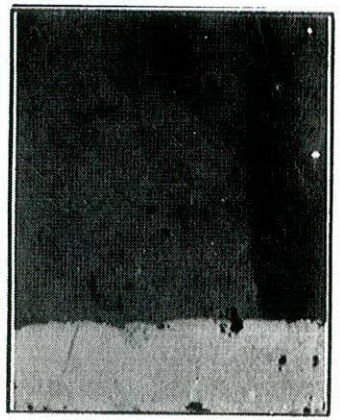


Figure 8

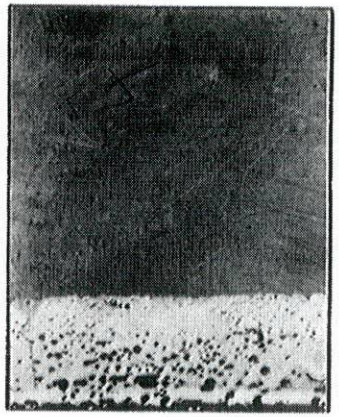
As Plated



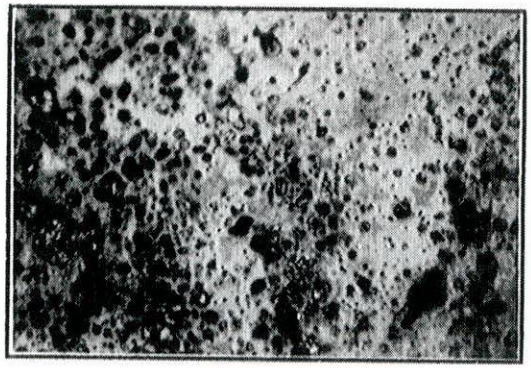
Ni = 50μ″
1.2 μm
Pd = 5μ″
0.12 μm

Steam Aged





Sulfurous Acid Vapor Test



Optical
Photo
10X

Gross Porosity

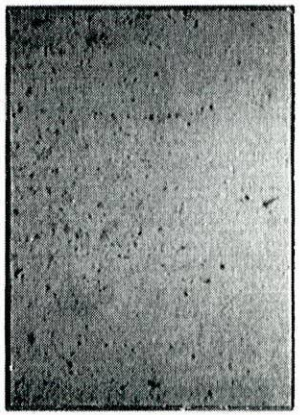
93BLM129.09

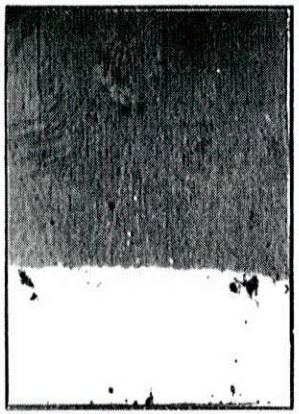
Figure 9

Au Flashed Pd

Porosity

Solderability

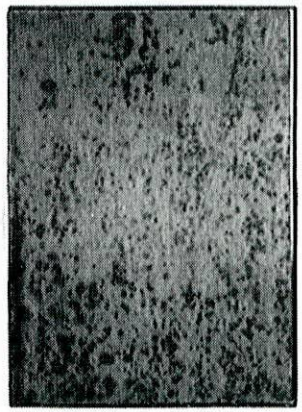




Pd = 10μ″
0.25 μm

Au = 1μ″
0.025 μm

23 Pores/cm^2





Pd = 10μ″
0.25 μm

Au = 1μ″
0.025 μm

110 Pores/cm^2

93BLM129.11

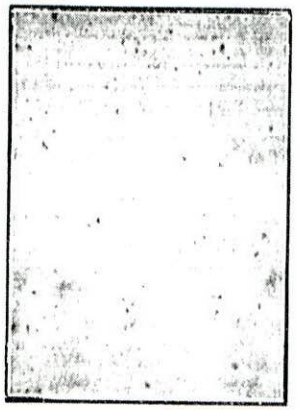
Figure 10

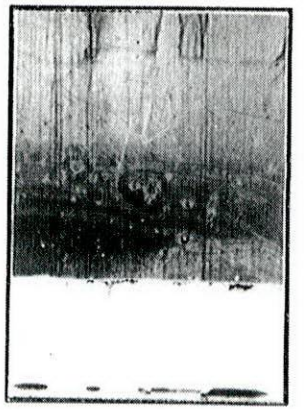
Au Flashed Pd

Porosity

Solderability

11 Pores/cm^2



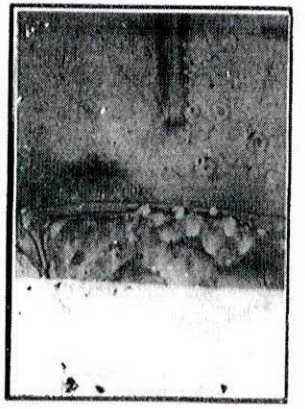


Pd = 10μ″
0.25 μm

Au = 1μ″
0.025 μm

13 Pores/cm^2





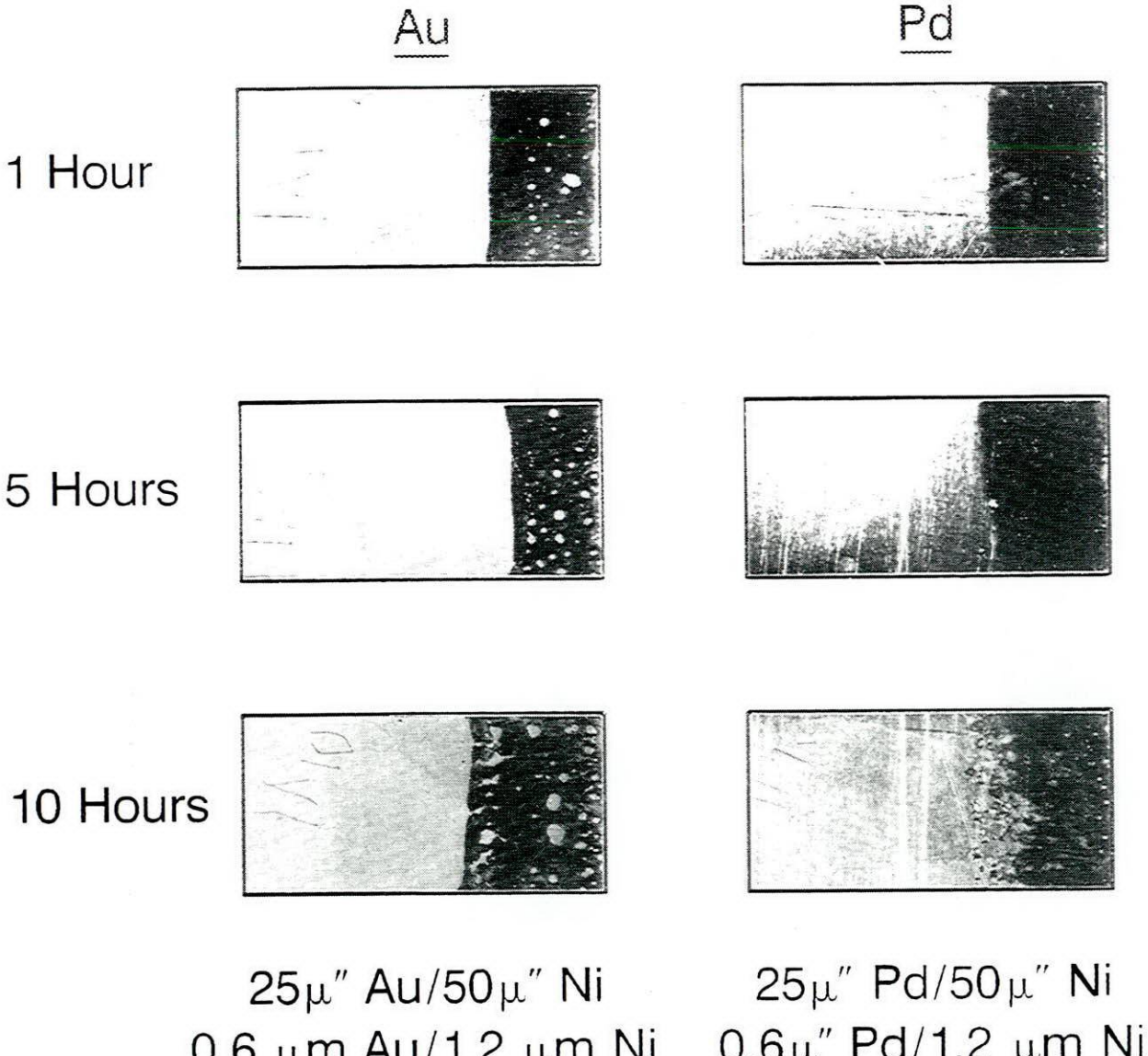
Pd = 10μ″
0.25 μm

Au = 1μ″
0.025 μm

93BLM129.10

Figure 10

Thermal Aging - 250°C

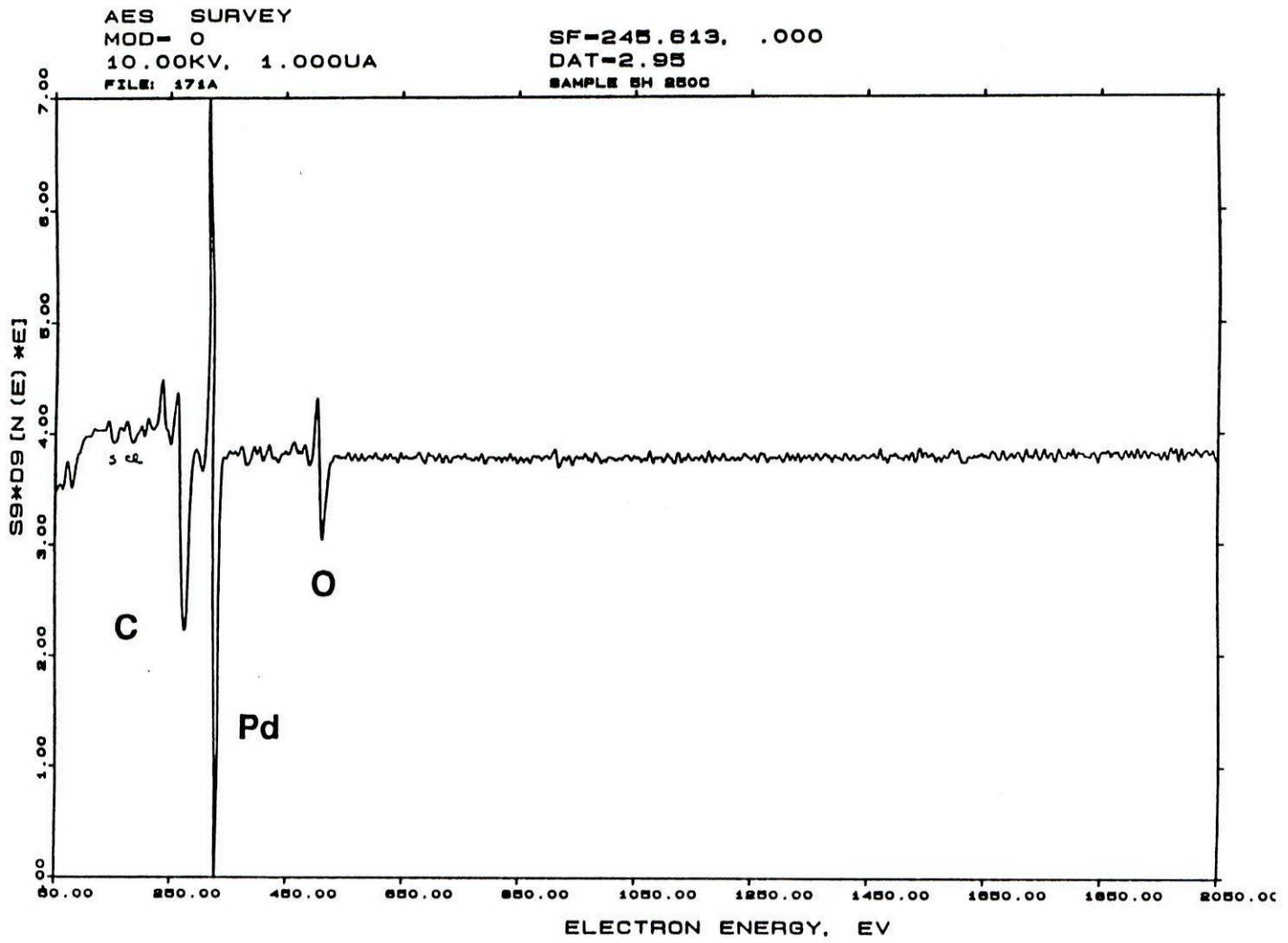


25μ" Au/50μ" Ni
0.6 μm Au/1.2 μm Ni

25μ" Pd/50μ" Ni
0.6μ" Pd/1.2 μm Ni

Figure 11

93BLM18.13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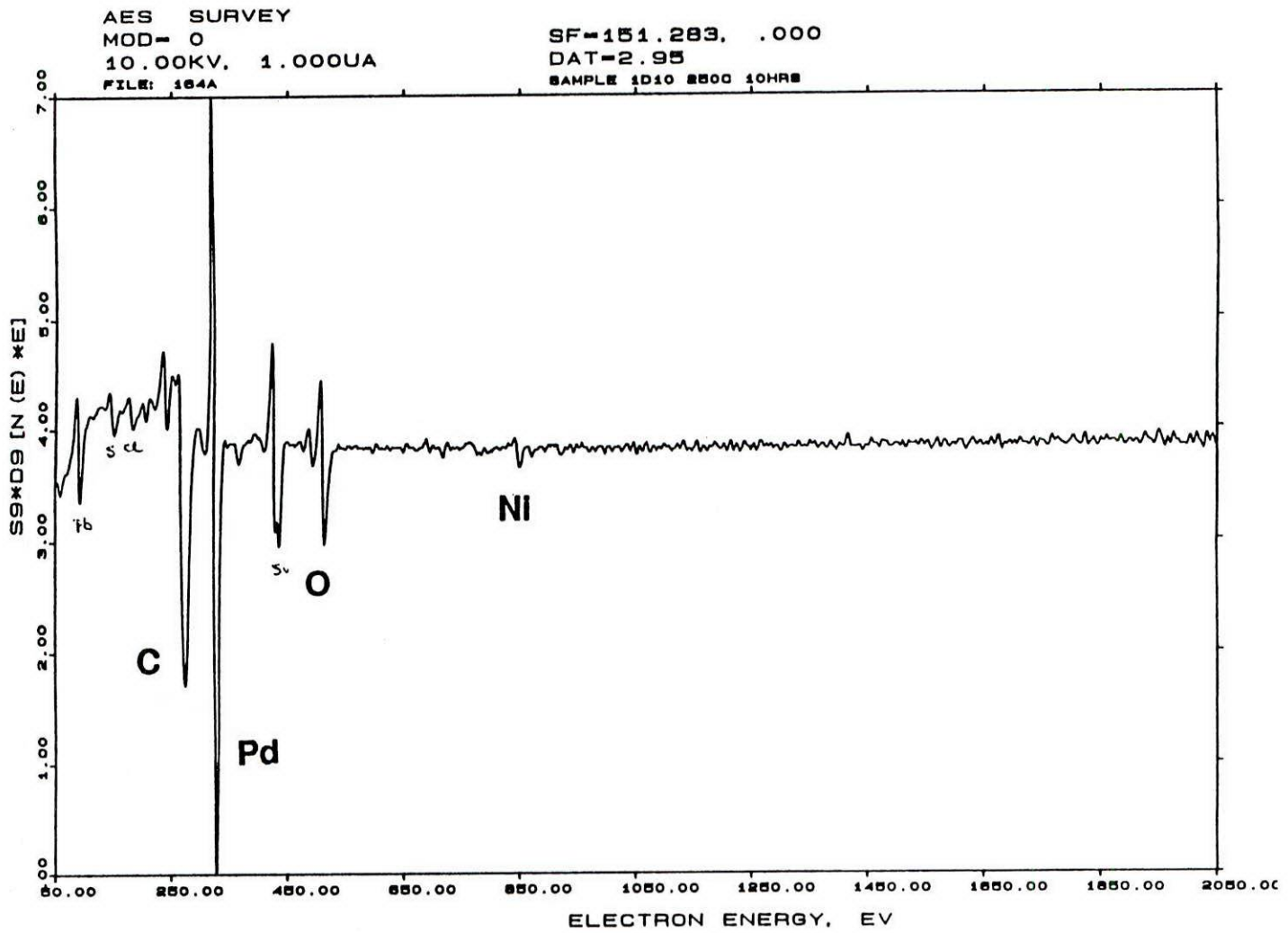
FILE: 171A
SF=245.613, .000
DAT=2.95
SAMPLE 5H 2500
S9*D9 [N (E) *E]
ELECTRON ENERGY, EV
C
Pd
O

Figure 11A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SF=151.283, .000
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S9*D9 [N (E) *E]
7.00
6.00
5.00
4.00
3.00
2.00
1.00
.00
C
Pd
O
Ni
50.00
250.00
450.00
650.00
850.00
1050.00
1250.00
1450.00
1650.00
1850.00
2050.00
ELECTRON ENERGY, EV

Figure 11B

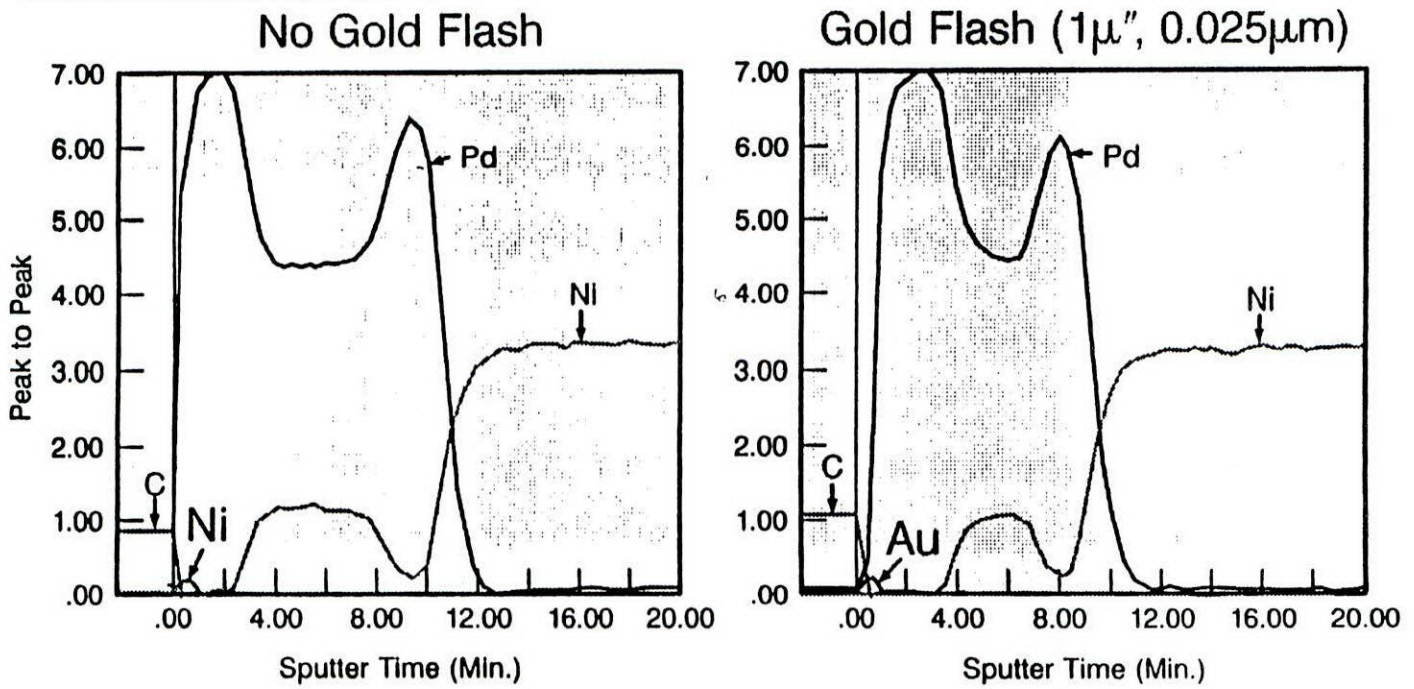
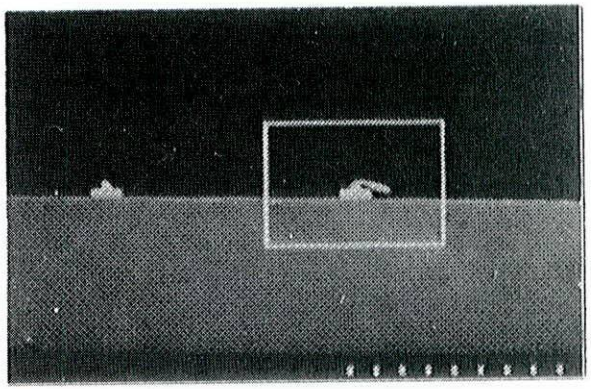
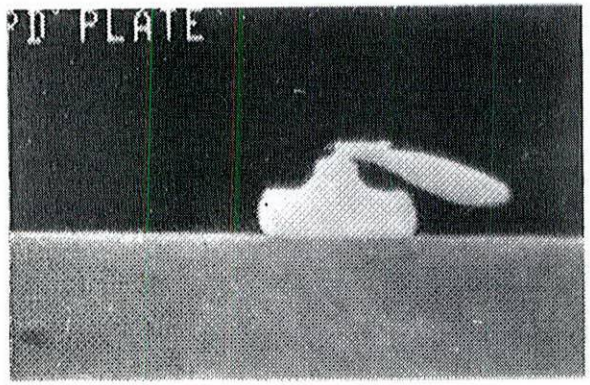

No Gold Flash
Gold Flash (1μ", 0.025μm)
Peak to Peak
7.00
6.00
5.00
4.00
3.00
2.00
1.00
.00
Pd
Ni
C
Ni
Au
.00
4.00
8.00
12.00
16.00
20.00
Sputter Time (Min.)

Figure 12

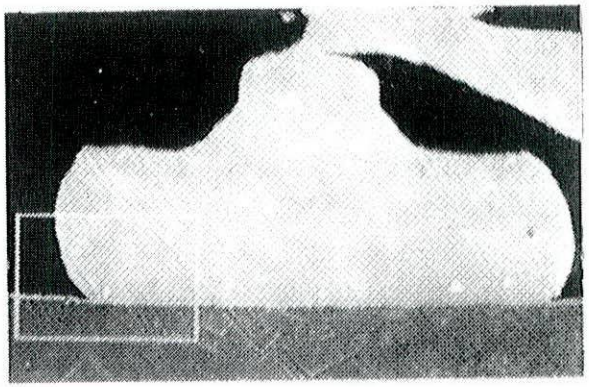
Cross Section of Ball Bond



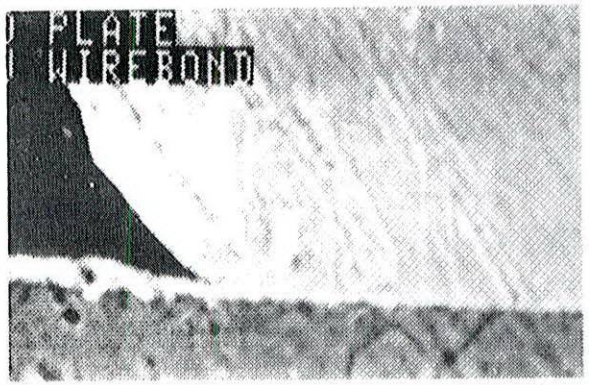
30 x



150 x



500 x

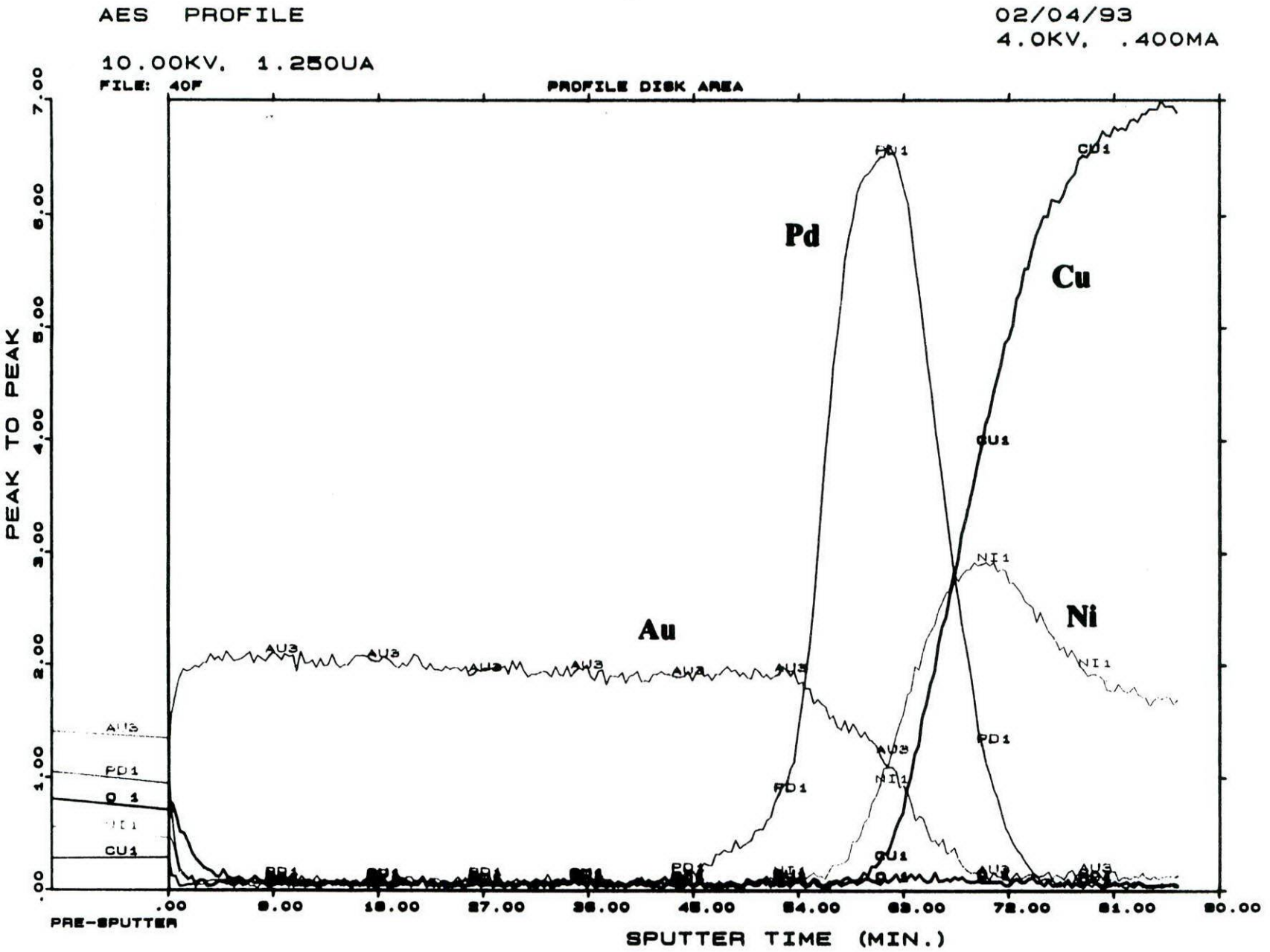


2500 x

93BLM19P.10

Figure 13

Figure 14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4.0KV, .400MA
PROFILE DISK AREA
PEAK TO PEAK
SPUTTER TIME (MIN.)
PRE-SPUTTER
Pd
Cu
Au
Ni
AU3
PD1
CU1
NI1
.00
9.00
18.00
27.00
36.00
45.00
54.00
63.00
72.00
81.00
90.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00

Paper Not Available In Time For Publication

Solderability—Non-Destructive Test, Quantitative, Evaluation and Predictability of Solderability of Electronic Devices

Michael Pavlov, Dr. Gene Chalyt, Dr. Peter Bratin and Rita Gluzman,
ECI Technology, East Rutherford, NJ

New solderability testing methods on the Sequential Electrochemical Reduction Analysis (SERA) technique will be presented. The basic principles of the method will be discussed. Experimental data for both plated-through holes and pads will be interpreted. Factors affecting the solderability of the plated wiring boards will be discussed, as well as the correlation between the experimental curve and the nature and quantity of oxides on the surface of the boards.

For copies of this paper please contact:

Michael Pavlov
ECI Technology
1 Madison Street
East Rutherford, NJ 07073
201/773-8686
FAX: 201/773-8797

Paper Not Available In Time For Publication

The Performance Characteristics of EN Films for Electronic Applications

Mark H. Suplicki and Dr. Alan J. Ruffini,
Fidelity Chemical Products Corp., Newark, NJ

Electroless nickel films have been widely accepted for protection against corrosion and wear. Their use, however, as functional engineering materials in the electronics industry is relatively new. The unique deposit properties of the various electroless nickel coatings available require careful consideration when selecting the appropriate one for an electronic application. Variables such as solderability, hardness, conductivity, wear, lubricity, corrosion inhibition and intrinsic stress of the deposit will be discussed relative to optimum performance characteristics.

For copies of this paper please contact:

Mark Suplicki
Fidelity Chemical Products
470 Frelinghuysen Ave.
Newark, NJ 07114
201/242-4110
FAX: 201/242-5796

A Novel Palladium Stripping Solution - Its Performance and Maintenance

H.K. Straschil
J.J. Maisano
I.V. Kadija
F. Humiec
J.A. Abys

AT&T Bell Laboratories
600 Mountain Avenue
Murray Hill, NJ 07974

ABSTRACT

Palladium finishes have become widely established in electronic and decorative applications. However, a reliable stripping solution for rework and metal recovery has not been commercially available. We have developed a three-component system which provides satisfactory and economical processing of palladium, gold-flash palladium or palladium-nickel finishes. The system is exceptionally selective for palladium and palladium-nickel vs copper. Recovery of the precious metal from the solution is relatively simple, using an electrolytic process. We present formulation data, etch rates, performance, maintenance, metal recovery, and analytical procedures associated with the process.

Introduction

In the fabrication of electronic devices and in the decorative industry, palladium and its alloys are often used to replace gold[1,2,3,4,5,6]; they are sometimes finished with a thin overlayer of gold. Palladium and its alloys, notably with nickel or cobalt, afford corrosion protection and superior wear, combined with excellent electrical properties[7,8,9,10,11]. Palladium is also useful for providing a barrier against diffusion, e.g. between gold and nickel. It is economically favorable because it costs significantly less than gold. But even though the metal cost is reduced, a reliable palladium and palladium alloy stripping process is highly desirable for two reasons: It will permit the recovery of precious metal from discarded or worn-out parts, and at the same time also the rework of expensive parts after faulty plating. Especially in the latter case, it is important that the substrate be fully preserved. Therefore, a stripping method is desirable that functions with a minimum of substrate corrosion, that is, with pronounced selectivity for the precious metal.

While the stripping of gold from base metal substrates is in common use, the stripping of palladium and its alloys is much less known. One reason may be that the processes which are in present use lack selectivity. The want for a generally accepted palladium stripping method presents an obstacle for the otherwise commercially attractive conversion from gold to palladium and its alloys.

The stripping solution[12] described in the following is selective for palladium with regard to nickel, copper, copper bronzes, and steel substrates. The proposed process easily dissolves any pure or hard gold finish on top of palladium or palladium alloy. If palladium is plated over nickel, both layers can be dissolved in the same solution, but nickel is removed more slowly than palladium by a factor of ten or more. In that case it may be preferable to strip the nickel separately. On the other hand, the large difference in stripping rates permits selective stripping of palladium from nickel wherever desired. The corrosion of copper or copper bronzes is so much inhibited that a clean removal of palladium or palladium alloy can be achieved virtually without loss of substrate material or change of shape. This leaves expensive work pieces re-usable after palladium stripping.

Although many procedures can be used, an electrolytic method has been found preferable for safe and efficient precious metal recovery from the spent solution.

Prior Developments

Palladium Stripping and Related Information

Both electrochemical and chemical stripping methods have been proposed for palladium removal. E. B. Saubestre[13] proposes anodic stripping in a solution of NaCl and $NaNO_2$ at pH 4-5, 2-4 V; similar methods are also given by N. Hall et al[14]. It appears, however, that most of the electroplaters prefer chemical methods, in which an oxidizing chemical is used to dissolve the metal. T. A. Shankoff[15] proposes the use of dichromate ion as the oxidizing agent and chloride

ion as the complexing agent. Concentrated sulfuric acid has been suggested as a solvent for chemical stripping with nitric acid added as an oxidant, and also as an electrolyte for anodic stripping.

Another group of oxidants in use for precious metal stripping includes "nitro-substituted aromatic compounds", which have been suggested for "dissolving metals of the class consisting of nickel, copper, cadmium, silver, zinc, and gold by chemical action alone etc." in 1949 by R. Springer and W. R. Meyer[16] . This class of oxidants is used in combination with ammonium and alkali cyanides, which, as the inventors point out, are rendered unstable or even explosive by inorganic oxidizing agents of high oxidizing potentials. J. J. Grunwald[17] proposes the use of complex tetracyanide ions, such as $[Zn(CN)_4]^{2-}$, in combination with nitro-substituted aromatics, for gold stripping with the aim to diminish the corrosion of the substrate metal, especially copper. L. R. Fountain[18] uses a solution of alkali cyanide and a nitro-substituted aromatic compound for removing a gold alloy braze having palladium or niobium in combination therewith. H. M. Solidum and R. C. Zobbi[19] recommend the use of a dry powder containing cyanides and nitrobenzene derivatives with an auxiliary agent for making up and replenishing stripping solutions for gold and silver (palladium is not mentioned). Nitrobenzoate derivatives as oxidant and alkali cyanide as ligand are also used in a palladium stripping solution proposed by A. Fletcher and W. L. Moriarty[20] (1985).

Corrosion Problems With Copper Substrates

Inhibitors are commonly in use for the selective stripping of nickel or gold from copper substrates. M. Weisberg and F. P. Butler[21] claim a long list of compounds of sulfur in the -2 oxidation state in combination with a nitro-substituted organic compound and an amine for removing metals, especially nickel, from bases, especially copper and its alloys. E. H. Too and D. R. Marx[22] propose the addition of an organo-mercapto compound for selectively stripping gold from a metal substrate, especially copper metal, in a solution also containing a ring-substituted nitrobenzoic acid compound, a bath-soluble cyanide, and a lead or bismuth compound. C. H. Huang[23] describes the function of benzotriazole as a corrosion inhibitor for copper in a sodium chloride solution.

However, none of these corrosion inhibitors has as yet been applied for stripping palladium from copper. We tested solutions as proposed by Too and Marx[22] for selective gold stripping, for the removal of palladium from copper substrates. The attack rates were 0.18-0.30 µm/min for palladium, and 4.5-4.8 µm/min for copper, at 40-43°C. These initial findings tend to imply that conventional copper inhibitors may be ineffective in palladium stripping.

Process Description

Palladium Stripping With Copper Passivation

While corrosion inhibitors for copper do not appear to be useful by themselves, we found that a suitable combination of additives with synergistic action can provide a good palladium stripping rate as well as very satisfactory copper protection. The resulting stripper satisfies all practical

demands with regard to speed of operation, selectivity, safety, and metal recovery. It is freshly prepared prior to each use from two liquid concentrates and a salt mixture containing cyanide.

Preparation and Operation of the Stripping Solution

To prepare one liter stripping solution, the following steps are performed in order:

1 g salt mixture are dissolved in 600 ml water,

2 add 250 ml/l "Concentrate I" (Oxidant) and mix well,

3 add 10 ml/l "Concentrate II" (Inhibitor) and mix well.

Upon addition of Concentrate II the solution becomes turbid and an insignificant amount of precipitate may form, which is not removed. Just before use, the solution is heated to 40-50°C; temperatures above 55°C should be avoided since solution decomposition with loss of stripping activity may set in. Before immersion, the parts are cleaned thoroughly and rinsed. Good agitation during stripping is essential. After stripping, the parts are rinsed repeatedly; water from the first rinse can be used to prepare more fresh stripper, or added to the spent stripping solution for eventual metal recovery. Cathodic cleaning of the parts is recommended before re-plating.

Solution Replenishment

The stripping rate drops during use due to various factors, such as depletion of oxidant and complexing agent. It can be largely restored through replenishment of the solution, as will be shown below. Replenishing can be based on the amount of metal stripped, or on the drop in stripping rate. Replenishing is performed after 10 g/l palladium have been stripped, or when the stripping rate has dropped to two thirds of the original rate. Concentrates I and II and the salt mixture are added in amounts proportional to the initial formulation, for instance: 100 ml/l of Concentrate I, 4 ml/l of Concentrate II, and 60 g/l salt mixture, after stripping of 10 g Pd per liter solution. The solution is replenished repeatedly, depending on factors like operating temperature, age of solution, and base metal concentrations in the solution. When replenishment does no longer improve the stripping rate, the solution is considered spent.

Performance Tests

Individual Metal Stripping Rates

Selectivity for palladium in the proposed stripping solution was evaluated by testing etch rates for individual metals, as well as for multilayer finishes. For the individual metal tests, electroplated palladium, electroplated nickel, rolled copper foil, and unplated Alloy 725 were used. The workpieces were immersed in the stripper for five subsequent periods of 30 seconds each, at 42°C and moderate agitation. After each interval, the pieces were rinsed, dried, weighed, and immediately re-immersed for the next interval. The etch rates are expressed in micrometers per minute and plotted at the end of each interval in Figure 1. The plot shows that the base metals

were much more slowly etched than palladium; furthermore, it shows that the palladium etch rate stayed constant over the whole 2.5 minute period, during which a total of 1.65µm (65 microinches) was stripped, while the nickel etch rate increased, and the copper etch rate decreased over the same period. Palladium-nickel alloy (20% Ni) behaves like palladium. Initial and final etch rates were:

Metal	Initial Rate (µm/min)	Rate After 2.5 min. (µm/min)
Pd	0.67	0.67
Ni	0.075	0.35
Cu	0.109	0.019
Alloy 725	0.094	0.043

Applying these rate figures to a multilayer finish, where palladium is plated over nickel on a copper substrate, the following can be expected: If only palladium stripping is intended with the nickel underplate to be left intact, the low initial nickel etch rate makes for clean palladium removal without much loss of nickel. (Quick testing procedures for monitoring the stripping progress are given below.) On the other hand, if also the nickel layer is to be removed, the autocatalytic acceleration of nickel etching, as expressed in the above numbers, is favorable; moreover, the nickel stripping rate can be increased by adding nickel salt to the stripper. Finally, the slight initial corrosion of the copper or copper-based substrate will be diminished further with time.

Stripping of a Multilayer Finished Workpiece

The above considerations were demonstrated on a multilayer finished leadframe strip with 50 - 100 microinches nickel and 5 - 10 microinches palladium plated over Alloy 725. The results of this experiment are shown in the table below:

Metal Layer Being Stripped	Immersion Time	Weight Loss	Comments
Pd	0.5 min.	6.8 mg	Palladium layer totally removed
Ni	1.5 min.	11.5 mg	Nickel layer totally removed
Alloy 725	> 2.5 min.	≤ 0.5 mg	No visible attack on leadframe pattern

This experiment shows how important a high degree of selectivity is in the stripping of pieces with coatings of uneven thickness, because in such cases two layers of metal may be exposed

simultaneously for relatively long periods. In the above instance, one might also have considered switching to a substrate-protecting nickel stripper after all palladium had been removed. No general preferences can be given here, for each application has to be judged by its own merit.

Stability of the Stripper Solution

The made-up stripper solution is fairly stable at room temperature, although it is recommended to mix it shortly before use. We tested the palladium stripping rate in a solution kept at 42°C, after 1, 2, 4, and 8 hours. The results are shown in Figure 2. The graph shows a small dip in the etch rate during the first hour, with subsequent recovery. The nature of the changes in the etch rate and in the cyanide content with time are under investigation; it is surmised that cyanide reacts slowly with the organic oxidant.

Aging of the Stripping Solution with Use

Due to the variety of stripped materials and stripping operations, the aging behavior of the stripping solution cannot be exactly predicted. In an attempt to obtain a useful simulation of actual operating conditions, incremental amounts of palladium metal powder were added to the stripping solution and permitted to react completely before the etch rate was determined. The results, presented in Figure 3 show a decline in the etch rate with the depletion of the reagents, caused by complexing of free cyanide with palladium, and reduction of the oxidant.

A connection between the etch rate of palladium and the availability of cyanide in the solution can be seen in the same Fig. 3, where also the "free" cyanide content of the solution (as determined by titration with silver nitrate) has been plotted against the amount of palladium metal dissolved; the curves for the etch rate and free cyanide run almost parallel to each other.

Effect of Replenishing

Etch rates approximating the initial conditions can be attained by replenishment of the components even if the stripping solution is used infrequently. A "spent" stripping solution containing 15 g/l palladium and 54 g/l free cyanide salt had an etch rate of 0.32 µm/min after being used intermittently for 13 days. The solution was replenished twice during this period, with 70 g/l salt mixture, 100 ml/l Concentrate I, and 5 ml Concentrate II; after each replenishment, the etch rate was found to be 0.65 µm/min, and 0.6 µm/min, respectively, recoveries of 80% of the initial rate. Similar effects are expected in larger-scale operation, although the results may vary. The results are presented graphically in Figure 4.

Metal Recovery

Choice of Recovery Methods

Most of the precious metal in the spent stripping solution (including gold) is present in the form of its cyanide complex(es). The simplest way to recover palladium from spent stripping solutions is to return them to the manufacturer for refining. However, existing regulations for the shipment of "hazardous waste" may render that option financially unattractive; in those cases, it is preferable to electrolytically recover the precious metal, which is more easily transported. The decision to ship the solutions to the refinery as such, or to send the recovered precious metal for refining, depends on a variety of economic and engineering factors which have to be weighed, such as:

1. Proximity of a precious metals refinery.
2. Volume and precious metal concentration of stripping sloution to be refined.
3. Cost of state and local government hazardous waste transportation permits.
4. Availability of chemical or electrochemical process equipment, air-borne emission exhaust system and wastewater treatment facility.

In-plant recovery of palladium can principally be effected by chemical or electrochemical methods; possibly also by a combination of them. Due to the extreme stability of the palladium cyanide complex, cyanide ions have to be removed or destroyed in all cases. Operation of the electrochemical equipment is possible in such a way that the cyanide in the solution is destroyed at the same time - a benefit for effluent management. Chemical methods utilize oxidants, for instance hypochlorite, for cyanide destruction; the electrochemical method proposed by the authors for the palladium stripper in hand takes advantage of its specific chemical properties, in combination with anodic and thermal oxidation processes.

Proposed Electrochemical Recovery of Palladium

Description of Process

Several methods were investigated to destroy cyanide and recover palladium from spent palladium stripper solution. Processing variables included pH, temperature, current density and the presence or absence of chloride and reducing agents (For reduction of the organic oxidant in the stripper concentrate). The palladium concentration was reduced from 15 grams per liter to approximately 1 gram per liter, and undetectable amounts of cyanide. Figure 5 the change in palladium and cyanide concentration as a function of amp hours per liter for a typical bench-scale electrolytic recovery experiment. The concentration of palladium was determined by atomic absorption spectrometry using the procedure described below. The free cyanide was monitored by titration with silver nitrate using potassium iodide as the indicator in a highly alkaline of ammonical buffer[24].This procedure, described below, is not EPA approved for use on the analysis of wastewater for municipal sanitary drain discharge, but served only as a process monitor during

this development effort. Cyanide destruction must be verified by an EPA approved procedure by a certified laboratory before solutions are deemed "cyanide-free".

Metal Recovery Experiments - Conclusions and Comments

The addition agents seemed to have no positive effect on the process. The solution was quite colored before the recovery experiments but became colorless when the majority of the cyanide was destroyed and metal plated out. The loss of color suggests that all organometallic compounds, nickel, copper and other metallic impurities, have been removed or destroyed. As expected nickel and copper were preferrentially removed as the cyanide concentration dropped, followed by plating of the bulk of the palladium. The cathode deposit became quite hot upon drying and was allowed to cool for several hours in the hood prior to further purification.

Experiments currently in progress in our laboratory suggest that commercially available electrowinning equipment could be utilized to accomplish this task.

Description of Analytical and Process Control Methods

Process Monitoring

When palladium or palladium-nickel is stripped from a nickel undercoating, the appearances of both layers are very similar, which makes it difficult to monitor the progress of stripping visually. The following test has been found useful:

1. Prepare 1 liter Metex® Nickel Stripper BR solution as follows:
2. Add 30 ml concentrated H_2SO_4 to 900 ml water,
3. heat to approximately 45°C,
4. add with agitation 120 g dry Metex® Nickel Stripper BR and dissolve,
5. heat solution to 65°C.
6. Dip a test piece into the heated solution for 1 minute with agitation.
7. Remove piece and rinse with water. Nickel surfaces appear dark gray to black, while palladium and palladium-nickel surfaces remain unchanged.
8. The dark coating on nickel can be removed with HCl (1:1), and the test piece reused.

Note: Metex® is a registered trademark of MacDermid Inc.

As an alternative, this simple spot test is recommended:

1. Rinse piece well with water and dry.
2. Place one drop of concentrated nitric acid on the test site.
3. If nickel is exposed in that spot, the drop turns green immediately. If palladium is on the surface, the drop turns yellow to amber slowly.

Determination of Palladium by Atomic Absorption

The solution is diluted with DI water to the 5 to 10 ppm level and compared with standards over the same range. Analytical recovery was 100 percent, precluding the need for acid digestion.

Analysis of Free Cyanide Titration Method

A 10 ml aliqout of stripper solution is placed in a 250 ml Erlenmeyer flask. Add 100 ml deionized water, 10 ml 30 % NH_4OH, and 2 ml 20% KI. Titrate with 0.1N $AgNO_3$ to a faint yellow turbid endpoint. For used samples, which can be dark brown in color, shining a flashlight beam through the solution aids in determining the endpoint turbidity. The accuracy in samples containing low levels of KCN can be improved using 0.01N $AgNO_3$, but the end-point is more difficult to observe in deeply colored solutions. A blank solution containing 50 g/l Na_2CO_3 and 250 ml/l stripper concentrate I and 10 ml/l of stripper concentrate II (without KCN) was titrated with 0.1N $AgNO_3$. The endpoint was observed after only 0.15 ml titrant. When 0.01N $AgNO_3$ was used, the endpoint was reached after 1.10 ml was added. Nickel and copper in the used stripper solution are also complexed by cyanide. This cyanide is not amenable to titration. The calculation for determining the concentration of free cyanide in the solution is shown below:

$$\frac{(\text{ml } AgNO_3 - \text{ml blank})\,(\text{N } AgNO_3)(2)(65.11)}{\text{ml Sample}} = \text{g/l free titratable KCN}$$

A fresh plating bath containing 55 g/l KCN was determined to have 53.6 g/l by the above titration method. After addition of 2.5 g/l Ni as $NiSO_4.6H_2O$ to the fresh stripping solution, the so;ution was determined to have 44.5 g/l free KCN. Assuming that the complex $Ni(CN)_4$ is formed, 11.0 g/l CN as KCN would not be amenable to titration. Thus the value determined by titration agrees with the expected value of 55 g/l when complexation with nickel is taken into consideration. Interference by palladium was also verified. Addition of 10 g/l of palladium as its tetrammine complex to an unused stripper bath yield a free KCN content of 29.4 g/l. Assuming 4 equivalents of cyanide is complexed by palladium, the "total cyanide" value by titration is 53.9 g/l, which agrees within experimental error with the 55 g/l actual KCN content.

Summary

A reliable stripping solution for rework and metal recovery has been developed which is comprised of a three-component system. This formulation provides satisfactory and economical processing of palladium, gold-flash palladium or palladium-nickel finishes. The system has been demonstrated to be exceptionally selective for palladium and palladium-nickel vs copper. The electrolytic recovery of the precious metal using standard equipment is also described. The relationships between the etch rate, dissolved metal and free cyanide concentration were also established, along with analytical methodologies useful for process control.

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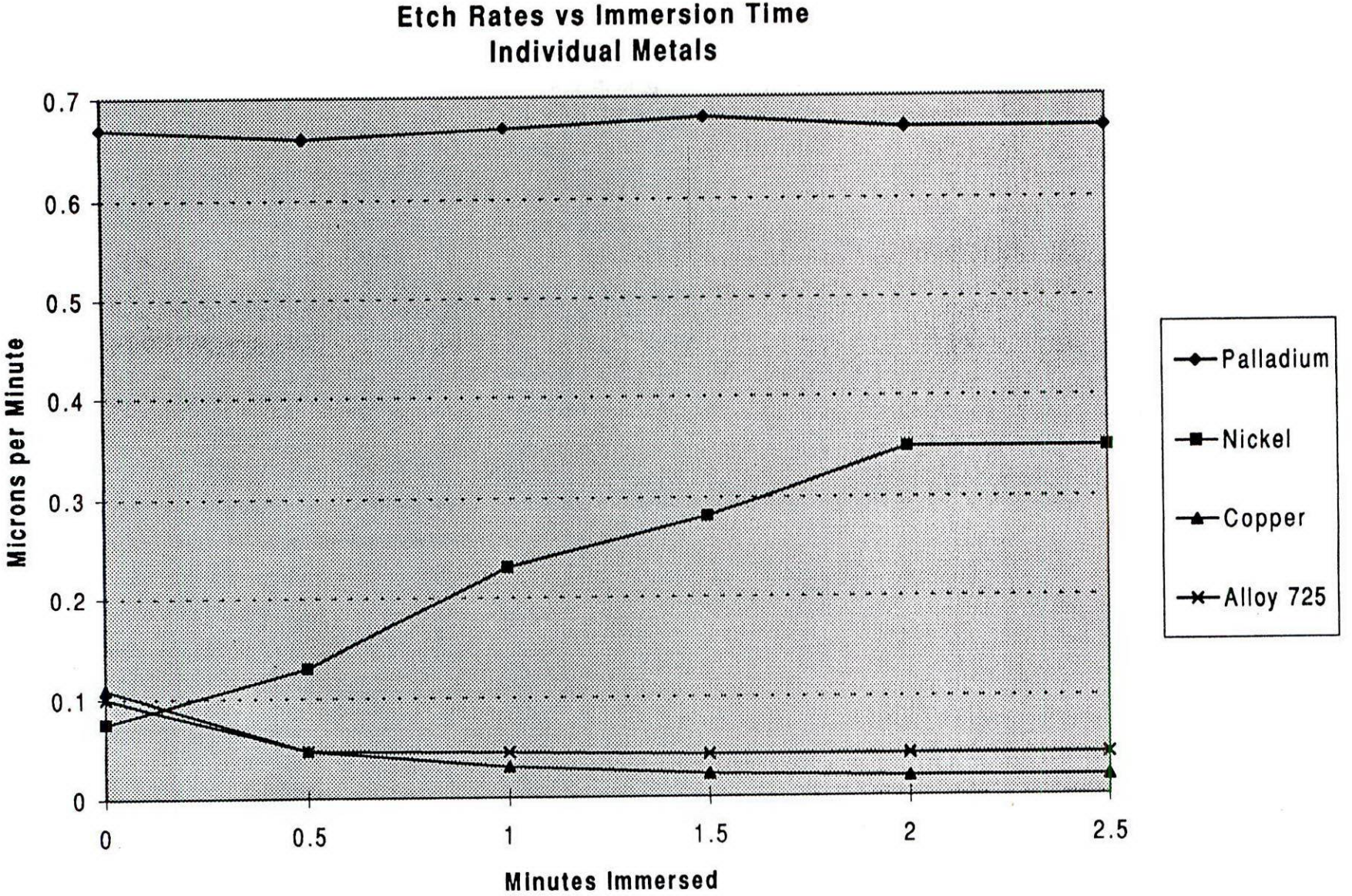
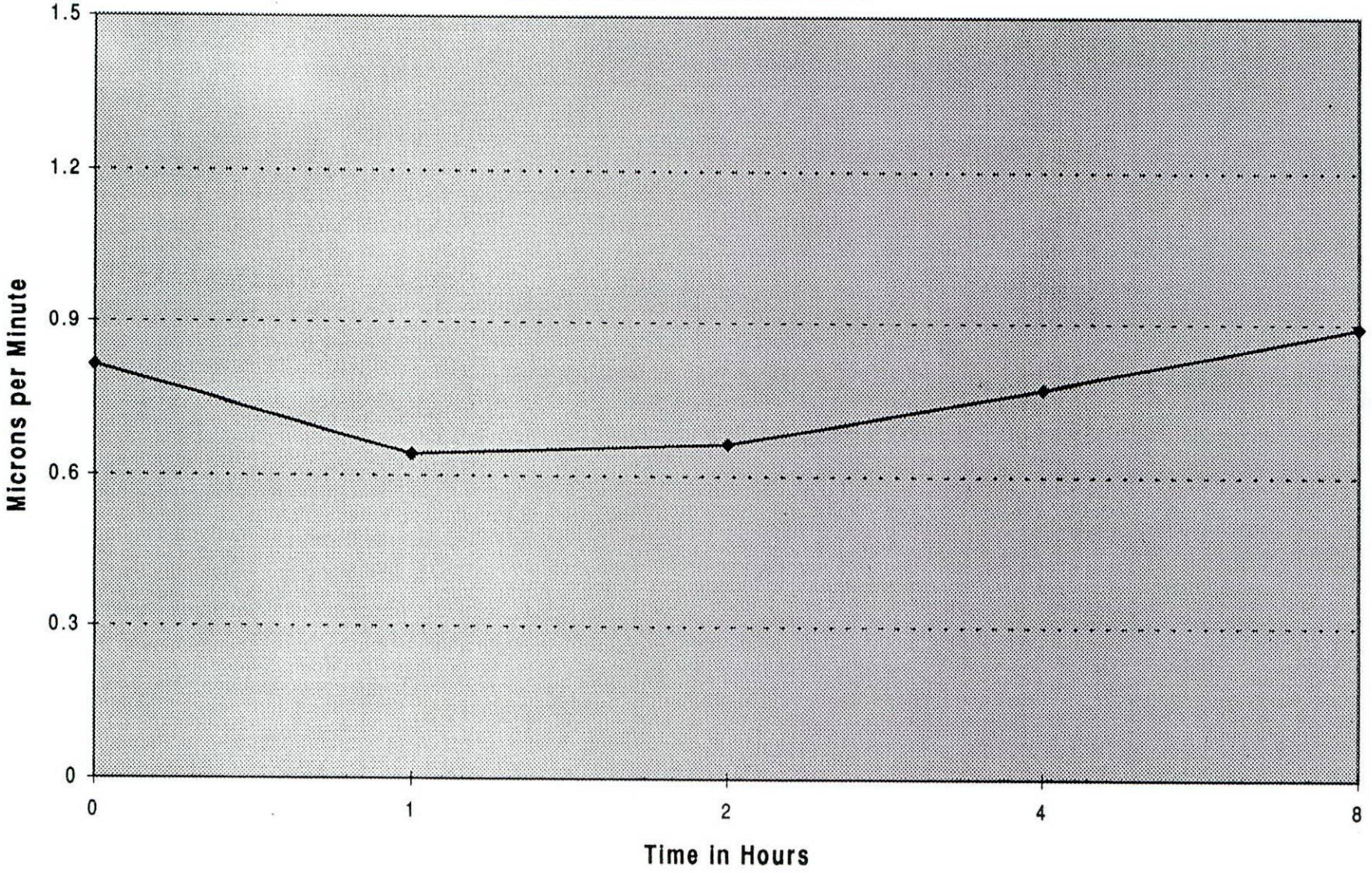
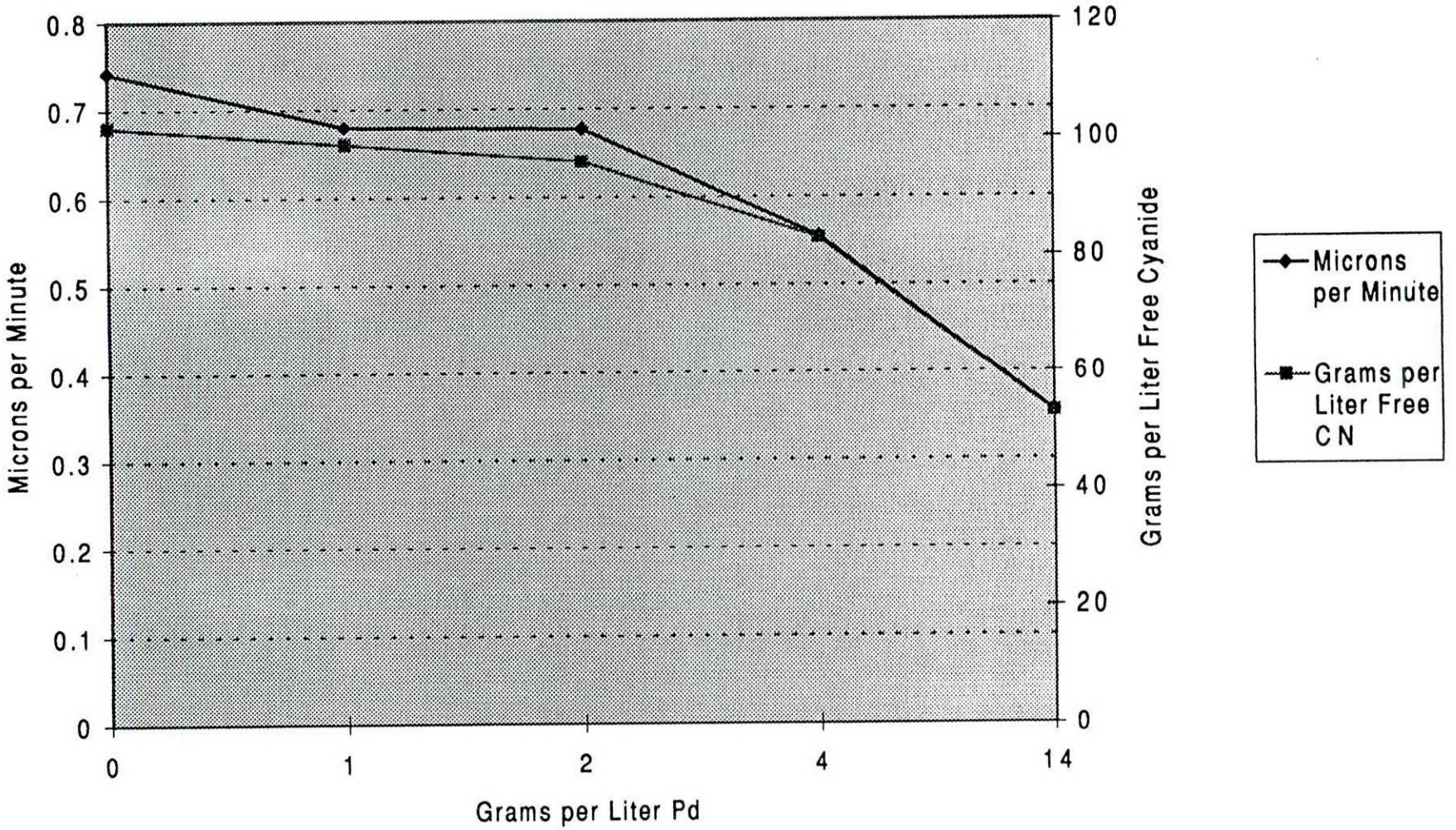

Etch Rates vs Immersion Time
Individual Metals
Microns per Minute
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.5
1
1.5
2
2.5
Minutes Immersed
Palladium
Nickel
Copper
Alloy 725

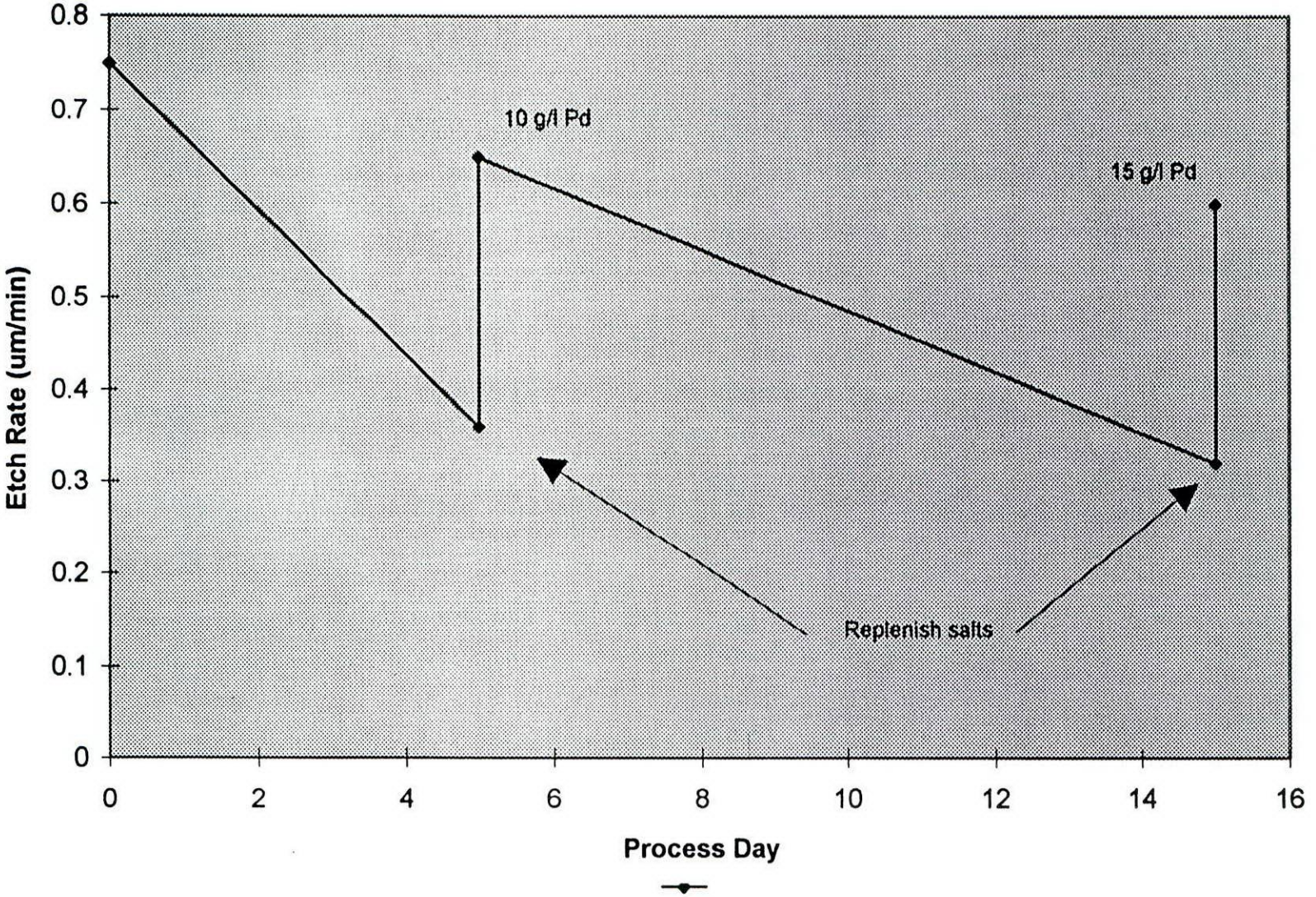
Stability of Stripping Solution -- Etch Rate vs Shelf-Life



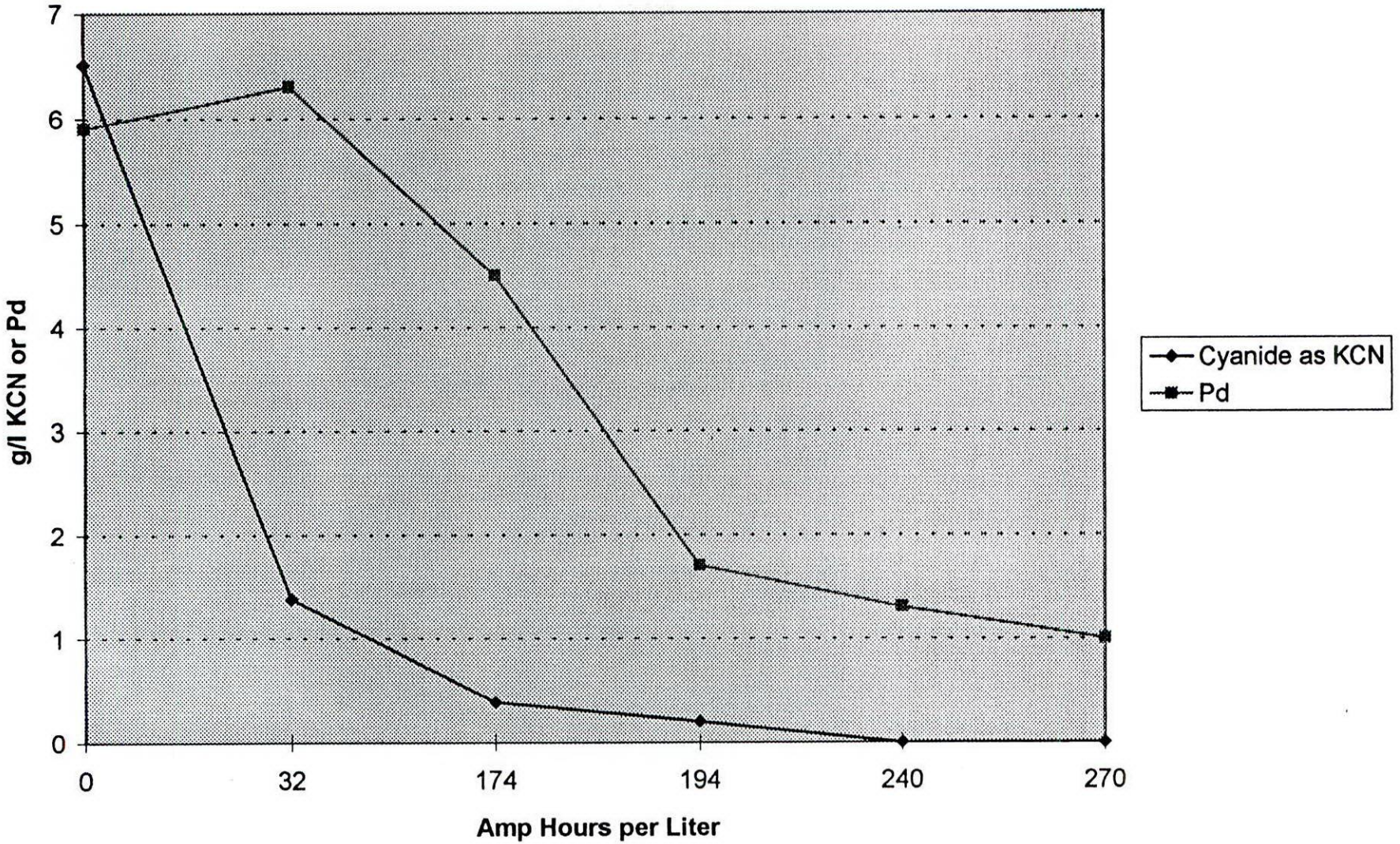
Aging of Stripping Solution with Use
Etch Rate vs Pd Concentration



Effect of Salt Replenishment on Etch Rate



Electrochemical Recovery of Palladium and Destruction of Cyanide



Removal of Metals from Metal Finishing Waste Water Using a Granular, Magnesium-based Adsorbent*

by Matthew D. Walter, Joseph T. Witkowski, and Aileen Reyes

This paper details a granular, Magnesium-based Adsorbent which has been used to remove various metals from surface finishing waste water streams. The metals treated in this study include copper, nickel, and zinc. Effluent concentrations of the treated metals are typically less than 0.5 mg/L.

Environmental regulations have become increasingly severe regarding the types and amounts of pollutants that may be released into the environment. In particular, metal finishers are commonly restricted to the metal concentrations and pH of waste water that may be discharged into natural waterways, municipal sewers, etc. Various treatments have been utilized to remove metal ions from water while rendering the pH suitable for discharge. The most widely used method for treating waste water streams is chemical precipitation. Using this method, the pH of the stream is raised with an alkali (e. g. $Mg(OH)_2$, NaOH, Lime, etc.) until the metals precipitate as the insoluble hydroxides. Often, chemical precipitation is not completely successful in reducing metal concentrations in the waste water stream to comply with discharge regulations. Additional treatment techniques such as reverse osmosis, ion exchange, and activated carbon are often necessary to reduce the metal concentration sufficiently for discharge. The adsorbent described herein is a novel Magnesium-based adsorbent from Martin Marietta Magnesia Specialties, Inc. that has been shown to remove heavy metal ions from mildly acidic to mildly alkaline surface finishing waste water while simultaneously neutralizing the acidic components of the waste. Three case studies are presented detailing the performance of this granular medium as well as information about how this granular, Magnesium-based product removes metals from solution.

Mechanism

The medium operates by the principal of ion exchange, where an Mg^{++} ion exchanges with a metal ion (M^{+x}) as shown in the following equation:

$$Mg(OH)_{2_{(adsorbent)}} + M_{aq}^{+2} \rightleftharpoons M(OH)_{2_{(adsorbent)}} + Mg^{+2}$$

Equation (1)

Though the metal is shown to be divalent in this equation for simplicity, it may be of any valence provided the ion exists as a cation in solution. Anionic species (e. g. $Cr_2O_7^{-2}$, Cu-EDTA, etc.) cannot exchange for the magnesium in the medium, and are, therefore, not adsorbable by this material.

A general tendency exists for the solubility of the hydroxides of successfully treated metals to be lower than that of $Mg(OH)_2$, as shown in Table 1.

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* **FloMag™ G is a product of Martin Marietta Magnesia Specialties, Inc., 2323 Eastern Blvd., Baltimore, MD 21220-0470, (800)-648-7400.**

In order for the medium to effectively remove target metals from solution a minimum empty bed contact time of eight minutes is recommended. Laboratory tests have shown that effluent metal concentrations can be lowered to 0.010 mg/L or less with sufficient contact time. Shorter contact times may result in insufficient removal of the target metal. The medium is regenerable with a dilute acid backwash. In addition, periodic backwashing with air and water is recommended.

Table 1: Solubility Data for Target Treatment Metals

Metal Hydroxide	Ksp	Solubility, mole/L	Temperature	Ref.
$Cu(OH)_2$	2.2×10^{-20}	2.8×10^{-7}	Room Temp.	1
$Cd(OH)_2$	1.7×10^{-15}	1.2×10^{-5}	25 °C	2
$Cr(OH)_3$	1.7×10^{-24}	1.2×10^{-8}	Room Temp.	3
$Ni(OH)_2$	6.5×10^{-18}	1.9×10^{-6}	Room Temp.	4
$Zn(OH)_2$	1.66×10^{-16}	5.5×10^{-6}	25 °C	5
$Pb(OH)_2$	1.1×10^{-20}	2.2×10^{-7}	22 °C	6
$Mg(OH)_2$	1.1×10^{-11}	2.2×10^{-4}	18 °C	7

Case Studies

Case Study #1

The first case study involves an electronics component manufacturer with copper in the waste water stream. Chemical precipitation with both $Mg(OH)_2$ and NaOH was first used to both adjust pH and precipitate copper as $Cu(OH)_2$. An inclined plate clarifier removed most of the sludge, while a paper filter further clarified the waste stream. A schematic of the treatment system is shown in Figure 1. The Magnesium-based granular adsorbent was added to the system (as shown in Figure 1) to reduce soluble copper levels from ~1.5 mg/L after the primary treatment to below 1 mg/L for discharge. Figure 2 shows the performance of the granular adsorbent in removing copper from this waste water stream. The stream, at a flow rate of approximately 5 Gallons per Minute (~18.9 Liters/Min), entered the column containing 300 pounds (~136 kg) of the granular,

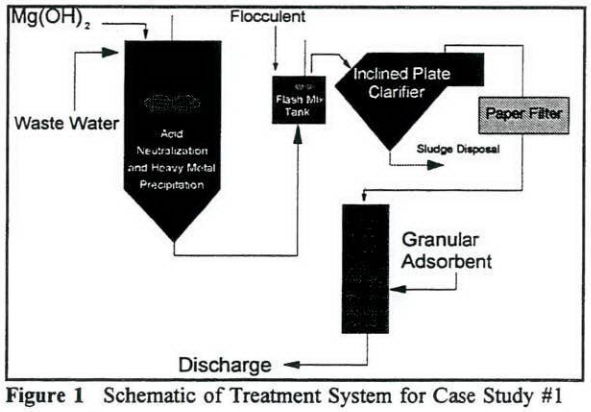

Figure 1 Schematic of Treatment System for Case Study #1

Magnesium-Based Adsorbent. This provided an empty bed contact time of approximately six minutes (as opposed to the recommended eight to ten minutes). All of the measurements showed the medium to substantially reduce the copper concentration in the effluent. For the most part, the effluent copper concentrations were 0.5 mg/L or less. One reading had a concentration of 1.36 thought to be the result of channeling in the bed.

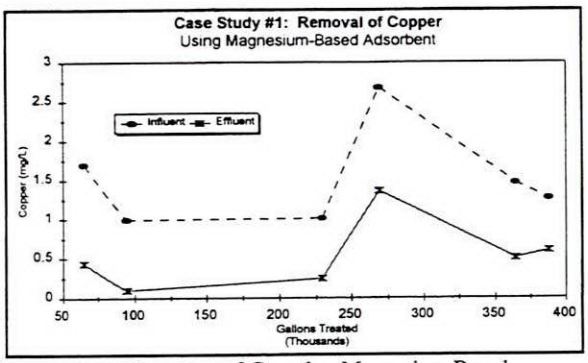

Figure 2 Performance of Granular, Magnesium-Based Adsorbent in Case Study #1.

Backwashing restored good copper adsorption in the subsequent measurements.

Case Study #2

The second case study involved a hardware plating shop treating a zinc-containing stream. In this application, primary treatments with NaOH to pH 10-11 had been unable to reduce the zinc concentration of the effluent to less than 5.75 mg/L on average, while the discharge limit was 2 mg/L. By incorporating the Granular, Magnesium-Based Adsorbent as a polishing filter, this company was able to reduce the target pH of the primary treatment to pH 8 while removing the residual zinc with the adsorbent. Specific influent data is not available but the monthly averages for the effluent are plotted in Figure 3. Even though the flow rate of 25 Gallons per Minute (94.6 Liters/Min) allowed only about three minutes empty bed contact time, the medium consistently reduced the zinc levels to well below the 2 mg/L discharge limit. The user regenerated the adsorbent approximately every one hundred days of operation, as shown in Figure 3, to restore the adsorption capacity of the medium.

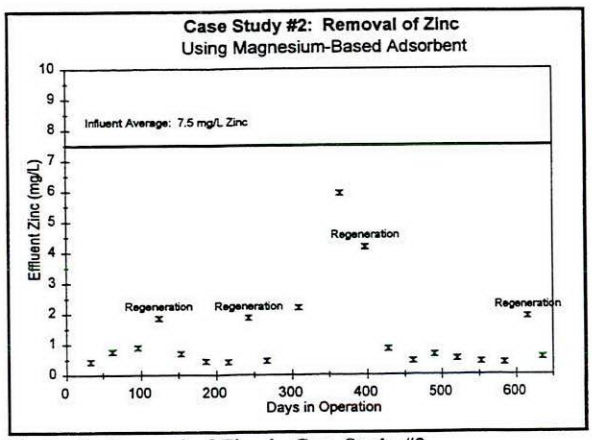

Figure 3 Removal of Zinc in Case Study #2

Case Study #3

The third case study involved a metal finisher with zinc, copper, and nickel in the waste water stream. Conventional chemical precipitation techniques using NaOH had been unable to consistently reduce the concentrations of the three target metals to below 1 mg/L. To reduce the metals in this 6 Gallons per Minute (22.7 Liters/Min) waste water stream, this plater added a column containing 300 pounds (136 kg) of the Granular, Magnesium-Based Adsorbent as a polishing filter. Even though the unit only has a 5.2 minute empty bed contact time, the company has not experienced a surge in any of the metal concentrations exceeding 0.98 mg/L. Figure 4 shows the metals content of the waste water stream

before the addition of the Granular, Magnesium-Based Adsorbent in March 1993, as well as the metals content of the stream after the addition of the polishing unit.

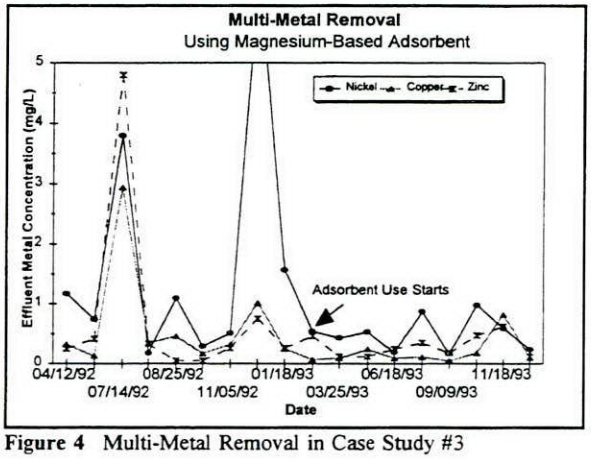

Figure 4 Multi-Metal Removal in Case Study #3

Conclusions

The Granular, Magnesium-Based Adsorbent is effective in removing many cationic metals from waste water streams. Laboratory testing, and small scale industrial trials have shown that metal concentrations of 0.01 mg/L or less may be achieved with this product when used properly. Though none of the case studies cited in this paper consistently achieved these levels, all consistently reduced the metal concentrations in the effluent to well below discharge limits. It is presumed that more appropriately sized units, providing the recommended eight to ten minute empty bed contact times, would result in even better performance.

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Paper Not Available In Time For Publication

Designing and Implementing a Medical Surveillance Program in the Electroplating and Surface Finishing Industry

Dr. Shirley A. Conibear, M.P.H., Carnow, Conibear & Associates, Ltd., Chicago, IL

OSHA requires medical examinations, including certain laboratory tests, when there is potential exposure to hazardous materials. Workers in the electroplating and surface finishing industry are at risk for exposure to hazardous materials. A well-designed medical program, however, can minimize injury and Workmen's Compensation claims, avoid inappropriate placement of workers while complying with the American Disability Act (ADA), and serve to provide peace of mind to both workers and management. This presentation will take a step-by-step approach, showing the listener how to assess his need for medical exams and testing, how to select tests and procedures, how to get them done, the kind of information and benefits that can be expected from a medical surveillance program and what the cost may be. Exposure to a variety of classes of materials will be considered, including heavy metals, organic solvents, heat stress and noise, as well as the stress involved in the use of various respirators.

For copies of this paper please contact:

Dr. Shirley Conibear
Carnow, Conibear & Associates
333 West Wacker Drive
Suite 1400
Chicago, IL 60606
312/782-4486
FAX: 312/782-5145

INTEGRATION OF MULTIPLE WASTEWATER MANAGEMENT TECHNOLOGIES IN A METAL FINISHING SHOP

Ali Ahmadi
Senior Marketing Engineer

Kenneth W. Linehan
Marketing Engineer

WHEELABRATOR/MEMTEK
28 Cook Street
Billerica, MA 01821

Abstract

A case study of a midwest plating shop which integrates multiple state-of-the-art waste recovery technologies to achieve its long-term compliance and cost minimization objectives.

Chemical and hydraulic characteristics of each individual waste stream were studied. Various compatible treatment and recovery technologies were evaluated which led to the implementation of combined ion exchange, microfiltration and reverse osmosis system design.

Application of the integrated techniques result in 90% water recycle. The economical assessment and design approach for the installed system will be presented.

Introduction

The plating company discussed in this case study is a midsized company located in Minnesota. Metal finishes performed by this company include zinc, copper, nickel, chrome and electroless nickel. Plating is done by both rack and barrel methods. Total rinses amount to 70 gpm flow. This company was utilizing ion exchange to remove heavy metals from the rinses prior to discharge to the sanitary sewer. Once exhausted, the ion exchange columns were sent off-site for regeneration. The spent concentrates were also hauled off-site for treatment. These services were provided by an outside vendor. No other treatment or waste management existed prior to the installation of an integrated wastewater management system. The high expense of water and sewer and the fees associated with services provided by the outside vendor prompted the company to design and install an on-site wastewater system to recycle 90% of the rinses. The block diagram of this system is shown in Figure 1.

Ten years ago water and sewer charges were not as expensive and compliance was loosely regulated, end-of-pipe treatment technology was the best and most economical treatment scheme. Today metal finishers have to face a totally different situation. Water and sewer fees have increased tremendously, compliance rules are more stringent, recycle and waste minimization rules are imposed more vigorously, plating processes have become more complex, the plating industry is more competitive, hazardous waste sites are being closed, dumping of sludge is becoming more and more difficult, dumping fees and hauling costs keep going up and liability of dumped sludge stays with the generator indefinitely. These factors create a great challenge to all platers. As a result, coming up with a good resource and waste management plan becomes vital for the present and future of today's plating operations.

These changing factors also impact on the wastewater treatment vendor. As the plating industry becomes more and more educated in waste management, the waste management industry becomes more and more educated with the various plating operations and the nature of wastes being generated. Consequently, the waste management industry will strive to develop more specific technologies to comply with the on-going demand.

Wastewater technologies that are currently commercially viable include: ion exchange for metal removal and water reuse, precipitation with clarifiers or micro-filtration, reverse osmosis, electrowinning, evaporation, recovery of baths through dialysis and electrodialysis, alkaline cleaner purification through ceramic microfiltration. Integration of these technologies varies from one shop to another and from one region to another depending on the specific governing factors. Even though integrating several systems is usually more complex and expensive, the fact that each system is responsible only for a portion of the total waste, may eleviate production problems if the wastewater treatment system is out of commission or requires maintenance. Using multiple technologies will usually prevent the shop from becoming totally crippled.

Plating Companies

These factors, as well as the plating shop's other corporate goals, needed to be considered in designing an integrated system to handle the 70 gpm of total rinses generated at the subject

operation from the following plating operations:

Automatic Barrel Acid Zinc Line

Alkaline Soak Clean
Alkaline Electro Clean
Acid Clean Dip
Acid Zinc Plate
Tri-Chromate
Hex-Chromate
Unload and Dry

Electroless Nickel Line

Alkaline Soak Clean
Alkaline Electro Clean
Acid Clean/Activate
Electroless Nickel
Chromic Acid
Unload and Dry

Cyanide Zinc Line

Alkaline Soak Clean
Alkaline Electro Clean
Acid Clean
CN Zinc Plate
Tri-Chromate
Hex-Chromate
Unload and Dry

Small Rack Zinc Line

Alkaline Soak Clean
Alkaline Electro Clean
Acid Dip
Acid Zinc Plate
Tri-Chromate
Yellow-Chromate or Black Chromate
Unload and Dry

Cyanide Copper/Nickel/Tri-Chromate Line

Alkaline Soak Clean
Alkaline Electro Clean
Acid Dip
Cyanide Copper Plate
Acid Nickel Plate
Tri-Chromate
Unload and Dry

Segregation of Rinses and Spent Concentrates

A thorough survey of the baths and rinses was conducted. Proper dragout rinses were suggested and implemented to minimize the total dissolved solids (TDS) of the rinses that were for reuse and recycle using cation/anion trains compatible to ion exchange systems. Rinses not compatible with ion exchange and those with high TDS were segregated for chemical treatment, precipitation and membrane microfiltration. Cyanide rinses were to be sent to a dedicated cyanide ion exchanger. Spent concentrate from electroless nickel and hexavalent chrome were sent directly to a batch treatment system. Regenerant from anionic column of cyanide ion exchange, along with other spent cyanide wastes, were sent to a cyanide destruct system utilizing chlorination.

Waste Stream Segregation

- Low TDS rinses, including chromium
- High TDS rinses
- Cyanide rinses
- Spent acid concentrates (excluding Electroless Ni and Cr^{+6})
- Spent alkaline concentrates (excluding cyanide)
- Spent cyanide concentrates
- Spent hexavalent chrome and electroless nickel

Wastewater Management Systems

Ion Exchange System for Reuse and Recycle

The ion exchange system provided in this project is an acid cation and base anion resin system with two cation columns and two anion columns. One cation and one anion column are in stand-by and are put in operation each time the columns on-line are saturated. As a result, the system will maintain the rinsewater quality without interruption during regeneration. The system is equipped with an adjustable TDS meter and a microprocessor to regenerate the columns. Sulfuric acid and caustic are used for regeneration.

An analysis of the representative rinse sample must be conducted to measure the

amount of TDS in order to determine the amount of resin required. The closed loop ion exchange system consists of: equalization/collection tank, carbon filtration, two cation/anion trains of resin, one acid regeneration tank, one caustic regeneration tank and associated instrumentation, controls and piping manifold.

Rinsewater from the plating area is collected in the equalization/ collection tank. The process pump transfers the rinsewater through the carbon filter and then through the cation/anion on-line columns. The deionized water then will flow back to the associated rinse tanks. Use of dragout tanks not only reduces the water usage, it also reduces the transfer of dissolved solids in the subsequent rinse tanks, ultimately making it suitable for the application of ion exchange and close looping. Typical total dissolved solids in this arrangement will range from 100-300 ppm.

A carbon filter is provided to prevent the fouling of resin columns due to organics and fine particles. The payback analysis for close looping with an ion exchange system is shown in Figure 2. The application of ion exchange in a plating shop is becoming more and more popular. However, ion exchange has its own limits. Generally strong oxidizers, chelators and organics are those chemicals for which one or more additional measures should be taken before applying ion exchange. In the case of close looping, the TDS of the solution, the frequency of the regeneration and the associated costs should also be evaluated carefully in order to justify the use of ion exchange. Reverse osmosis systems are shown to be more economical for TDS over 500 ppm.

In cyanide systems, the rinses will be treated as described above, however, the sizing of the columns, timing of the regeneration and regeneration itself, are more crucial because cyanide has different chemical characteristics than other elements in the wastewaters.

Membrane Microfiltration

As shown in Figure 3, the high TDS rinses are collected in an equalization tank with about 2 hours retention time. From the equalization tank the rinses are pumped into a two-stage precipitation system. In the first stage the pH is maintained at ~4.0 s.u. and ferrous sulfate is added as a co-precipitant. In the second stage reaction system, the pH is raised causing co-precipitation of the metals and iron. Polymer addition and particle enhancement is not required since precipitation is followed by cross-flow membrane microfiltration. The precipitated rinsewater then overflows to a concentration tank located ahead of the microfiltration skid. As shown in Figure 3, the major components of a microfiltration system are:

- Concentration Tank
- Recirculation Pump (Process Pump)
- Microfiltration Modules
- Chemical Cleaning and Waterflush Tanks
- Cleaning Pump
- Effluent (Permeate) Flow Meter
- Sludge Draw Pump
- Backpulse

Unlike the case for reverse osmosis where there are a great number of manufacturers with similar module design, there are a limited number of manufacturers of micro-filtration modules, each with a different type of module design. The materials of construction also vary from one manufacturer to another. Typically, microfiltration modules which are applied in the wastewater industry are made of bundled porous tubes with a support structure and housing. Typical diameters of tubes used vary from 1/4" to 1". The smaller the tube, the more tubes that can be bundled in a housing which results in higher permeate flow per unit.

However, there is a risk involved in plugging the smaller diameter tubes with solids greater than 1-1/2%. Once the tubes are plugged with solids, cleaning usually is very difficult. On the other side of the scale are 1" diameter tubes. Since the surface area of the whole bundle is not as high as the smaller tube bundle, the flow rate of permeate per module is less, but it will tolerate solids as high as 6% (60,000 ppm). The nominal pore size of the membrane is 0.1 microns.

The microfiltration operation starts with a high flow pump drawing wastewater containing suspended solids from the bottom of the concentration tank and recirculating it through the membrane modules. High flow is necessary to

provide high velocity flow in the module tube, keeping the flow in the turbulent flow range at the tube wall to self clean the surface of the tubes. The higher the velocity, the higher the flow rate.

Backpulsing of the modules with filtrate causing flow in the opposite direction of the normal filtrate flow will also add additional cleaning of the module tube surface by purging the build-up of particles on the surface of the tube back into the stream. This is very crucial in modules with a smaller diameter, but not as critical in the larger more open tube designs.

As the precipitated rinsewater recirculates through the membrane, the clean water permeates out of the membrane and suspended solids stay in the loop, resulting in an increase in the level of suspended solids in the concentration tank. Once the solids level increases to the range of 2-5%, any additional solids will be bled to the filter press for dewatering. Since polymer is not used in this process, the slurry resulting from microfiltration is higher in solids than those of a clarifier and dewaters better usually by 5-10% higher solids in the filter cake. Unlike clarifiers where gravity is the solids separation mechanism, microfiltration requires less chemicals for co-precipitation and no polymer for particle enhancement. Compliance with microfiltration is more consistent and reliable.

The high degree of particle removal and lack of polymers are very important to the application of reverse osmosis for water recycling after metals removal. It is impractical to apply reverse osmosis to the effluent from a clarifier and still meet the EPA categorical limits.

Alkaline Cleaner Filtration System

Organics such as oil and grease and surfactant from an alkaline cleaning process of parts are detrimental to the chemical precipitation process. Rinsewater containing a high level of organics is costly and cumbersome to treat; more chemicals are necessary for precipitation of solids and permeate flow enhancement. In addition, sludge generation will increase as well, resulting in additional hauling and disposal costs. The use of an alkaline cleaner filtration system is suggested to filter the oil and other particulates out of the bath.

The main components of an alkaline cleaner filtration system are a high pressure pump, one or more microfiltration modules and a tank. A backpulsing feature is also necessary to continuously clean the inside surface of the modules. These systems are usually made of stainless steel to handle the high temperature of the cleaning bath. The module is typically made of high-temperature resistant material with a pore size of 0.1-0.8 microns. In an alkaline cleaning bath, only the oil and grease and particulates are filtered out and the surfactant and cleaner pass through the filter and return to the bath. Consequently, the life of the bath will be elongated, resulting in lower cleaner purchasing costs, less dumping of the cleaner and lower treatment chemical costs. Figure 4 is a flow schematic of an alkaline cleaner filtration system.

Reverse Osmosis System

As was pointed out in the ion exchange section, reverse osmosis is an excellent water recycling tool for waters containing high TDS. Reverse osmosis systems have been in operation for many years in various fields. Many types of membranes are available. Cellular acetate and thin film composite types were developed for specific applications.

To design the RO system, a composite sample of the feed water to be treated and processed through the membrane microfiltration is absolutely necessary. A sample of effluent to be used for RO feed was analyzed for constituants. Computer software utilized the data to project the system design.

In this case the high TDS rinses amount to 30 gpm. The RO system is targeted to recover 75-80% of the water. The reject will flow to sewer. It should be noted that using an RO will concentrate the level of heavy metals by the recovery factor. This means if recovery is 75% and the zinc concentration prior to RO is .5 ppm (for example), it will increase to 2 ppm after the RO process (0.5/25%).

Payback Analysis

The following treatment technologies were considered for this analysis:

1. Clarifier for discharge
2. Microfiltration followed by reverse osmosis for recycle
3. Combination of microfiltration, ion exchange and reverse osmosis for recycle
4. Existing outside services (ion exchange for discharge and off-site disposal of spent concentrates)

In the long term Option #3 was the most attractive. Option #2 was slightly less expensive in capital cost, but considering 90% recycle, it was overall more expensive. Option #1 was most attractive in capital cost, but not a good long term alternative in terms of operating cost or compliance reliability. Option #4 was extremely expensive in operating cost with unknown future reliability. Refer to Figure 5 for comparison of Options #1, #2 and #4.

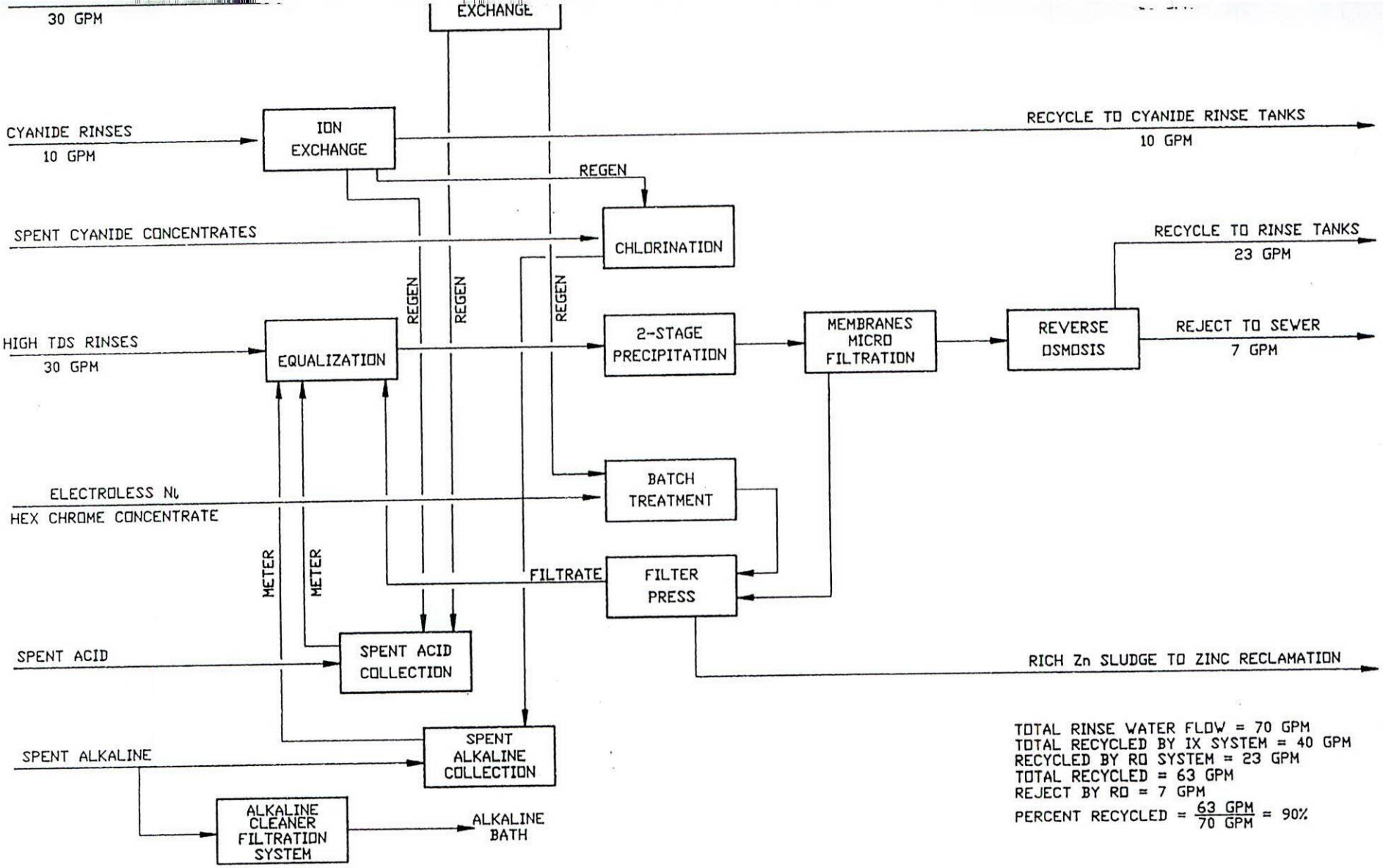
The following assumptions were used in this analysis:

- Cost of chemicals, labor, electricity and sludge hauling remain unchanged.
- Cost of outside services for Option #4 remain unchanged.
- Installed cost of clarifier and integrated systems were considered.
- Plant Operation: 70 gpm, 16 hours/day, 5 days/week, 52 weeks/year.
- Water Cost: $2.86/1000 gals or $50,000/year.
- Sewer Connection: $70,000.

Conclusion

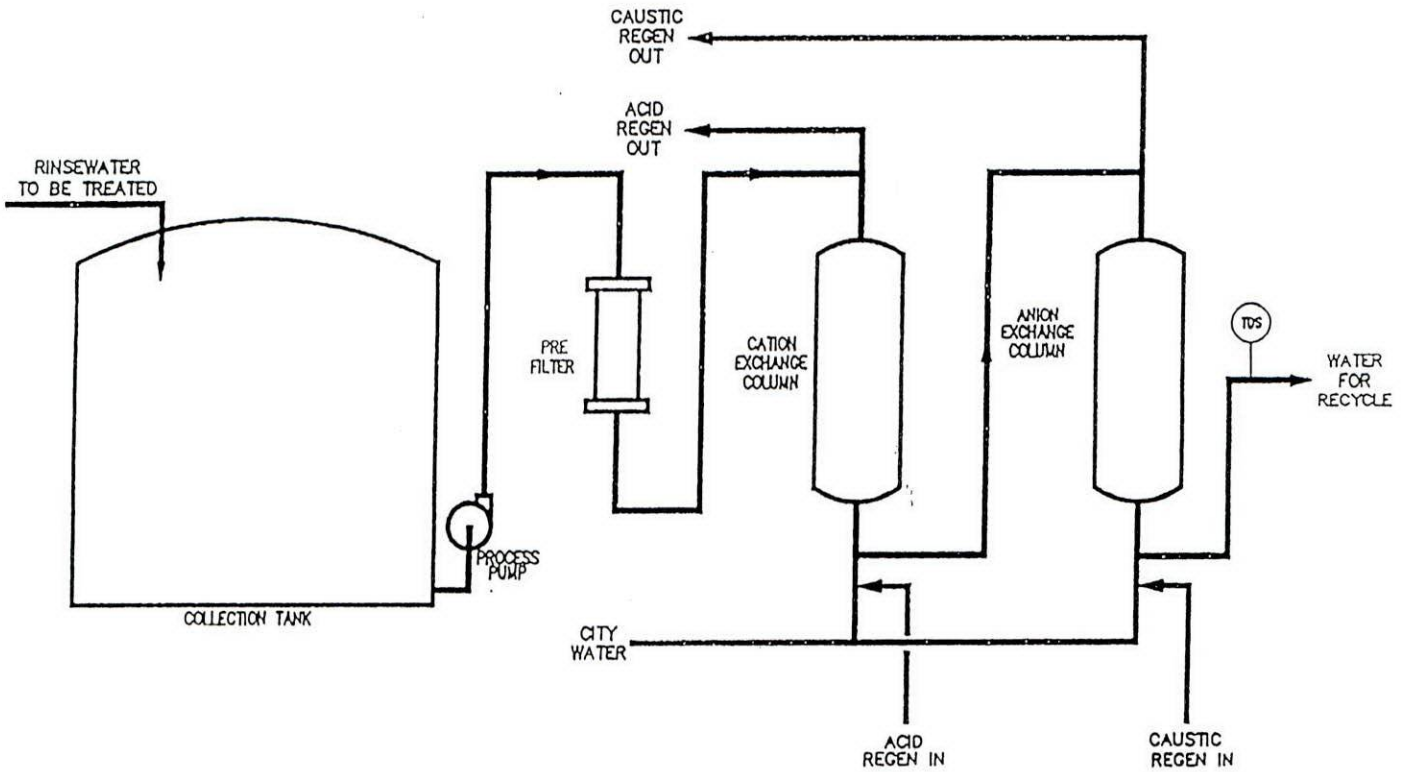
In conclusion, when designing a complete wastewater treatment system for water reuse and recovery with an aim toward waste minimization, many factors and appropriate technologies must be used to achieve the best and most economical treatment approach. The choice of a vendor to supply such a system is critical as the vendor must have a wide and thorough knowledge of various treatment techniques, costs and operating parameters.

The system design must take into consideration all the technical and economic factors noted in this paper, as well as the customer's and regulator's specific requirements and operational limitations. However, with a complete understanding of the customer's operation, the regulations and the overall cost parameters, a successful system can be designed and implemented.



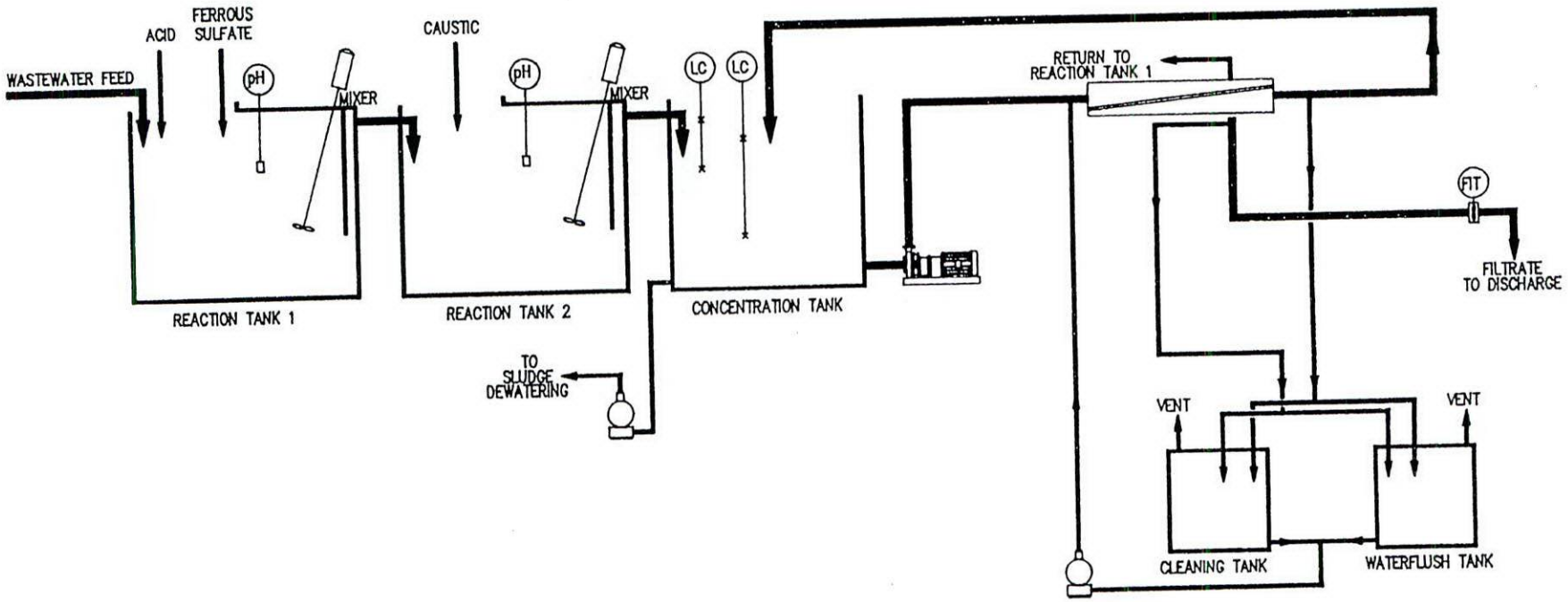
OVERALL WASTEWATER MANAGEMENT
BLOCK DIAGRAM

FIGURE 1



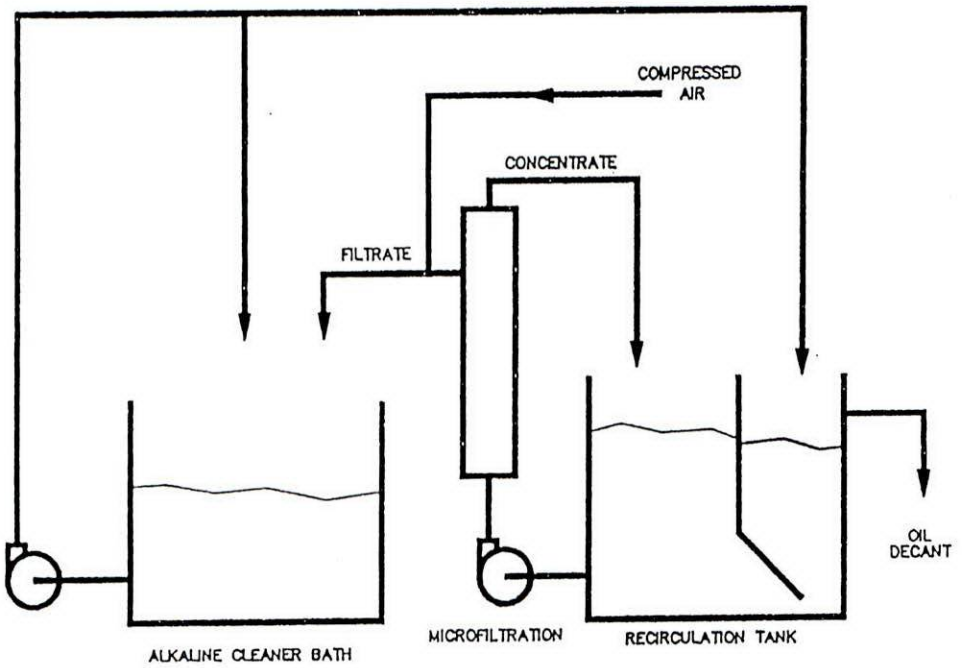
ION EXCHANGE SYSTEM
FOR CLOSED-LOOP

FIGURE 2



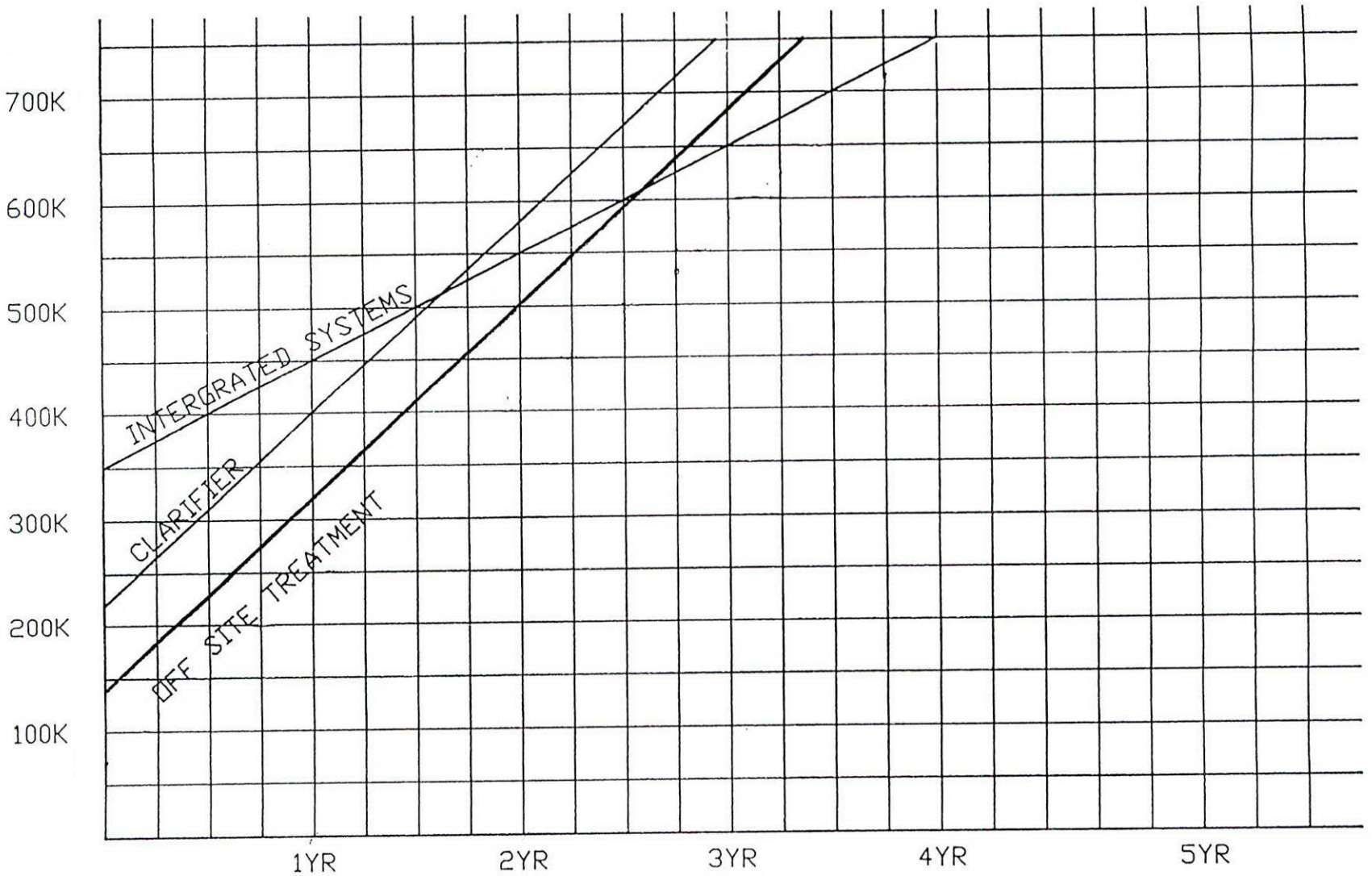
CHEMICAL PRECIPITATION & MICROFILTRATION SYSTEM

FIGURE 3



ALKALINE CLEANER FILTRATION SYSTEM

FIGURE 4



COST ANALYSIS FOR THREE
WASTEWATER TREATMENT ALTERNATIVES

FIGURE 5

Paper Not Available In Time For Publication

Electroplaters in Southwest Ohio Demonstrate Waste Reduction Techniques

Craig Melvin, Institute of Advanced Manufacturing Sciences (IAMS), Cincinnati, OH

Under a grant from the Ohio Environmental Education Fund, the IAMS worked with electroplaters in southwestern Ohio to reduce wastes and encourage pollution prevention. The Institute worked directly with seven platers to develop opportunities for waste reduction and to determine which of these waste reduction processes and alternatives were most effective. This information was then transferred to local electroplaters through a manual, seminars and meetings. This paper will summarize the results of the project.

For copies of this paper please contact:

Craig Melvin
Institute of Advanced Manufacturing
1111 Edison Drive
Cincinnati, OH 45216
513/948-2036
FAX: 513/948-2109

Waste Water Treatment with a Combined Adsorption / Flocculation Process

Joseph M. Ragosta
Graver Chemical Company

Abstract
The metal finishing industry has made a great deal of progress on the development of new processes for recovery or treatment of waste water containing heavy metals. Even so, precipitation is still the most widely used process for waste water treatment. Unfortunately, this process is difficult to use properly and often causes users to be out of compliance.

Alternative processes are more reliable, but many small metal finishing shops can not afford to upgrade their facilities. Because of these problems, an improvement in precipitation technology would greatly benefit the industry.

We have developed a series of insoluble flocculants that improve the removal of heavy metal species. While all flocculants are capable of removing the insoluble particles, these new flocculants remove soluble species, as well. Since effluent limits are near the solubility limit for several metals, this ability to remove soluble species is important for reliable operation of a waste water treatment system.

Introduction
Precipitation is commonly used in treatment of waste water. In this process, the pH of the waste water is adjusted to a level which minimizes the solubility of heavy metals. The metal hydroxides are then allowed to settle and separated. In most cases, a polymer is added to speed settling or to improve final water quality.

Because of the nature of metal solubility as a function of pH and the very low effluent levels needed, most waste water operations operate near the solubility limit of the metals in question. This has the unfortunate effect that metals are generally present in waste water both as soluble and insoluble species. The presence of both types of metals results in many plants operating near their legal effluent limits and having difficulty staying in compliance.

Waste Water Treatment
Precipitation processes are familiar enough that a description of the process is not needed. Unfortunately, it is subject to several limitations.

pH Limitations
In many older systems, pH control is the limiting factor in optimizing metal removal. This is because metal solubility is a function of pH (Figure 1). For each metal, there is an optimum pH. When the pH is outside this optimum the metal concentration in the effluent will be increased.

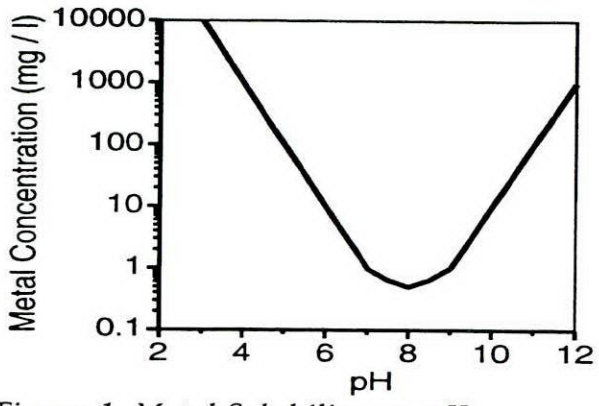


Figure 1. Metal Solubility vs. pH

Unfortunately, there is an even more important factor in controlling pH. When more than one metal is present, it is necessary to choose a pH that may be less than ideal for each of the metals because the pH for minimum solubility is different for different metals. Some examples are shown in Table 1.[1]

Table 1. Optimum Precipitation pH

Metal	pH Range
Cr	8
Cu	8-11
Ni	10
Zn	9-10
Fe	4.5-12

Solubility Limits

A second factor is important even if a waste water containing only one metal is optimized to the ideal pH. In any precipitation process, there is a minimum metal concentration that can be achieved. This concentration is the solubility limit. Even for a well-operated waste water treatment system, it is not possible to reduce metal concentrations below this value.

Unfortunately, the solubility of several heavy metals is close to the maximum level allowed by the EPA or local regulatory agencies (Table 2).[1]

Table 2. Minimum solubility of metals (mg / l)

Metal	Minimum Solubility
Cr	0.3
Cu	0.5
Ni	1.0
Zn	1.2
Fe	0.1

These two problems with precipitation processes combine to limit the performance of waste water treatment systems. The only way to improve these systems is to combine the precipitation step with a process which removes the soluble species which remain in solution.

Flocculation

Flocculants are used as an aid in precipitation processes. A flocculant does not typically change the metal solubility. Rather, it causes precipitation to occur much faster, reducing the size of settling tanks needed.

There are a large number of polymer flocculants, but all serve the same purpose. However, they have two limitations. First, if too much flocculant is added, the particles tend to remain in solution rather than settle out. Second, polymer flocculants can cause membrane filters to foul.

The use of an insoluble flocculants has been practiced. In cases where maximum precipitation performance must be achieved, the availability of an insoluble flocculant offers significant advantages. Figure 2 shows a comparison between a conventional soluble polymer (Betz 1175) and an insoluble flocculant related to the type presented in this paper.[3]

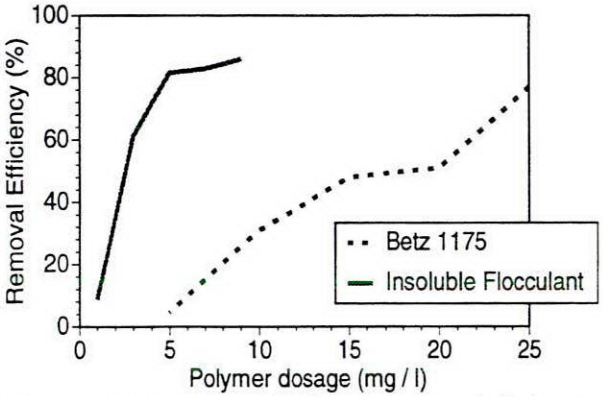


Figure 2. Removal of humic and fulvic acids from water

This example is much like the treatment of metal finishing waste water. Even though precipitation will remove some of the undesired material, the solubility is relatively high. The use of an adsorptive flocculant is much more effective than a conventional flocculant. At equivalent removal efficiency, flocculant dosages are reduced by about 75 percent.

Adsorption

Adsorption processes have been widely used in metal finishing waste water treatment. Of these processes, ion exchange is the most widely used.[2] Ion exchange is a very useful technique which can often reduce metal concentrations to low ppb levels. Unfortunately, its use has been limited by the cost of installing and operating ion exchange systems.

A combination of filtration (for removal of the bulk of the heavy metals) and ion exchange adsorption for removal of the final traces of metals would be ideal if it could be accomplished at reasonable cost.

Insoluble Flocculants

Clearly, precipitation processes can be improved by the use of a flocculant which is also capable of removing soluble species from solution.

The materials used in the humic / fulvic acid example above are not commercially available.[4] They are very expensive to produce and purification is difficult. Therefore, we have developed a product with similar properties.[5]

These materials are available in a range of particle sizes ranging from an average of about 0.5 microns to 75 microns. The optimum particle size will depend on the application, but the best performance has been with particles around the low end of this range.

A variety of materials can be used to make these flocculants. When using adsorbents for treatment of metal finishing waste water, it is well known that different adsorbents are needed for different situations. For example, Table 3 lists ionic form of a number of different metal species.

Table 3. Ionic Forms of Soluble Metals

Cationic	Most uncomplexed metals
Anionic	Metal cyanides, chromate Alkaline zinc, Some complexed metals
Neutral	Many metals at high pH, Some complexed metals

The adsorbent needs to be tailored to the species being removed from solution. Our ability to tailor the flocculant / adsorbent for different applications means that this technology can be used in a wide range of applications.

Metal Finishing Waste Water

To demonstrate the effectiveness of this flocculant / adsorbent, a synthetic waste water was prepared containing 58 mg / l copper, 19 mg / l zinc, and 19 mg / l iron at pH 3.5. This material was

treated with caustic alone, with caustic and a commercial flocculant, and with caustic and the new flocculant. The results for caustic alone and caustic and the commercial flocculant agreed very well with literature values.[6]

For copper, the results showed that the new flocculant outperformed conventional flocculants by a factor of

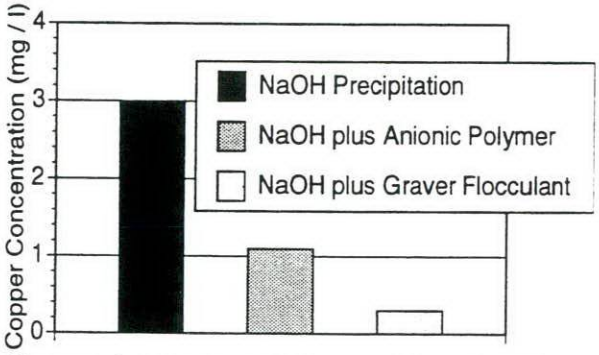


Figure 3. Residual Copper Level with New Flocculant

four (Figure 3). This result is significant in that the conventional flocculant gives results that are close to legal effluent limits. The new flocculant provides a good safety margin. The difference between caustic alone and caustic with polymer appears to be due to better separation of precipitated particles. The improvement from the adsorbent is due to the addition of adsorption into the system.

The same result was observed for zinc (Figure 4). Here the new material was a three-fold improvement over conventional flocculants.

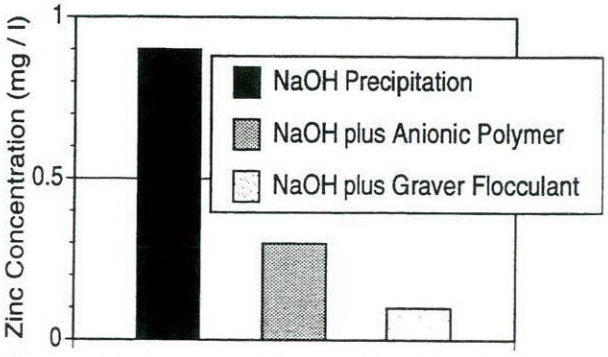


Figure 4. Residual Zinc Level with New Flocculant

Again, the difference between the new flocculant and the conventional polymer seems to be the ability of the new polymer to adsorb soluble metal species.

The new polymer is especially interesting in that in most cases it can be used without any equipment changes. This reduces the cost of changeover to an acceptable level.

Future Work

We are working to determine the minimum effluent level obtainable with the new flocculant. While the effluent level of 0.3 ppm copper meets the limit for most customers, lower levels are needed in some locations.

We continue to optimize both the adsorption and flocculation properties of this product. We are also exploring partnerships which will allow us to better understand the industry's needs and develop materials to solve specific problems.

Conclusions

A new flocculation technology has been developed for waste water treatment. This technology consists of the removal of both soluble and insoluble species by a combined flocculation / adsorption process. It offers a number of advantages over alternative processes:

- Better effluent quality than conventional precipitation / clarification systems
- Lower cost than ion exchange or ultrafiltration systems
- Can be tailored to the specific separation problem
- Requires little or no investment in capital equipment
- Low viscosity even at 10% solids simplifies handling
- Cost effective for any size system

This new flocculation / adsorption technology offers metal finishing operations the ability to greatly improve the performance of their waste water treatment systems at very low cost. This is especially valuable for locations which operate near their effluent limits and frequently experience excursions which take them out of compliance.

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Waste Water Treatment with Adsorptive Precoats

by
Joseph M. Ragosta, PhD
Graver Chemical Company

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Indianapolis, IN

Waste Water Treatment with Adsorptive Precoats

Joseph M. Ragosta
Graver Chemical Company

Abstract

Waste water treatment in metal finishing operations is complicated by the fact that metals are generally present in both soluble and insoluble forms. For any waste water treatment process to be effective, it is necessary to remove both forms. Most conventional processes are limited to effective removal of only one of these forms.

This article describes a new precoat medium that solves this problem. It is an effective precoat filter for submicron filtration. The unique feature of this material is that the precoat contains an adsorbent which will remove soluble species as well.

A new patented technology allows both filtration and adsorption to take place in a single step at flow rates which greatly exceed conventional precoat filtration. This process is effective even for difficult to treat electroless copper-containing systems.

Introduction

Environmental regulations have hit the metal finishing industry hard in recent years. Some estimates indicate that as many as 50% of metal finishing operations have closed or will close before the end of the century due to regulatory requirements. While other industries have suffered as well, the small size of most metal finishing operations makes the impact especially painful.

What has been neglected is that some of this difficulty stems from a technical problem with metal finishing waste water. While it is difficult to do much about regulations, it is possible to deal with technical problems.

Because of the nature of metal solubility as a function of pH and the very low effluent levels needed, most waste water operations operate near the solubility limit of the metals in question. This has the unfortunate effect that metals are generally present in waste water both as soluble and insoluble species. The presence of both types of metals results in many plants operating near their legal effluent limits and having difficulty staying in compliance.

Waste Water Treatment

Conventional waste water treatment processes are designed to handle either soluble or insoluble metals or both. Filtration and clarification are meant to handle particulate species. Ion exchange and reverse osmosis handle soluble species best. Precipitation is limited by the solubility of the metal (typically about 0.1 to 1 ppm). It is not practical for a precipitation process to reduce metal concentrations below this level.

While in principle a two step process (i.e., precipitation / clarification followed by filtration) has the potential to improve performance, the metals can change form. If the soluble metals are removed, some insoluble species can redissolve before the second purification step, leading to high effluent levels.

These problems are compounded when chelating agents are present. Electroless copper is an especially severe problem. It has been well documented that the presence of EDTA or other chelating agents will interfere with the removal of copper with either ion exchange or precipitation.[1] The chelating agent works to keep the metal in solution, working against the precipitation process. It also competes with ion exchange processes, although the mechanism is slightly different. Ion exchange or membrane processes can be plagued by fouling of the resin or membrane, reducing performance. A treatment process is needed which can remove sub-ppm levels of metals even in the presence of chelating agents.

The best solution to the metal purification problem is to identify a purification process that removes both soluble and insoluble species. Since precoat filtration has been identified as a process with excellent performance for removing insoluble species, it is a good starting point for development of a new process. In principle, all that is required is to develop an effective precoat filter that also contains an adsorbent to remove soluble species. One company has attempted that and sells precoats which contain a mixture of powdered activated carbon (PAC) and diatomaceous earth (DE).

In practice, however, the process is not that simple, as shown by the lack of success of the mixed precoat media currently available. For example, the simple physical mixture of PAC and DE has poor hydraulics, short run lengths, and inefficient contaminant removal. It is also incapable of removing most soluble metal species.

We have invested about 20 years of research into product development and improvement and have now identified a series of products which offer both effective filtration and adsorption of soluble species.[2,3] These precoats are typically applied to a variety of filters, including plate and frame, candle filters, and bag filters.

This discussion is divided into two sections: adsorption and filtration. However, it is important to remember that the advantage of this process is that both filtration and adsorption take place simultaneously. In fact, because of the dual mode of action, the effluent water quality is substantially better than can be achieved by either method alone.[4]

Filtration

Precoat filtration is a well-known technology which is used extensively in waste water treatment. As such, it will be familiar to many readers. The new technology is best considered an extension of precoat filtration.

However, like any fine precoat filter, the use of high levels of solids will tend to plug the filter quickly. This product is best used to polish either clarified or prefiltered waste water which is relatively low in suspended solids. When solutions with higher solids must be treated, the use of a body feed technique or a coarse DE overlay is recommended.

Adsorption

Adsorption is a well-known phenomenon and has been the subject of many books and reviews.[5] For the purposes of this paper, it is enough to state that adsorption efficiency is limited by both selectivity and kinetics. In addition, any process must have sufficient hydraulic performance to handle reasonable flow rates.

Selectivity
Selectivity is a measure of how much affinity the adsorbent has for the species of interest. For waste water treatment of metal finishing operations, there is no one adsorbent which will remove all contaminants.[1] Different metals have different charges in solution, as shown in Table 1.

Each of these ionic forms requires a different type of adsorbent. Any new process will need to offer the flexibility to use the best adsorbent or combination of adsorbents for a given application.

Table 1. Ionic Forms of Soluble Metals

Cationic	Most uncomplexed metals
Anionic	Metal cyanides, chromate Alkaline zinc, Some complexed metals
Neutral	Many metals at high pH, Some complexed metals

Kinetics
Adsorption kinetics is a measure of adsorption rate. The smaller the adsorbent particle size, the faster the adsorption will occur (Figure 1).[5] This translates into better effluent quality and the use of less adsorbent. Therefore, it is desirable to use the

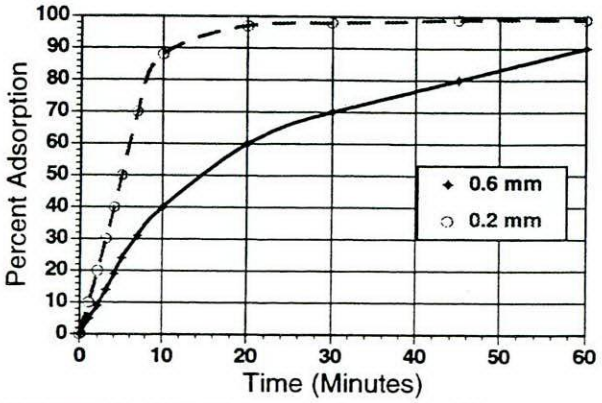

Figure 1. Kinetics vs. Particle Size

smallest particle size adsorbent possible. However, fine mesh adsorbents are very difficult to use because the pressure drop across a vessel bed is inversely proportional to particle size (Figure 2). This creates a dilemma: very small particles of adsorbent are needed for good adsorption performance, while large particles are needed for good hydraulics.

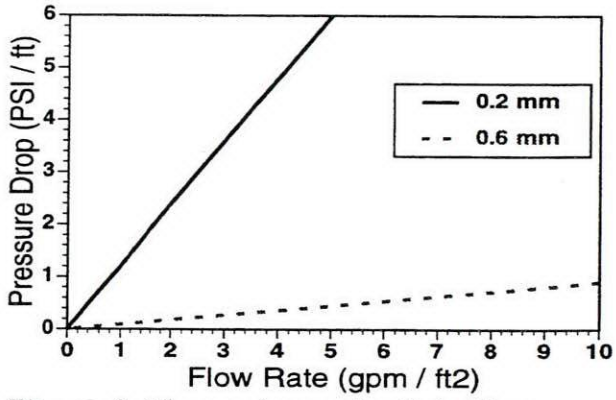

Figure 2. Flow rate vs. Particle Size

The adsorptive precoat technology solves this problem by offering the best of both worlds. We choose extremely fine particles or grind larger particles to a small size. For example, typical ion exchange resins are 300-1200 micron beads. To get the maximum benefit in this process, they are powdered to around 15 microns before use. Other adsorbents are even smaller.

Hydraulics
If these adsorbents were used in a precoat, the pressure drop would be too high for any useful flow to be achieved. A simple solution would be to blend the adsorbent with a filter aid. This can improve permeability by a factor of two to ten. This is still insufficient to obtain good flow rates, so we have developed a flocculation process for creating a "fluffy" precoat. A graphical simulation of this process is shown in Figure 3.

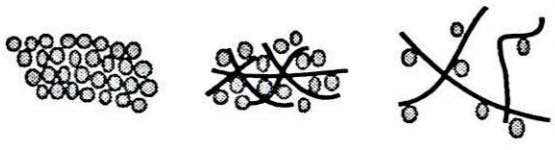

Figure 3. Adsorptive Precoat Structure

This is done by modifying surface charges to create an affinity between the particles.[3] Permeability improvement can be as much as two thousand times the permeability of the powder alone.[6] Relative permeabilities are shown in Figure 4.

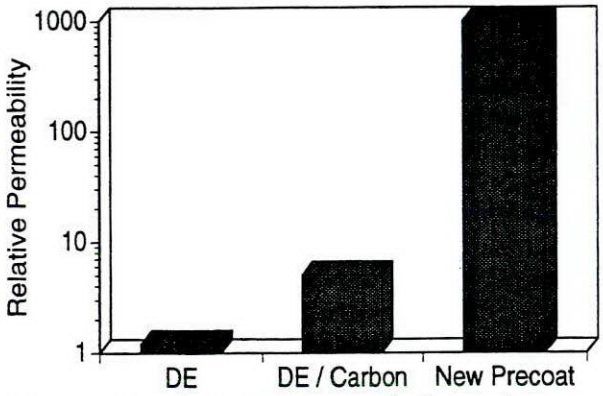

Figure 4. Relative Permeability of Precoats

The product is very simple to use. It is slurried in a small amount of the water to be treated, then applied to a filter (almost any type of filter has been shown to work, although candle filters generally offer the highest surface area / cost ratio). The waste water is then passed through the precoat.

Since the adsorption capacity is limited, the product is best used for polishing conventional waste water treatment systems. The waste water is treated with a conventional precipitation / clarification processes, and is then passed through a thin (5-20 mm) layer of adsorptive precoat on a filter. Several metal finishing plants are now using this technology to improve their waste water treatment operations.

Printed Circuit Board Manufacturer

One plant is a printed circuit board manufacturer using a variety of processes. As is usually the case, electroless copper causes them problems in meeting a 0.5 ppm copper limit. They have added specialty precipitating agents to break the electroless copper complex and have even invested in an expensive precoat filtration system which used a physical mixture of DE and powdered activated carbon. None of these processes has solved their problem.

Precipitation alone gives them copper concentrations around 1.5 ppm. Post-treating with precoat filtration only brings their effluent levels to around 0.5 to 1.0 ppm. This is because even the most effective filtration will not remove soluble metals. By replacing their conventional precoat with the new adsorptive precoat, they are able to easily meet their 0.5 ppm copper limit.

This customer has estimated the adsorptive precoat to act as an 0.8 micron filter, based on particles

leaving the system. This indicates that filtration performance is excellent, as well. In addition, the adsorbent is removing not only the complexed copper in solution, but some detergents which were previously causing a foaming problem. Other customers have seen similar benefits.

While this customer did not offer cost data, we have found in other industries that the direct cost is very close to conventional precoat filtration with DE. This is because our precoat cycle is generally considerably longer than the standard precoat.

Economics will be much more favorable in the metal finishing industry. Since materials contaminated by metals are very expensive to dispose of, the volume of waste generated is critical. In most applications, the adsorptive precoat reduces waste volume by 50-80% compared to conventional precoat filtration. The total operating cost is therefore usually lower than conventional precoat filtration.

Metal Plating Shop

In bright nickel plating, the plating bath becomes contaminated with organics and particulate material which interfere with efficient operation. To remove these contaminants, one plant used two precoats per week of a mixture of fiber (filter aid) and PAC.

By switching to the adsorptive precoat formulation, they were able to reduce precoat frequency to one precoat every one to two weeks and saved about 400 hours per year (>50%) in labor costs. In addition, product quality has been greatly improved due to the improved efficiency of the adsorptive precoat compared to a physical mixture of filter aid and adsorbent. They have reduced solid waste generation by 80%, as well.

Future Work

We are working to determine the minimum effluent level obtainable with the adsorptive precoat. While the effluent level of 0.5 ppm copper meets the limit for most customers, lower levels are needed in some locations. In addition, the product should work even better when no chelating agents are present.

To study performance in the laboratory, we prepared a simulated waste water which would resemble the effluent from a conventional clarifier. This waste water contained about 0.2 ppm of several metals as shown in Figure 5. After simple filtration, the metal levels were largely unchanged. After treatment with an adsorptive precoat, seven of the eight metal concentrations were undetectable. At the time the work was done, our detection limit was 0.05 ppm. We believe better levels are achievable.

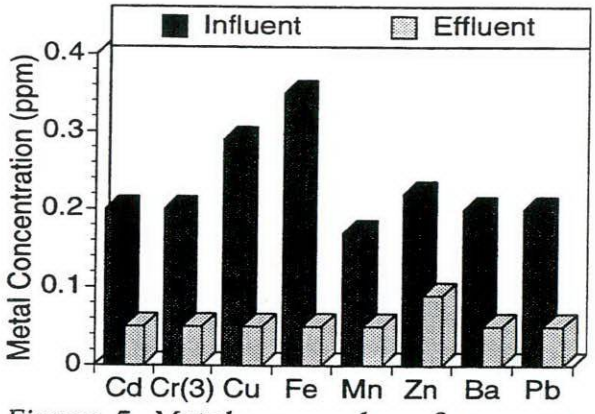

Figure 5. Metal removal performance

Future developments in this area will involve the development of customized adsorptive precoats. For some applications, a specialty adsorbent may be needed to effectively treat the waste water. New developments also indicate the potential for significantly

increasing the run length of the precoat, reducing costs.

We continue to optimize both the adsorption and filtration properties of this product. We are also exploring partnerships which will allow us to better understand the industry's needs and develop precoats to solve specific problems.

Conclusions

An adsorptive precoat is a useful technology for waste water treatment. It offers a number of advantages over alternative processes:

- Better effluent quality than precipitation / clarification systems, even those with post-filtration
- Lower cost than ion exchange or ultrafiltration systems
- Can be tailored to the specific separation problem
- Effective for chelated systems like electroless copper
- Requires little or no investment in capital equipment
- Cost effective for any size system

Adsorptive precoat filtration offers metal finishing operations the ability to greatly improve the performance of their waste water treatment systems at very low cost. This is especially valuable for locations which operate near their effluent limits and frequently experience excursions which take them out of compliance.

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5. See for example, R. Kunin, Ion Exchange Resins, 1990, R.E. Krieger, Malabar, FL.
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VITRIFICATION OF F006 PLATING WASTE SLUDGE BY REACTIVE ADDITIVE STABILIZATION PROCESS (RASP)[1]

by

H. Lee Martin, Carol M. Jantzen, and John B. Pickett
WESTINGHOUSE SAVANNAH RIVER COMPANY
Aiken, South Carolina 29808

INTRODUCTION

Fuel and target assemblies for the nuclear reactors of the Savannah River Site (SRS) were fabricated in 300-M Area metal finishing and aluminum forming operations. With the end of the cold war, these components for production of nuclear weapons materials for the U.S. Department of Energy are no longer being fabricated. However, 500,000 to 600,000 gallons of nickel plating line sludge, which is a F-006 mixed (hazardous and radioactive) waste, will remain in RCRA permitted interim storage tanks after the supernatant from those tanks has been processed by the wastewater treatment facility. Technologies have been developed by the SRS to convert the sludge to a solid stabilized waste form for permanent disposal.

The M Area Liquid Effluent Treatment Facility (LETF) is an end-of-pipe industrial wastewater treatment facility, that uses precipitation and filtration which is the EPA Best Available Technology economically achievable for Metal Finishing and Aluminum Form Industries. The physical and heavy metal characteristics of the sludge are similar to the F-006 waste sludge generated from wastewater treatment in commercial industry, except it also contains uranium and more than the normal concentration of nickel. There was no market to justify recovery of radioactive nickel from the Watts plating bath. Achieving the Environmental Protection Agency (EPA) Land Disposal Restrictions (LDR) for nickel concentration by the Toxic Characteristic Leaching Procedure (TCLP) has been difficult during commercial F-006 waste stabilization, but the technologies developed by the SRS reliably achieve the LDR standard and greatly reduce the volume of waste for final disposal.

Vitrification was one of those alternative technologies, and full scale demonstration of this Reactive Additive Stabilization Process (RASP) at SRS is scheduled in 1995 and 1996. Vitrification into simple glass compositions was achieved by tailoring the glass composition to take advantage of the common glass constituents of silicon, aluminum, sodium, and calcium that are already in the waste. Stabilization of the heavy metals in the glass is achieved by use of reactive additives such as diatomaceous earth, perlite, rice husk ash, and/or precipitated silica These filter aids are also already in the waste. The process and product models developed for high level radioactive waste glass were utilized to develop glass formulations which optimize processability (viz. viscosity) and product durability.[2] Vitrification produces durable waste forms at volume reduction of 50% compared to commercial cement stabilization of this F-006 sludge and a volume reduction of 10% compared to the Filtration & Stabilization (FIST) process alternative.[3] An 89% total reduction and delisting of the final waste form in M-Area is anticipated.

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1 Patent pending.

2 C. M. Jantzen, "Relationship of Glass Composition to Glass Viscosity, Resistivity, Liquidus Temperature, and Durability: First Principles Process-Product Models for Vitrification of Nuclear Waste," CeramicTransactions, V. 23, American Ceramic Society, Westerville, OH, 37-51 (1991).

3 H. L. Martin, J. B. Pickett and C. A. Langton, "Radioactive and Hazardous Waste Sludge Treatment and Stabilization by Filtration," J. Advances In Filtration and Separation Technology, V.6, American Filtration Society, Chicago, IL, 195-199 (1992)

DISCUSSION

Experimental

The nickel plating line waste glasses were made of the actual nickel plating line sludge and the spent perlite filter aid from supernatant wastewater treatment by adding reagent grade chemicals. Waste loadings varied from 90 to 70 wt%. Other mixed wastes were also tested to demonstrate the RASP. All glasses were melted at a temperatures of 1150°C in high purity Al_2O_3 crucibles for 4 hours. Small amounts of glass, ~100 gram batches, were made to optimize the best compositions for further testing.

Each vitrified sample was submitted for x-ray diffraction (XRD) analysis so that the homogeneity of the resulting glass could be determined. For glasses which were not homogeneous, the crystalline phases were identified by XRD. If analysis by XRD was inconclusive, elemental scans by x-ray fluorescence (XRF) were substituted.

A modified EPA Toxic Characteristic Leaching Procedure (TCLP) was performed at the Savannah River Technology Center on representative homogeneous glasses.

Nickel Plating Waste Sludge

M-Area nickel plating line waste sludge plus the spent filter aid from the associated supernatant treatment are examples of RASP stabilization. Representative samples of the RCRA F006 sludge in each of the M-area tanks, including the tank with the spent filter aid, was analyzed. The X-ray diffraction analysis of the sludge dried at 90°, 300° and 600°C allowed the chemical phases to be identified and a molar mass balance calculation to be performed (Table 1). The aluminum is present primarily as $Al(OH)_3$, while the Na is present as $NaNO_3$. Using the current and projected tank volume inventories a calculated composite waste composition based on a dry calcine basis was determined (Table 1).

Table 1. M-Area Calculated Composite Sludge Composition.*

Oxide	Wt%	Oxide	Wt%	Speculation	Wt% **
Al_2O_3	17.47	TiO_2	0.04	$Al(OH)_3$	23.18
CaO	0.48	K_2O	1.48	$NaNO_3$	17.88
Fe_2O_3	0.88	P_2O_5	3.22	SiO_2	43.44
MgO	0.20	BaO	0.02	$Na_6U_7O_{24}$	3.48
MnO	0.28	PbO	0.11	Ca-zeolite	3.15
Na_2O	10.83	MoO_3	0.01	$AlPO_4$	4.32
NiO	0.93	ZnO	0.59	SUM	95.44
SiO_2	43.58	CuO	0.03		
Cr_2O_3	0.01	SO_4	0.03		
B_2O_3	0.03	NO_3	13.05		
UO_2	3.00	SUMS	96.28		

* Current inventory plus additional filter aid projected from continued supernatant treatment.
** Species identified by x-ray diffraction analysis.

Vitrification

The high SiO_2, Al_2O_3 and Na_2O content of the M-Area waste indicated that stabilization in either sodium borosilicate or SLS glass was feasible. The addition of only one additive, B_2O_3, borax ($Na_2O{\cdot}2B_2O_3{\cdot}10H_2O$), or $Na_2O{\cdot}B_2O_3$ enabled the waste mixture to be made into a borosilicate

glass (Figure 1, Table 2) while the addition of only $CaCO_3$ or a mixture of $CaCO_3$ and Na_2CO_3 allowed solidification into SLS glass (Figure 2, Table 2). The use of only one additive simplifies processability of the waste as only two components need to be adjusted in order to optimize processability and waste loading (Figure 1).

Vitrification was achieved in both borosilicate and SLS glass at waste loadings varying between 70 to 90 wt% waste (Table 2). Higher waste loadings were achieved at higher melt temperatures. Homogeneous glasses formed at temperatures between 1150° and 1300°C at waste loadings of 70 to 80 wt%. The borosilicate system is a well known glass forming system used to make commercial pyrex and vycor glasses which are very stable but are phase separated. Many types of high-level radioactive wastes are being solidified in borosilicate glasses which are in the known glass forming region of the Na_2O-B_2O_3-SiO_2 system, but away from the known region of phase

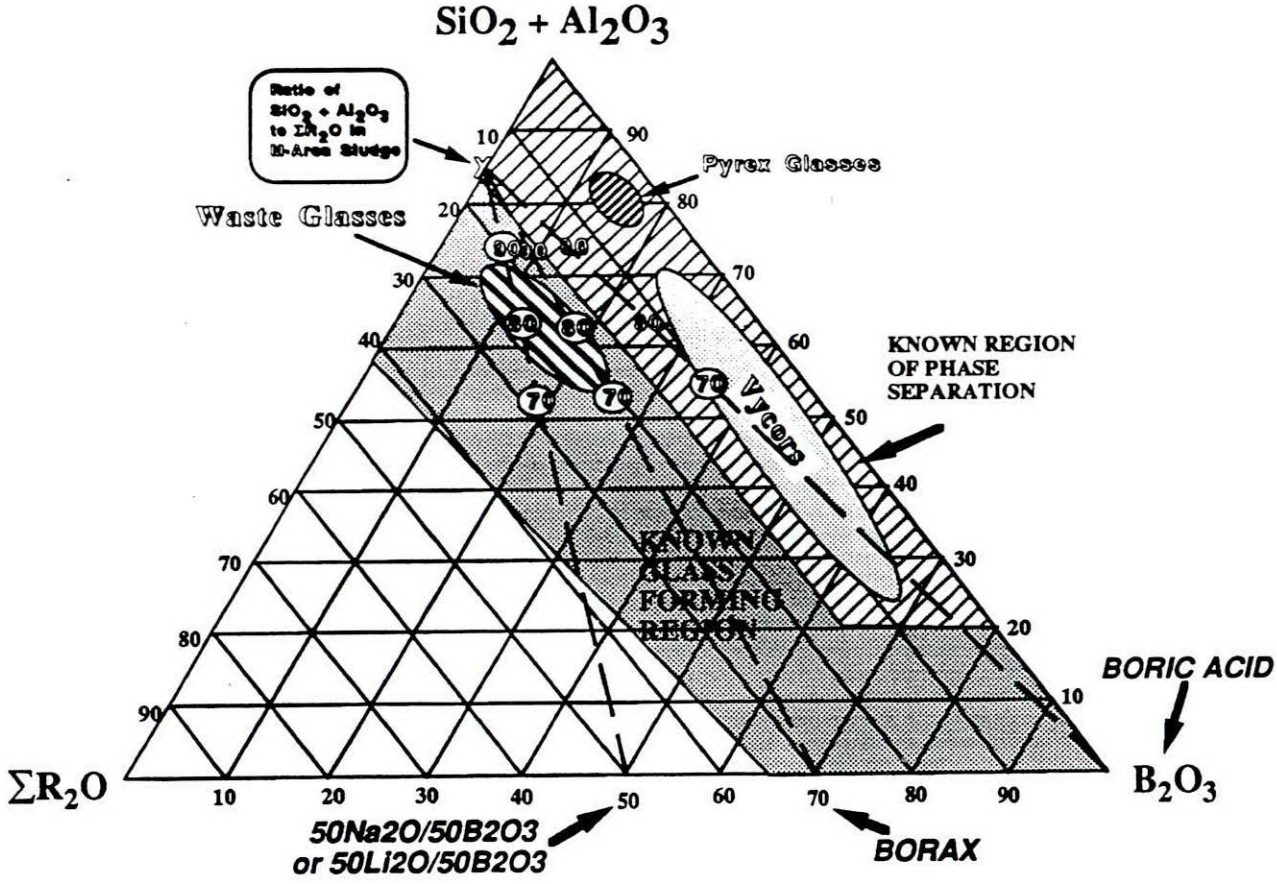

Figure 1. Ternary phase diagram for the system Na_2O-B_2O_3-SiO_2 with the glasses formulated for M-Area sludges superimposed (wt%). The "X" indicates the ratio of SiO_2 + Al_2O_3 to the alkali oxides (R_2O) in the M-Area sludge and filter aid. The stippled area indicates the known glass forming region in the Na_2O-B_2O_3-SiO_2 system. The cross hatched area indicates the known region of phase separation and includes the commercial pyrex and vycor glasses. Glasses in the region of phase separation tend to be less durable than glasses in the other region of the Na_2O-B_2O_3-SiO_2 system.

separation.[4] Phase separation is undesirable for waste stabilization because phase separated glasses tend to be less durable than homogeneous glasses.[5]

Table 2. Glass Formulations and Additives for M-Area Sludge with Spent Filter Aid

Glass	Waste Wt%*	Temp. (°C)	Type of Additive	Type of Glass	Results
M-1	90	>1300	Borax	Borosilicate	Poorly Melted
M-2	85	>1300	Borax	Borosilicate	Poorly Melted
M-3	90	>1300	H_3BO_3	Borosilicate	Poorly Melted
M-4	90	>1300	$CaCO_3$	SLS	Poorly melted
M-5	80	>1250	$H_3BO_3 + Na_2CO_3$	Borosilicate	Poorly melted
M-6	70	1150	Borax + Na_2CO_3	Borosilicate	Homogeneous Glass
M-7	80	>1150	$CaCO_3 + Na_2CO_3$	SLS	Poorly melted
M-8	70	1150	Borax	Borosilicate	Homogeneous Glass
M-9	70	1150	$CaCO_3 + Na_2CO_3$	SLS	Homogeneous Glass

M-area waste glass formulations are being optimized in the region of the borosilicate system-where the high-level radioactive waste glasses are known to form stable homogeneous glasses. The process models developed for high level borosilicate waste glasses can be utilized to calculate the glass viscosity and durability as a function of temperature.

The SLS glass forming system is a well known system used to make window glass and it has been extensively studied by glass chemists since 1925.[6,7,8,9] Soda-silica glass is known to readily incorporate heavy metals.[10] SLS glass formulations have been used for In-Situ Vitrification (ISV) to solidify contaminated soils.[11,12] and a barium analog (soda-baria-silica)

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glass has been used at Fernald to solidify residues from uranium ore processing that contain large amounts of uranium, radium, and lead.[13] For Fernald waste solidification the barium rich glass was chosen due to the high barium content of the waste. SLS glasses have also been successfully fabricated from reactive sodium metal contaminated during efforts to develop sodium-cooled fast breeder nuclear reactors.[14] For the M-Area wastes, Figure 2 demonstrates that the use of reactive silica, in this case the spent filter aid already a part of the waste, extends the known glass forming region in the SLS system.

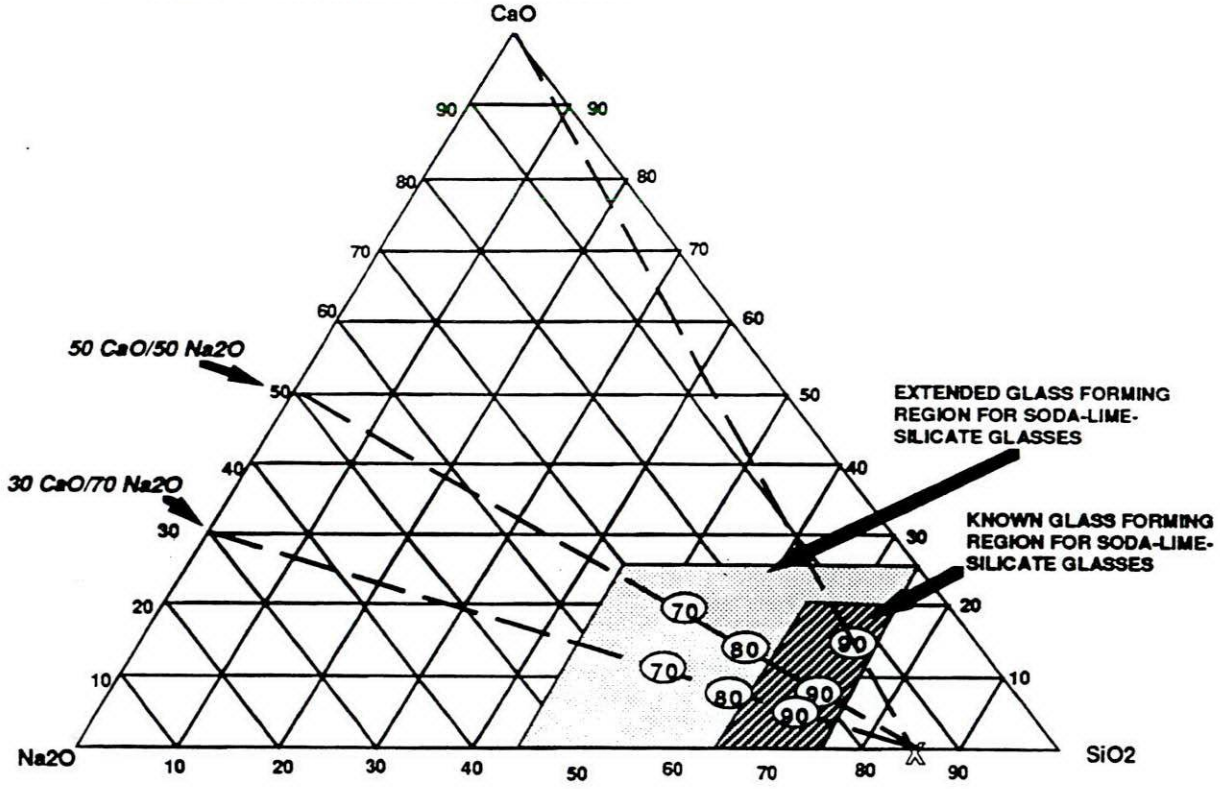

Figure 2. Ternary phase diagram for the system Na_2O-CaO-SiO_2 with the glasses formulated for M-Area sludge superimposed (wt%). The "X" indicates the ratio of SiO_2 + Al_2O_3 to the sum of the alkali oxides (R_2O) in the M-Area sludge + spent filter aid. The cross hatched parallelogram represents the known glass forming region in this system while the larger shaded parallelogram represents the extended glass forming region determined in this study by use of reactive silica additives.

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[12] R.A. Callow, L.E. Thompson, J.R. Weidner, C.A. Loehr, B.P. McGrail, and S.O. Bates, "In-situ Vitrification Application to Buried Waste: Final Report of Intermediate Field Tests at Idaho National Engineering Laboratory," U.S. DOE Report EGG-WTD-9807, Idaho National Engineering Laboraoty, Idaho Falls, ID (August, 1991).

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[14] R. Kumar and J.E. Helt, "Improved Treatment/Disposal of Reactive Metals. Phase II: Technical Research and Development," U.S. DOE Report ANL-91/21, Argonne National Laboratory, Argonne, IL (May, 1991).

To date the TCLP leaching procedure has been performed on one borosilicate glass (M-6) and one SLS glass (M-9). Both of these glass formulations contained 70 wt% waste on a dry basis (Table 1). Both glass formulations had melted to a homogeneous glass at 1150°C. Both glasses passed the TCLP leachate limits for Pb, Ba, and Cr. The borosilicate glass formulation was superior to the SLS glass formulation for retention of Ni and U (Table 3). The SLS glass (M-9) did not meet the Land Disposal Restrictions for Ni but the borosilicate glass (M-6) did.

Table 3. Toxic Characteristic Leaching Procedure (TCLP) and Land Disposal Restriction (LDR) Limits and Response for M-Area Glasses.

Element	Wt% Sludge	Wt% Glass M-6*	Wt% Glass M-9*	Waste Code	LDR Limit (ppm)**	TCLP Leachate M-6 (ppm)	TCLP Leachate M-9 (ppm)
Pb	0.10	0.074	0.074	F006	0.51	<0.2	<0.2
Ba	0.018	0.013	0.013	N/A	100	1.85	1.40
Ni	0.73	0.51	0.51	F006	0.32	0.17	0.74
Cr	0.007	0.005	0.005	F006	5.2	<0.04	<0.04
U	2.65	1.85	1.85	N/A	N/A	0.10	0.45

* M-6 and M-9 contained 70 wt% waste on a calcine oxide basis

** 40 CFR 148, et. al., Land Disposal Restriction for Third Third Scheduled Wastes Final Rule, 55 FR 22 250, June 1, 1990.

The RASP has been independently verified by a waste treatment company, which has been awarded the contract to vitrify the nickel plating sludge. A temporary wastewater treatment facility will be constructed in M-Area. The glass melter is now being designed, and full scale demonstration of the RASP will begin in 1995.

CONCLUSION

Reactive high surface area silica, as a waste form additive, was determined to greatly enhance the solubility and retention of hazardous, mixed and heavy metal species in glass. Highly reactive silica was found to increase the solubility and tolerance of Soda(Na_2O)- Lime(CaO)-Silica(SiO_2) glass (SLS) and borosilicate (B_2O_3-SiO_2) glass formulations to atomistically bond the waste species. Highly reactive silica lowers glassification temperatures, increases waste loadings which provides for large waste volume reductions, and produces EPA acceptable glasses.

The Reactive Additive Stabilization Process (RASP) can be used to vitrify the Metal Finishing Industry wastes of (1) filter cakes from wastewater treatment, (2) waste sludge, (3) filter media, (4) asbestos or glass fiber filters, (5) ion exchange zeolites, and (6) waste cement formulations in need of remediation into glass.

ADVANCES IN THE COLORING OF ANODIZED ALUMINUM

The process of anodizing aluminum goes back several decades, however several new advances and changing environmental needs have changed the coloring methods over the years. The purpose of this paper is to review the history & practices today as well as discuss what the future might bring.

Anodized aluminum can be colored using the following methods:

- INTEGRAL COLORING
- CHEMICAL DYEING
- ADSORPTIVE DYEING
- ELECTROLYTIC COLORING
- COMBINATION DYEING
- INTERFERENCE COLORING
- OTHER COLORING METHODS

INTEGRAL COLORING

Integral color anodizing took advantage of the metallurgical history of the aluminum alloy being colored. It also made use of organic acids in conjunction with sulfuric acid. The process became unpopular during the energy crisis due to the fact that high current densities were employed to achieve the desired "earth tones".

From a finishing standpoint, the process was touchy and required constant monitoring. It was also very alloy dependent, which helped lead to it's demise as a popular finishing process. Electrolytic coloring (which replaced integral coloring) gave all

the advantages without all of the headaches.

CHEMICAL DYEING

In this method of coloring the coloring matter is distributed in the hard aluminum oxide and is inseparably bound to the aluminum. The most common color using this method is various shades of gold that look like brass. The brass shades are produced using either Ferric Sodium Oxalate or Ferric Ammonium Oxalate. The ferric Sodium Oxalate chemical seems to be more stable in the tank and is also more desirable from the environmental aspect. Other colors like bronzes and grays can also be produced using this method but are not very popular.

ELECTROLYTIC COLORING

This method of coloring utilizes alternating current in a metal salt solution. The anodic coating which acts as a capacitor rectifies the current at the barrier layer and allows positively charged ions to electrodeposit at the base of the coating. this metal at the base causes the light to scatter and the degree of scattering determines the color obtained. Generally, the lower the deposit content the lighter the shade.

Using electrolytic coloring can be done using several metals like Co, Ni, Cu, Ag, Sn etc., however the most popular method uses Sn as the metal of choice. Advantages and disadvantages of coloring using Stannous Sulfate are as follows:

ADVANTAGES

- Most conductive
- Easily available
- Less sensitive to contaminants
- Shades produced are widely used in practice
- Colors are very stable
- Sn is not a regulated metal in most treatment facilities
- Multiple colors from one tank

DISADVANTAGES

- Blacks are harder to obtain
- Sn is unstable and so chemical depletion is high
- Chemical cost is high
- Breakdown products sometimes difficult to filter
- Capitol investment in electrical equipment required
- Cannot use titanium racks
- Load size is limited as compared to dyes
- Limited color shades available
- Common stabilizers for Sn are Phenolic and not desirable

ADSORPTIVE DYEING

This method of coloring is the oldest and most widely used. The chromophore of the organic dye is adsorbed throughout the coating and is inseparable after the coating is sealed. The lightfastness of the color is dependent on the amount of dye adsorbed into the coating. Factors that effect dyeing are as follows:

- pH
- Water Quality
- Temperature
- Dyeing time

The advantages and disadvantages of organic dyeing are listed below.

ADVANTAGES

- Very widely used and accepted
- No need for additional capitol equipment
- Reduced tooling costs
- Wide range of colors
- Excellent color stability can be obtained with several dyes
- Blacks are deeper and more intense
- Excellent weathering characteristics can be achieved
- Decades of experience on applicability

DISADVANTAGES

- Improper dyeing can cause fading
- Sealing mechanism more critical
- Some dyes contain Chrome complexes
- Need for waste treatment

COMBINATION COLORING

This method combines the benefits of Electrolytic coloring and organic dyeing to broaden the range of colors that can be obtained. The electrolytically colored deposit which is at the bottom of the coating is applied first followed by organic dyeing.

The advantages and disadvantages using this method are listed below:

ADVANTAGES

- Wider range of colors
- Colors are more muted
- Very light and weather fast colors can be obtained.
- Minimum capital investment required.
- Excellent field data on performance available.

DISADVANTAGES

- Need for aluminum tooling
- Dyes are metal complex
- Sealing very critical

INTERFERENCE COLORING

This method was invented several years ago but has not found widespread applicability because of the complexity of the method. The method involves a reanodizing stage after the conventional anodizing to modify the pore structure. The modified pore structure causes an additional level of interference to the flow of light. This can produce shades of blues, greens, grays and essentially any colors in the spectrum. The advantages and disadvantages are listed below.

ADVANTAGES

- Several colors can be produced from one tank
- Colors are light and weather fast
- Electrolytic coloring method well accepted

DISADVANTAGES

- Process involves several additional tanks
- Additional electrical needs
- Color difficult to control
- Phosphoric acid in reanodizing step difficult to rinse
- Sealing method very important.
- Poor throwing power of coloring tank

OTHER COLORING METHODS

Several other methods are published and patented which use different wave forms and combination of different chemicals that claim to produce colors in the blue and green shades. Some of these are not practical because of the complex electrical requirements and because of the complexity of scaling up using alternating current. A process that we are working on produces shades of blues, greens and grays using techniques that do not require an additional reanodizing tank. With this method we can broaden the range to include blues, grays and greens. There is extensive work going on with different colors using electrolytic methods and the future looks very promising with this technology.

Paper Not Available In Time For Publication

New Electrocoloring Process of Anodized Aluminum

Mores Basaly, Novamax Technologies, Inc., Atlanta, GA

Two-step electrocoloring is a well-developed and well-known process for coloring anodized aluminum. The process has increased in use in the U.S. market since the late '70s and early '80s. It offers many attractive advantages over other techniques of coloring aluminum, such as integral color, dyeing and the over-dye process. The most common used metals are nickel, copper, cobalt, tin or a mixture of their salts. It produces a color range from champagne, light and dark bronze and black. One of the major disadvantages is the process limitation of providing a wide color range. The new process offers attractive new color, while still offering the same advantage of the traditional one.

For copies of this paper please contact:

Mores Basaly
Novamax Technologies
1615 Johnson Road NW
Atlanta, GA 30313
404/799-1292
FAX: 404/799-1873

Neutralization Titration Curves Of Electrolytic Coloring Baths For Anodized Aluminum

By T. Sato and K. Kaminaga

Abstract

Titration curves are plotted to study the co-deposition of metal and metal hydroxide, which markedly affect the shade of colored films and give rise to possibilities of attaining novel colors such as opaque gray and blue.

Introduction

Anodized aluminum is colored when electrolyzed in a solution containing metal ions by alternating current or cathodic current. Metal hydroxides deposit in the pores of anodized aluminum in three different forms, as side reactions of metal deposition when anodized aluminum is electrolytically colored. Control of these metal hydroxides during the electrolytic coloring process is very important for achieving uniformly colored products and for developing novel colors such as red, green, gray, and so on. The authors have studied the neutralization titration curves of electrolytic coloring baths.

Experimental methods

100 ml of the electrolytic coloring bath was titrated with 1 normal sodium hydroxide to obtain the neutralization curve of the electrolytic coloring bath. The concentrations of the baths are shown in Table 1. The generation of precipitate by the neutralization reaction was observed by naked eyes. In the experiments for coloring of anodized aluminum, aluminum plate (99.5% Al) was anodized in 15% H_2SO_4 bath at a voltage of 18 V to obtain anodic oxide film of 10μm, and the oxide film was electrolyzed in the coloring bath by cathodic current.

Experimental results

Three different formations of metal hydroxide

Metal hydroxides are formed in the pores of anodized aluminum in three different ways. This topic is discussed here before the neutralization curves of coloring baths to emphasize the importance of hydroxides in the electrolytic coloring process.

Table 1

Concentrations Of Electrolyzing Baths

Bath	Concentration	Bath	Concentration	Bath	Concentration
H_2SO_4	pH=2.0	$ZnSO_4$	30g/l	$NiSO_4$	30g/l
				H_3BO_3	30g/l
H_3PO_4	10ml/l	$Al_2(SO_4)_3$	10g/l	$NiSO_4$	30g/l
				H_2SO_4	pH=2.0
H_3BO_3	30g/l	$Al_2(SO_4)_3$	10g/l	$NiSO_4$	30g/l
		H_3PO_4	10ml/l	H_3BO_3	30g/l
				$Al_2(SO_4)_3$	10g/l
$NiSO_4$	30g/l	$ZnSO_4$	30g/l	$NiSO_4$	30g/l
		H_3BO_3	30g/l	$Al_2(SO_4)_3$	30g/l
				H_3PO_4	10ml/l

(1) Metal hyrdoxide formed by cathodic polarization of anodic oxide film in sulfuric acid bath

The curve (1) in Fig. 1 shows the relationship between cathodic voltage and electrolyzing time when anodized aluminum is cathodically polarized in the sulfuric acid bath of pH 2.0 by a constant current of 1.0 A/dm^2. The cathodic voltage increases up to 28 V, then it decreases. The rise in cathodic voltage is due to the formation of a gel layer of aluminum hydroxide at the base of the pores. The reason for this formation is explained in detail below.

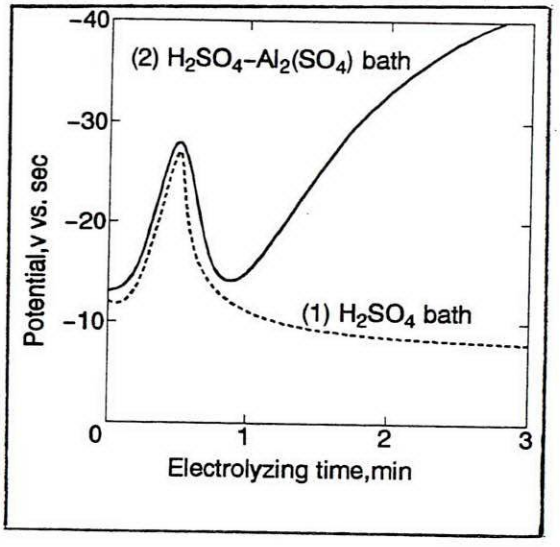

Fig.1– Cathodic polarization of anodized aluminum at constant current density.

Fig. 2 shows the pore structure of anodized aluminum, according to

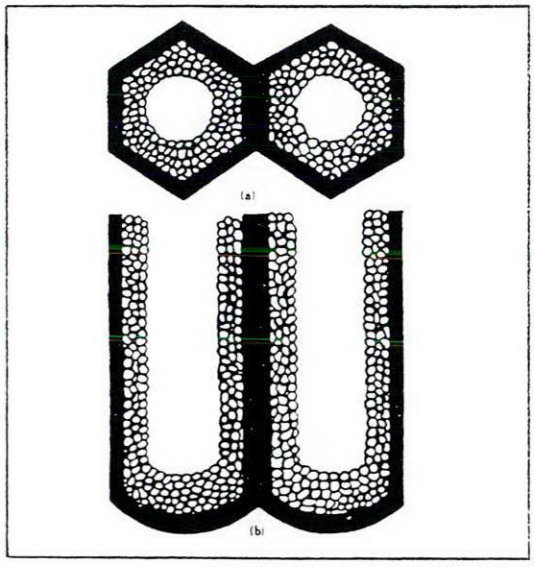

Fig.2-The pore structure of anodized aluminum proposed by Thompson and Wood.

Thompson and Wood. [1] The inner surface of the pores is covered by the sol layer of aluminum hydroxide. The pH of the solution in the pores changes from acidic to alkaline due to the reduction of H^+ ions in the pores when anodized aluminum is cathodically polarized. The sol layer of aluminum hydroxide changes to gel layer, which is an electrically resistive material. [2] This is the reason for the rise in cathodic voltage. The formation of aluminum hydroxide layer when aluminum foil is etched in HCl solution by alternating current, was also reported by Alwitt.[3]

The drop of cathodic voltage in the curve (1) of Fig. 1 after reaching the maximum voltage is due to the destruction of the barrier layer of the anodic oxide film. Many spallings of oxide film can be observed by the naked eyes.

When anodized aluminum is electrolyzed in the $NiSO_4$- H_3BO_3 coloring bath by constant cathodic voltage or by constant alternating voltage, oxide film is colored because of the deposition of nickel in the pores. The cathodic current decreases also. This decrease in cathodic current is due to the formation of gel layer of aluminum hydroxide at the base of the pores.

(2) Metal hydroxide formed by cathodic polarization of anodic film in the $NiSO_4$-H_3BO_3-$Al_2(SO_4)_3$ bath

The concentration of Al^{3+} ions increases after many oxide films are colored in the $NiSO_4$-H_3BO_3 bath, and the shades of the colored films change to a light color since aluminum hydroxide is easily formed in the coloring bath containing more Al^{3+} ions.

Anodized aluminum is not colored when $Al_2(SO_4)_3$ is added to the $NiSO_4$-H_3BO_3 coloring bath. The reason for the non-coloration is also due to the formation of aluminum hydroxide in the pores.

Curve (2) in Fig. 1 shows the relationship between the cathodic voltage and electrolyzing time when anodized aluminum is cathodically polarized in the H_2SO_4-$Al_2(SO_4)_3$ bath at a constant

cathodic current of 1.0 A/dm^2. Two increases of cathodic voltage are observed on curve (2) in Fig. 1. The first increase in cathodic voltage is due to the formation of gel layer of aluminum hydroxide at the base of the pores. The second increase in cathodic voltage is due to the change of Al^{3+} ions to $Al(OH)_3$ precipitate in the pores.

(3) Metal hydroxide formed by cathodic polarization of anodic oxide film in the $NiSO_4$ bath

Green precipitate is observed on the surface when anodized aluminum is electrolyzed in $NiSO_4$ solution by cathodic current or by alternating current. Since the solution on the surface or in the pores of anodized aluminum is alkaline due to cathodic reduction of H^+ ions, nickel hydroxide is formed.

Neutralization curves of electrolytic coloring baths are plotted to investigate the relationship between the formation of metal hydroxide and color shades of anodized aluminum.

Neutralization curves of $NiSO_4$-H_3BO_3 coloring bath

Fig. 3 shows three neutralization curves of the $NiSO_4$ bath, the H_3BO_3 bath, and the $NiSO_4$-H_3BO_3 bath. The black triangle marks on the curves show the locations where precipitate of metal

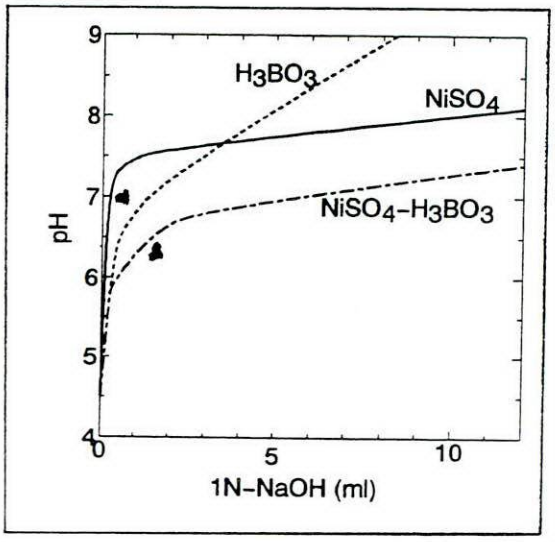

Fig.3-Neutratization titration curues in H3BO3, NiSO4 and NiSO4-H3BO3 baths.

hydroxide was observed by naked eyes. The precipitate of $Ni(OH)_2$ was observed at a pH of 6.8 in the $NiSO_4$ bath, while the precipitate of $Ni(OH)_2$ was generated at a pH of 6.2 in the $NiSO_4$-H_3BO_3 bath. The pH of $Ni(OH)_2$ precipitation in the $NiSO_4$-$H3BO_3$ bath is lower compared to pH of precipitation in the $NiSO_4$ bath. Therefore, it is assumed that nickel hydroxide is formed more easily in the $NiSO_4$-H_3BO_3 bath than in the $NiSO_4$ bath, and the oxide film is assumed to be not colored. However, the result of the electrolytic coloring process contradicts this assumption. Anodized aluminum is not colored in the $NiSO_4$ bath and green precipitate deposits on the surface. The anodized aluminum is

colored in the $NiSO_4$-H_3BO_3 bath because of the electrodeposition of nickel in the pores. This contradiction can be explained by the fact that the ease of formation of hydroxide in the pores does not depend on the pH value of precipitation, but on the titrated amount of NaOH for precipitation of metal ions. The precipitation of hydroxide with a small amount of NaOH means the precipitation of hydroxide by short time electrolysis. On the other hand, precipitation of hydroxide with a large amount of NaOH implies the formation of hydroxide after a longer period of electrolysis.

When 0.01 ml of 1N NaOH is titrated in the $NiSO_4$ bath, the pH of the solution increases to 6.8 and a precipitate of $Ni(OH)_2$ is formed. This means that the pH of the solution in the pores increases rapidly to 6.8 and $Ni(OH)_2$ precipitates by electrolysis in the $NiSO_4$ bath, while the pH of the $NiSO_4$-H_3BO_3 bath has a pH of 6.2 and green colored precipitate is formed when 1.16 ml of 1N NaOH is titrated in the $NiSO_4$-H_3BO_3 bath. The amount of 1N NaOH required to generate a precipitate of $Ni(OH)_2$ in the $NiSO_4$-H_3BO_3 bath is 11.6 times more than that required to generate a precipitate of $Ni(OH)_2$ in the $NiSO_4$ bath. This shows that the time required to generate the precipitate of $Ni(OH)_2$ in the pores of the anodic oxide film in the $NiSO_4$-H_3BO_3 bath by cathodic current is 11.6 times greater than that in the $NiSO_4$ bath. In other words, the precipitate of $Ni(OH)_2$ is formed rapidly in the pores in the $NiSO_4$ bath and the precipitate of $Ni(OH)_2$ is not formed in the pores until a longer time has elapsed in the $NiSO_4$-H_3BO_3 bath, and therefore, oxide film is colored by electrodeposition of nickel in the pores. The results of titration of coloring bath and the results of electrolytic coloring coincide, as explained above.

About the relationship between the coloring of oxide film and the neutralization curves of coloring baths, the amount of titrated NaOH required to precipitate hydroxide is more important than the pH value of the hydroxide precipitation.

Neutralization curves of the coloring bath containing $Al_2(SO_4)_3$

Fig. 4 shows the neutralization curves of the $Al_2(SO_4)_3$ bath, the $NiSO_4$-H_3BO_3 bath, and the $NiSO_4$-H_3BO_3-$Al_2(SO_4)_3$ bath. $Al(OH)_3$ is formed at a pH of 3.8 in the $Al_2(SO_4)_3$ bath. The precipitate of $Al(OH)_3$ is formed at a pH of 4.1 in the $NiSO_4$-H_3BO_3-$Al_2(SO_4)_3$ bath. The titrated amounts of 1N NaOH are 0.63 ml in the $Al_2(SO_4)_3$ bath, and 0.32 ml in the $NiSO_4$-H_3BO_3-$Al_2(SO_4)_3$ bath. The reason for the non-coloring of the anodized aluminum in the coloring bath containing

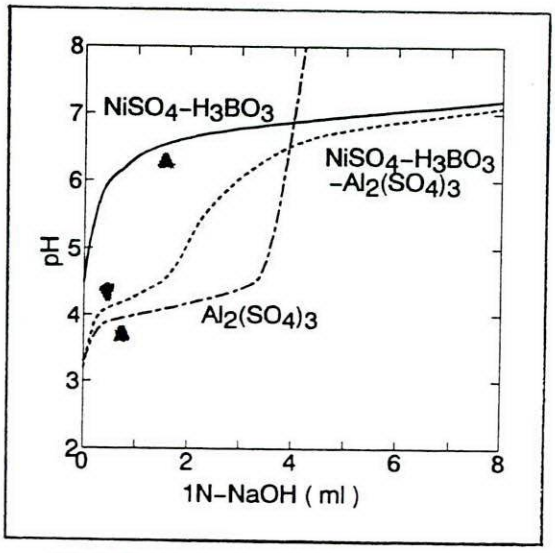

Fig.4-Neutralization titration curues in $Al_2(SO_4)_3$ $NiSO_4$-H_3BO_3,$NiSO_4$ -H_3BO_3-$Al_2(SO_4)_3$ baths.

Al^{3+} ions can be explained by comparing the titration curves of the $NiSO_4$-H_3BO_3 bath and $NiSO_4$-H_3BO_3-$Al_2(SO_4)_3$ bath. In case of the $NiSO_4$-H_3BO_3 bath, the precipitate of $Ni(OH)_2$ is formed by titrating 1.16 ml of 1N NaOH, while the precipitate of $Al(OH)_3$ is formed by titrating 0.32 ml of 1N NaOH in the $NiSO_4$-H_3BO_3-$Al_2(SO_4)_3$ bath. The results of the neutralization curve show that the oxide film is colored lightly or not colored at all in the coloring bath containing Al^{3+} ions, because the precipitate of $Al(OH)_3$ is formed just after the start of coloring electrolysis. Also, the results suggest a strict control of concentration of Al^{3+} ions in the coloring bath to obtain the same shade for colored films.

The precipitate of $Al(OH)_3$ is formed at a pH of 4.1 with 14.50 ml of 1N NaOH in the $Al_2(SO_4)_3$-H_2SO_4 bath. This result shows that $Al(OH)_3$ is not formed easily in the $SnSO_4$-H_2SO_4 bath, which is a popularly used coloring bath in European countries and the United States. In case of acidic tin sulfate coloring bath, the shades of colored films are almost the same even if the concentration of Al^{3+} ions is not controlled strictly.

Neutralization curves of coloring bath containing H_3PO_4

Fig. 5 shows the neutralization curves of $Al_2(SO_4)_3$-H_3PO_4 bath, $NiSO_4$-H_3BO_3-$Al_2(SO_4)_3$ bath, and $NiSO_4$-$Al_2(SO_4)_3$-H_3PO_4 bath. Precipitate is formed at a pH

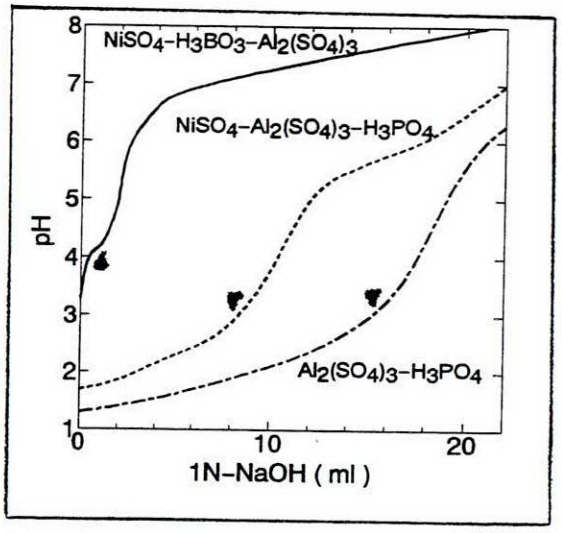

Fig.5-Neutralization titration curues in $Al_2(SO_4)_3$ -H_3PO_4,$NiSO_4$-H_3BO_3-$Al_2(SO_4)_3$ -$NiSO_4$-$Al_2(SO_4)_2$-H_3PO_4 baths.

of 3.0 in the $Al_2(SO_4)_3$-H_3PO_4 bath and also in the $NiSO_4$-$Al_2(SO_4)_3$-H_3PO_4 bath. The precipitate of $Al(OH)_3$ is formed at a pH of 3.8 as shown in Fig. 4. The precipitate formed in the $Al_2(SO_4)_3$-H_3PO_4 bath and in the $NiSO_4$-$Al_2(SO_4)_3$ - H_3PO_4 bath is not $Al(OH)_3$. For chemical conversion films of phosphate compound on aluminum, the crystalline compound of $AlPO_4$ is formed at a pH of 3.0. Therefore, the precipitate formed in the $Al_2(SO_4)_3$-H_3PO_4 bath and in the $NiSO_4$-$Al_2(SO_4)_3$-H_3PO_4 bath is a compound of $AlPO_4$. This precipitate sedimentates rapidly in water, as the compound consists of fine crystalline particles. Therefore, even if the precipitate of $AlPO_4$ is formed in the pores of anodized aluminum, the decrease of cathodic current in the pores is small. $AlPO_4$ also is formed in the pores of anodized aluminum treated with H_3PO_4 by immersion treatment or by re-anodizing. These oxides treated with H_3PO_4 are colored blue by electrolytic coloring. This special function of H_3PO_4 treatment is due to the formation of $AlPO_4$, and $Al(OH)_3$ is not formed by cathodic reaction. Therefore, metal can deposit uniformly in each pore and the colored film shows a blue color.

It is well known that these blue color films cannot be sealed by conventional sealing methods using hot water. The reason for this is also due to the formation of $AlPO_4$ on the walls of the pores of anodized aluminum. Since reactions at the aluminum sites on the anodized aluminum have already occurred, a reaction with water to form a corrosion-resistant $Al(OH)_3$ layer cannot occur.

Neutralization curves of coloring bath containing $ZnSO_4$

Fig. 6 shows the neutralization curves of the $NiSO_4$ bath, $ZnSO_4$ bath, $NiSO_4$-H_3BO_3 bath, and $ZnSO_4$-H_3BO_3 bath. When 0.05 ml of 1N NaOH is titrated in the $ZnSO_4$ bath, the pH of the bath increase to 6.2 and a precipitate of $Zn(OH)_2$ is formed. The pH of the $ZnSO_4$-H_3BO_3 bath

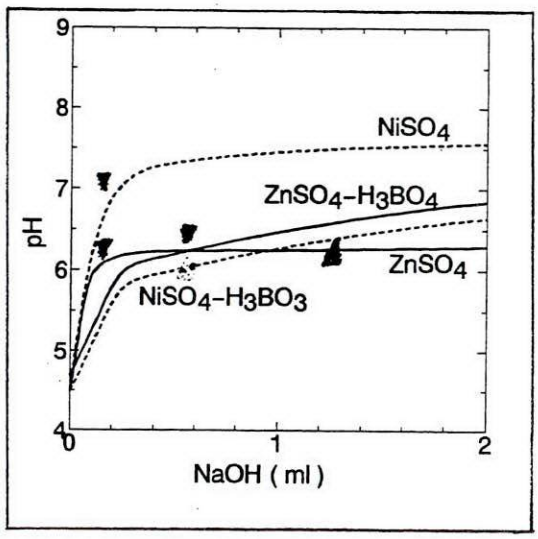

Fig.6–Neutration titration cutues of $NiSO_4$, $ZnSO_4$,$NiSO_4$–H_3BO_3,and $ZnSO_4$ –H_3BO_3 baths.

increases to 6.1 and the precipitate of $Zn(OH)_2$ is formed by titrating 0.60 ml of 1N NaOH. The neutralization curve of the $ZnSO_4$-H_3BO_3 bath is almost the same as that of the $NiSO_4$-H_3BO_3 bath, and the pH value of the hydroxide formation is also almost the same in both baths. However, the amounts of 1N NaOH required to generate the hydroxide is different for the two baths. In the $ZnSO_4$-H_3BO_3 bath, the precipitate of $Zn(OH)_2$ is formed by titrating 0.60 ml of 1 N NaOH, and 1.16 ml of 1N NaOH is titrated in the $NiSO_4$-H_3BO_3 bath to generate the precipitate of $Ni(OH)_2$. This difference is the reason why the anodized aluminum is not colored in the $ZnSO_4$-H_3BO_3 bath, but colored in the $NiSO_4$-H_3BO_3 bath. The precipitate of $Zn(OH)_2$ is easily formed in the pores of anodized aluminum and it prevents the flow of cathodic current. Therefore, the oxide film is not colored in the $ZnSO_4$-H_3BO_3 bath.

Novel colors by co-deposition of metal and metal hydroxide in the pores of anodized aluminum

The addition of $MgSO_4$ to the $NiSO_4$-H_3BO_3 bath has been carried out since a long time in Japan. Stable production of light brown color film is possible in this bath. Fig. 7 shows the cathodic polarization

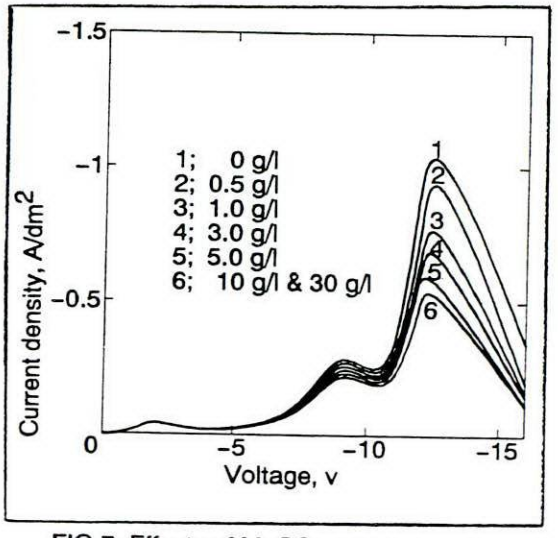

FIG.7–Effects of $MgSO_4$ addition on the cathodic polarization curves of anodized aluminum in the $NiSO_4$ -H_3BO_3 coloring bath.

curve in the $NiSO_4$-H_3BO_3-$MgSO_4$ bath. The amount of $MgSO_4$ added to the coloring bath is changed from 0.5 g/l to 30.0 g/l. There are three current peaks on the cathodic polarization curve. The first peak is due to the reduction of H^+ ions. The second peak is due to the reduction of the dissolved oxygen in the coloring bath ($O_2 + 4H^+ + 4e = 2H_2O$), and the third peak is due to the reduction of Ni^{2+} ions. When $MgSO_4$ is added to the coloring bath, only the third peak decreases. The deposition of nickel in the pores of anodized aluminum is suppressed by the precipitate of $Mg(OH)_2$. However, even if more than 10 g/l of $MgSO_4$ is added to the coloring bath, the third peak does not decrease any more.

This enables stable coloring of the oxide film to a light brown color to be obtained.

Cathodic polarization curves of anodized aluminum in the $NiSO_4$-H_3BO_3-$Al_2(SO_4)_3$bath are shown in Fig. 8 for comparison. The larger the amount of $Al_2(SO_4)_3$ in the coloring bath, the lower is the third peak. The difference between these two polarization curves (Fig. 7 and Fig. 8) indicates that $Mg(OH)_2$ suppresses the nickel deposition moderately and $Al(OH)_3$ suppresses the nickel deposition strongly. The co-deposition of nickel and $Mg(OH)_2$ enables light brown coloring to be obtained. Also, the co-deposition of metal and metal hydroxide enables novel colors to be obtained by the electrolytic coloring process. When anodized aluminum is treated in the H_3PO_4 bath by immersion or by re-anodizing, the sol layer of $Al(OH)_3$ at the bottom of the anodized aluminum changes to the $AlPO_4$ layer. Therefore, the gel layer of $Al(OH)_3$ is not formed and the current decrease or voltage rise in curve (1) of Fig. 1 does not occur. $AlPO_4$ or $Al(OH)_3$ can deposit in the pores when this oxide film is electrolyzed in the $Al_2(SO_4)_3$ bath and the film shows an opaque white shade.

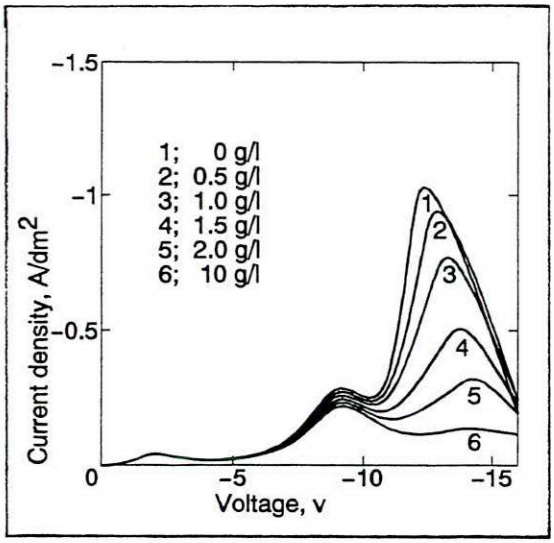

FIG.8–Effects of $Al_2(SO_4)_3$ addittion on the cathodic polarization curves of anodized aluminum in the $NiSO_4$ –H_3BO_3 coloring bath.

Opaque gray film can be obtained in the $NiSO_4$-$ZnSO_4$-H_3BO_3 bath by electrolytic coloring of anodized aluminum pre-treated in the H_3PO_4 bath before coloring. In this case, nickel and $ZnPO_4$ deposit in the pores of anodized aluminum, and the oxide film shows an opaque gray color. Opaque gray or opaque blue films can be obtained in the $NiSO_4$-$Al_2(SO_4)_3$ bath, $CoSO_4$-$Al_2(SO_4)_3$ bath and $NiSO_4$-$MgSO_4$ bath by AC coloring of oxide film pre-treated in H_3PO_4 bath. The biggest problem of these films with novel colors is the low corrosion resistance because of poor sealing effect, and poor light fastness_because of the decomposition of deposited compounds, such as AlPO3, $Al(OH)_3$ or $Zn(OH)_2$.

Blue, green, red, and violet colors can be obtained by electrolytic coloring in the $SnSO_4$-H_2SO_4 bath without pre-treatment of anodic oxide film with H_3PO_4. [4] In this case, the anodized aluminum is re-anodized

in the H_2SO_4 bath or in the $SnSO_4$-H_2SO_4 coloring bath at low voltages between 3 to 5 volts. The reason for the pre-treatment before the coloring process is to avoid the formation of gel layer of $Al(OH)_3$ in the base of the pores and to create a thin barrier layer of the oxide film. These preparations make the metal deposition uniform in each pore and enable blue, green, red, and violet colors to be obtained.

Conclusion

When anodized aluminum is electrolyzed in the coloring bath, metal hydroxide deposits in the pores of the oxide film as a side reaction of metal deposition. Control of this metal hydroxide formation is very important for the AC coloring of anodized aluminum. This is important not only from the point of obtaining uniform coloring but also for development of novel colors by the electrolytic coloring process.

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Electrocolour and Integral Colour Anodizing of Aluminium Alloys

By Xavier Albert Ventura, Ph. D. in Chemistry

The properties produced by integral coloured anodic oxide films and sulphuric acid, oxalic acid, maleic acid and different anodizing aluminium alloys -Si, Mg, Fe, Cu- are studied. A two stage anodizing procedure was employed. The influence of alloy and solution composition, temperature, concentration, voltage, ampere, time from optimization simplex and anodizing conditions are considered.

An oxide disordered structure is formed in the initial stage while an oriented structure is obtained in the second stage.

The changes in colour parameters obtained with complex forming electrolytes are explained.

Anodizing solutions: sulforsalicylic acid, sulphuric acid, sulfamic acid.

Anodic Oxidization

Unlike the electrocoating processes in which the layer towards the electrode outer part, in anodic oxidization the layer growth is towards the inner part of the metal and therefore consuming it. If we concentrate on the faradic conversion of Al to oxide, we observe that for each gram of metal consumed, 1.889 grs. of oxide is obtained. The coating relation is defined as the oxide amount formed per gram of reacted aluminium, which experimental value double weighting measurement show us the efficiency of the anodic process.

The classification of the anodized layer during the formation process, can be made in accordance with the dissolvent amount of the electrolyte in that layer.

Non-Porous Layer

The non porous layers are those which do not retain dissolvent in the formed oxide layer and therefore, are compact, dielectric and thinner. The layer thickness initially depends on the applied potential and temperature. In a dielectric environment if the potential applied is high enough, a strong discharge is produced, thus perforating the layer. We call this effect layers breakage.

The electrolytes causing this type of breakage are aqueous dissolutions of borates, tartres, succionates, citrates, phosphates and carbonates. The breakage potential for the non porous layers, oscillates between 500 and 700 V and refers to thickness between 7,000 to 10,000 Å. If the applied potentials are lower, the current density becomes almost zero and the layer growth is gradually slowed down until becoming non-existent.

The velocity formation in the initial layer increases lineally in relation to the current density and the coating relation value near to the theoretical value of 1.889 as for a process that has not secondary reactions.

Porous Layers

Porous layers are those which do not hold dissolvent in the formed oxide layer. They are gelatinous and therefore thick and soft. In the porous layer the coating relation has a value of 1.35 to 1.56 due to the existing competitive effect of dissolution against that of oxide formation. The porous layer because of its physical characteristics cannot serve the purpose of being a protective layer. This is achieved through sealing. This seems to transform the superficial layer in small crystalline nuclei of hidratated oxide which several authors believe to be boehmite.

Characteristic Regarding Definition of Porous and Barrier Layers

Anodic aluminium oxide structures fall into two general categories: The porous layer structures and the non porous, or barrier-layer structure. Porous layers are so named because of the microscopic pore channels that run perpendicular (or at a slight angle) with respect to the metal substrate. These pore channels may be well ordered throughout the layer, or they may be fever and more randomly distributed, depending on the anodizing conditions and electrolyte.

A particular type of anodizing response is generally used to classify an anodic oxidized porous layer oxide. The voltage vs. time curve, for anodizing at constant current density, will generally be flat or will rise only slowly. Once anodizing is established, little or no voltage increment is required to maintain a

constant current density, all other anodizing conditions being unchanged, and the film continues to grow to inappreciable thickness. Electrolytes that tend to dissolve aluminium oxide, either through complex formation or direct solubility, can be made to yield anodic porous layers. A common example is sulphuric acid. Porous oxide are also formed with phosphoric, chromic and many dicarboxylic acids, including polyfunctional mixed acid electrolytes such as 5-sulfosalicylic plus sulphuric acid, or other acids containing functional groups that contribute to complexing -chelating- ability. Some of these, however, require a continued voltage increase in order to maintain a constant current density, but these voltage increments are still less than that characterized by barrier type anodizing response, to be discussed next.

The non-porous or barrier layer, oxides are generally characterized by a glass-like insulating structure. This high dielectric oxide comprises most of the voltage barrier-voltage drops during anodizing. While this oxide is always found along with porous-layer films, lying next to the metal substrate, below the porous layer, it can also be prepared by itself. The anodizing response that characterizes only the formation of this type of oxide layer is entirely different from that of a porous-layer film, which contains both barrier and porous layers. The anodizing voltage vs. time relationship is usually linear but with a sharp upward slope, at constant current density. Unlike that of the porous layer, the applied voltage must be continually increased in order to maintain a constant current density. Also unlike the porous layer situation, the anodizing current density will rapidly fall down toward zero if applied voltage is held at a constant value. For a pure barrier layer electrolyte, where no porous layer is formed, the final voltage reached during anodizing is thus an indirect measure of the quantity of coulomb spent in film formation: a constant current/time relationship as the voltage is increased, with negligible current passing after the applied voltage reaches some preset maximum value. A voltage to film thickness relationship is often applied to this situation: between 10 and 20 Å/volt, depending on the electrolyte and anodizing conditions employed. Pure barrier layer oxide may be prepared in electrolytes with little or no complexing or solubility toward alumina, although, to this end, the anodizing conditions need to be rather specific. Boric acid or near-neutrality ammonium tartrate provide this type of aqueous electrolyte.

There are, however, some apparent anomalies in the formation of barrier and porous layer oxides. If aluminium is first anodized in sulphuric acid, a barrier layer will form first, followed by, and above this, the growth of a thicker, clear and colourless, porous layer. If this anodized metal is next anodized in an integral colour electrolyte, the coloured porous layer -a characteristic of this electrolyte- will be situated between the barrier layer and the first formed clear sulphuric acid film. Reversing this situation and anodizing first in the integral colour electrolyte, will put the coloured porous layer above the clear -sulphuric anodized- porous layer. It therefore appears that the first layer to form will appear above subsequent layers, when the coating is prepared step-wise in successive anodizing electrolytes.

But why, then, is the barrier layer always situated beneath the porous layer or layers? Anodizing first in boric acid -a "pure" barrier layer electrolyte- and then in sulphuric acid produces the same results as anodizing first in sulphuric and last in boric acid. The barrier layer is situated next to the metal substrate and underneath any porous layers that might have been formed. While many diverse explanations have been set forth to explain this, the more plausible involve a series of oxide transformation mechanisms.

Electrochemical Process

Anodizing is that on the anodic half-cycle, at each electrode, when film formation takes place and that on the cathodic half-cycle film reduction does not take place and the continuous film growth can occur.

On the anodize half-cycle the main reaction is clearly oxide film formation expressed simply as

$$2\,Al + 6\,OH^- \rightarrow Al_2O_3 + 3H_2O + 3e^-$$

As the voltage is increased some film dissolution occurs, leading to conventional porosity

$$Al \rightarrow Al^{+3} + 3e^-$$

$$Al_2O_3 + 3\,H_2O \rightarrow 2\,Al^{+3} + 6OH^-$$

or

$$Al_2O_3 \rightarrow 2\,Al^{+3} + 1/2\,O + 6e^-$$

and some direct oxygen evolution may occur:

$$4OH^- \rightarrow 2H_2O + 4e^-$$

A side reaction also take place at higher voltage but probable not to any significant extent, oxidation of sulphate

$$2\,SO_4^{2-} \rightarrow Sx\quad O_2^{-2} + 2e^-$$

On the cathode half-cycle hydrogen evolution is the main reaction

$$2\,H^+ + 2e^- \rightarrow H_2$$

With the reduction of sulphate as a minor side reaction

$$SO_4^{-2} + 8H + 6e^- \rightarrow S^o + 4\,H_2O$$

or

$$SO_4^{-2} + 10\,H + 8e^- \rightarrow H_2S + 4H_2O$$

Its occurrence is clear from both the smell of H S and the presence of sulphur in anodic film present ad S or S and quite distinct from SO_4^{-2} which is usually trapped residual acid electrolyte (4-8).

Two other reactions, theoretically possible at higher voltage, do not in practice occur and can be disregarded. They are alumina reaction

$$Al_2O_3 + 6H^+ + 6e \rightarrow 2\,Al + 3\,H_2O$$

and aluminium electrodeposition

$$Al^{+3} + 3e \rightarrow Al$$

Any process improvement based on the electrochemistry will normally relate to elimination of the sulphate reduction reaction and two possibilities exist.

Firstly, the overvoltage for sulphate reduction could be raised or the overvoltage for hydrogen evolution lowered, thereby making sulphate reduction less favourable. Secondly, allowing sulphate redaction to take place but directing the sulphur or sulphide, thus formed away from the film preferably as some soluble species.

Experimental

The majority of the work to be discussed was carried out on commercial purity aluminium. Samples measuring 50 mm x 50 mm were cut from the sheet.

The following pre-treatment was employed, prior to nickel fluoride cold sealing and hot water sealing.

Cleaning: All samples were cleaned for 10 minutes, at 50-65°C,in a 50-60 gr/l solution of proprietary alkaline cleaner.

Rinse.

Etching: Samples were etched for 10 minutes,at 60°C, in a proprietary long life solution, containing 60 ml/l etch bath, approximately equal to 50 gr/l of free caustic soda.

Rinse.

Desmutting: First,the surface was wiped with cotton wool under tap water,then, dipped in 20% nitric acid, at room temperature,for two minutes.

Rinse.

Anodizing: Direct-current anodizing was performed at a constant current density of 1.5 A/dm, in an electrolyte containing 165 gr/l sulphuric acid in deionized water at 20°C.

Rinse.

Electrocoloring Process, Electrochemical Parameters and Integral Colour

Cold Sealing:

Cold sealing took 15 minutes at 25°C in a 6 gr/l Ni F .4H O solution, at a Ph of 6.

The two final rinses removed excess chemical from the surface.

Hot Sealing:

Hot sealing in deionized water with cobalt acetate, 1 gr/l, time 40 minutes,temperature 96°C.

Finally samples were rinses once more in deionized water at 60°C

The Aluminium Substrate/Porous oxide/Electrolyte System

The oxide film formed on aluminium during anodization consists of a highly complex porous outer region and an inner barrier-type oxide. The simplified cross-section representation of the oxide layer, given in Fig. 1, identifies both the barrier and porous layers. The base of each hexagonal shaped cell is scalloped as a result of localized anodizing current distribution.The exact distribution of pores across the surface primarily dependent upon the topography of the substrate. High resolution scanning electron micrographs show that cells grow perpendicular to the substrate and that numerous pore termination sites exist. While the complexity of the oxide makes it impossible to obtain an exact electrochemical model for the anodized surface, generalized models assuming idealized pore structures have been

developed. Fig. 2 gives an equivalent circuit model for the anodic oxide.

The circuit has been laid out to allow a direct comparison between the model and the schematic model ALCOA. The barrier layer can be viewed as a semiconductor,having a breakdown potential E above which electrons will flow. The pores act as conductive pathways between the bulk electrolyte and the barrier layer,the limiting factor being the resistance of the solution within the pore. The bulk oxide is resistive in nature, exhibiting a characteristic capacitance when in contact with electrolyte. The entire oxide can, therefore, be represented by a complex series-parallel RC network. The non porous regions of the oxide are represented by a resistor (Ro) in parallel with a capacitor (C_o). The electrochemical response of the porous regions is modeled by the pore resistance (R_1) in series with a parallel with a capacitor (C_1). The electrochemical response of the porous regions is modeled by the pore resistance (R_2) in series with a parallel RC network (R_2C_2) representing the barrier layer. Each of the electrical parameters above are dependent upon the chemical composition of the oxide, the type of electrolyte and/or the structure and thickness of the oxide.

The electrolytic colouring of anodized aluminum involves the application of an AC voltage between the work and appropriate counter electrodes. The electrochemical response of the anodized surface to the applied potential Fig. 3,4 can be seen, typical current and voltage-time profiles for electrolytic colouring using a tin-based electrolyte. A delay in the current response for the system is observed during the first few seconds of the voltage ramp. This delay corresponds to the time it takes for the voltage to surpass the leak potential of the barrier layer. A sharp rise in the current is observed near the breakdown potential and is accompanied by the onset of tin deposition as well as hydrogen and oxygen evolution. Therefore, the breakdown potential corresponds to the overpotentials for these three reactions on the barrier oxide. The current is observed to peak at approximately the same time as the colouring voltage is reached, then fall rapidly to less than 50% of the peak value. The current is then observed to fall logarithmical as the colour cycle continues.

The total current-time profile presented in Fig. 3 is useful for obtaining information about the overall reaction kinetics but is insufficient for evaluating colouring efficiency. The anodic and cathodic current-time profiles for the cycle are required for this evaluation. Colouring will proceed only if there is a net cathodic current flowing in the system.When a pure sinusoidal waveform is applied to a reversible to a reversible system,the rate of deposition will equal the rate of dissolution, that the current waveform is catholically rectified during the colour cycle.The degree of current rectification is observed to change over time. Analyzing the system it becomes obvious that the source of the rectification is the barrier oxide which has already been shown to be semiconductive in nature. Researchers have observed that the barrier oxide thickness, and eventually flattens out, during the anodic half cycle. The properties of the oxide are, therefore, continuously changing accounting for the variations in current rectification.

The equivalent circuit for the anodic oxide given must be modified to take into account the rectifying characteristics of the barrier layer. A rectifier circuit consisting of four diodes and two resistors has been added in parallel with R_2 and C_2. The introduction of these components to the circuit has little effect on the overall impedance response of the system.

Factors Influencing the Electrochemical

The electrochemical response of the system during two-step colouring is dependent upon a number of factors including the thickness and nature of the oxide,the electrochemical characteristics of the colouring electrolyte, the electrochemical characteristics of the colouring electrolyte, racking and tank geometry, the counter electrodes and the counter electrode-to-work surface area ratio, system inductance, and the magnitude and shape of the applied voltage-current waveform. Each of these factors in and of itself can influence colour quality and colouring efficiency. However alloy these variables are interactive and the proper combination is required to obtain optimum efficiency.

The thickness and nature of the oxide, particularly of the barrier layer, effects the impedance and semiconductor characteristics of the system. The thickness of the barrier layer has been shown to greatly influence the rectification of the current waveform. The breakdown potential for the oxide increases with thickness as does the total impedance. The composition of the oxide influences overall conductivity. While the anodized film on pure aluminium exhibits a uniform distribution of aluminum and oxygen through the oxide the distribution of these species through the oxide formed

on an alloy can be altered as a result of cation inclusions or vacancies. The presence of the copper prevents rectification and, therefore, inhibits colouring. An ion incorporation in the oxide can also influence conductivity.

The electrochemical characteristics of the electrolyte dictate the proton, electron and ionic transport mechanisms and the reaction kinetics. The solution resistance must be low to minimize the voltage IR drop between the work and counter electrodes. There should also be a high degree of ionic mobility to assure good transport of the depositing species to the work. The electrolyte also influences the magnitude of the reaction overpotentials on both the work and counter electrodes. Additives are available to reduce specific reaction pathway and lower the activation energy. Improved colouring efficiency is, therefore, achieved by increasing electron and ion transport into recessed areas about the work and altering the reaction kinetics to allow deposition to occur at a greater rate.

Proper racking is critical to assuring good colouring efficiency. The rack must have a low internal resistance and be capable of carrying high current with minimum Joule
heating (which, in turn, increases electrical resistance. Junction potentials between work pieces and the rack must be minimized by utilizing similar alloys. The spacing between work pieces on a rack is regulated by the throwing power of the bath, reaction kinetics and ionic diffusion.

When a reaction occurs at an electrode, the concentration of the reacting species becomes depleted near the electrode surface. A concentration gradient develops with the reacting species reaching the surface by diffusion along the gradient or via migration. The size of the concentration gradient depends upon the reaction rate and the migration or diffusion coefficient for the reacting species. Close racking minimizes the number of available diffusion pathways. The evolution of hydrogen or oxygen further inhibits ionic diffusion. Thus, the spacing between work pieces must be such as to allow uniform diffusion/migration of ionic species to all surfaces.

The overall geometry of the colouring tank is another factor which dictates colouring performance. A side from the tank dimensions, tank geometry includes the configuration (size, shape and positioning) of the counter electrodes. The current between two electrodes follows "lines of flux". These lines of flux are usually non-linear, the degree of non linearity being dictated by the shape of the work or counter-electrode. (It should be noted that lines of flux always originate and end perpendicular the electrode surface). Thus, it should be possible to "direct" electron and ion flow by carefully choosing the shape of the counter-electrodes. The spacing between the work and counter-electrodes in actual production situations diminishes the effect of counter-electrode shape. Shapes such as tubular, angle, and channel have been effective in electrolytic colouring application.

In conjunction with the tank geometry, the counter-to working electrode surface-area ratio must be taken into account to assure efficient colouring. In addition to dictating the density of the lines of flux, the surface-area ratio decreases below 1.0, the current density across the counter electrode surface increases in order to support the deposition reaction. More work must be done on the electrode to overcome so called "polarization resistance", an intrinsic tendency to resist current flow when an external potential is applied. Thus, the maximum allowable surface area ratio will be determined by the current limit under polarization.

The degree of counter electrode polarization is dictated by the type of electrode material. Stainless steel is highly corrosion resistant and is a common electrode material due to its long life in acid solutions. However, the same factors which improve corrosion resistance also result in a high polarization resistance Rp. Steels which are less corrosion resistant exhibit lower Rp values and allow current to flow more readily. Electrodes made from the deposition material (tin in the case of this sulphate baths) are only slightly polarized. Graphite electrodes do not polarize allowing unrestricted current flow. It should be noted that the work-to-counter electrode surface area ratio for graphite is limited by the localized current throw of these electrode. Thus, current flux can also be influenced by selection of the counter electrode material.

One factor which is often overlooked when evaluating the colouring process is the influence of system inductance. An inductor, such as a coil, produces an electromagnetic field which does work on the system.

This work manifests itself as an increase in potential at the tank. The system inductance is proportional to I (I being the current) and, therefore, the inductive effects are more severe for larger loads. One source of the system inductance has been traced by the bussing between the power supply and the

tank. Bussing techniques have been developed to virtually eliminate inductance problems.

The voltage ramp rates and hold (or delay) times are critical for obtaining uniform metal deposition. The charging characteristics of the barrier layer, as well as the overall polarization/relaxation responses of both the work and counter electrodes, are dependent upon not only the frequency of the waveform but the rate at which the potentials applied. During slow ramps a charge builds across the potential is applied. During slow ramps a charge builds across the barrier layer limiting the peak current densities. Increasing the ramp rate reduces the amount of capacitive charging thereby allowing more current to flow. Spalling occurs when the instantaneous reaction rate greatly exceeds the diffusion/migration rate of hydrogen and oxygen from the base of the pores. The uniformity of deposits within the pores is dependent upon the current distribution, electrical field strength and the migration/diffusion rates of the electrolytic species. A high electrical field strength, resulting from too rapid a voltage ramp, can lead to metal reduction within the pore rather than at the pore base. Metal deposition high within the pore could result in overplating as the colour density of the deposit. The structure of the deposit and the location within the pore effect the refractive properties of the surface and, therefore,the perceived colour.

Oxide layer modification

Method for altering the electrochemical response of anodized aluminium is to modify the surface oxide, in particular the barrier layer. Several two-stage anodizing techniques have been introduced in recent years as a means of modifying the structure of the porous layer. While the barrier layer does undergo modification during the second anodizing treatment, it is the altered metal deposition pattern during AC application which has the greatest effect on colouring. During DC/AC colouring the work is subjected to an anodic treatment while immersed in the colouring electrolyte. The DC ramp rate and hold time are set to give the most uniform current distribution across the surface. The DC treatment is then followed by a standard AC colour cycle.

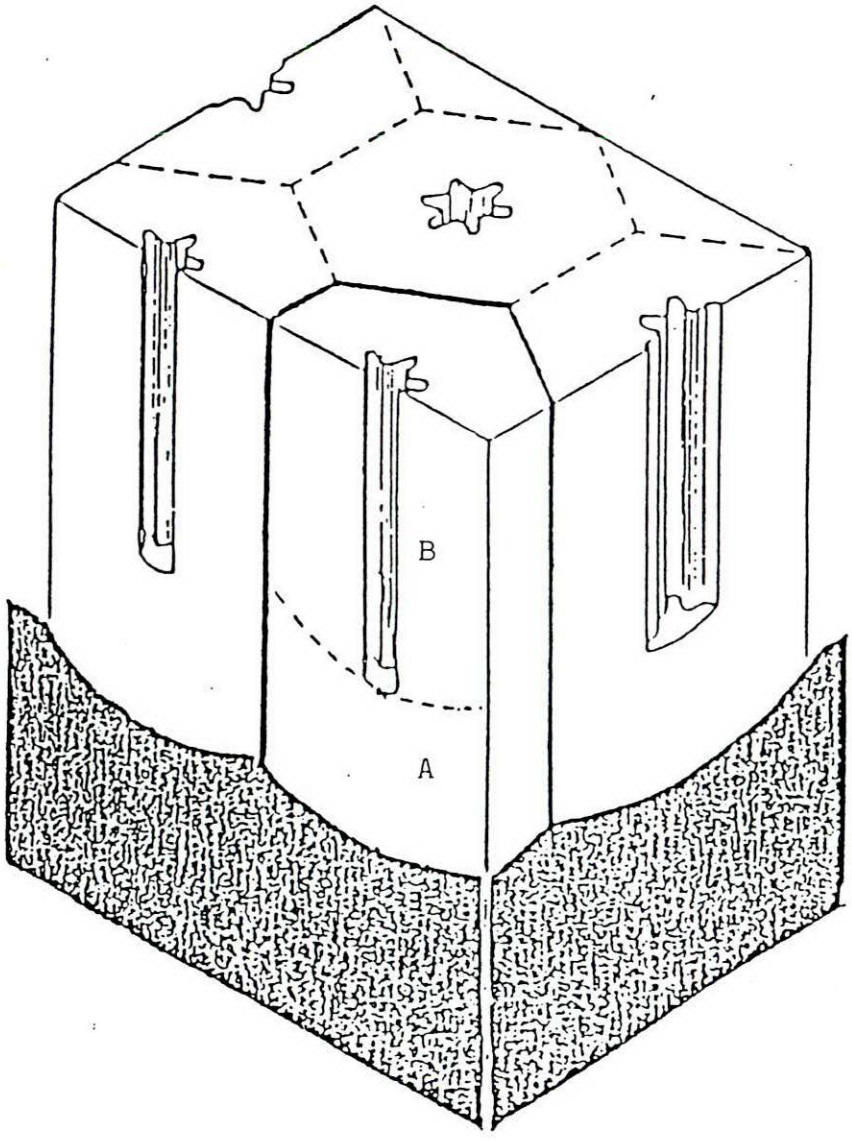
Two changes in the electrochemical response of the system have been observed as a result of the DC treatment. First there is often an increase in the peak AC current density, a manifestation of the increased impedance and modified rectification characteristics of the barrier layer. The second effect is an apparent increase in throwing power, with improved colour uniformity. What is actually observed is the inhibition of colouring on surface closest to the counter electrodes as a result of preferential treatment. The preferential treatment of the outermost surfaces is readily accepted when the throw characteristics of the bath are taken into account. The AC current flow across these surfaces is decreased resulting in a more uniform metal deposition between outer and inner surfaces.

The application of DC/AC offers little benefit in reduction of colouring time in the electrolytic process, but the improved colour uniformity (throwing power) observed for DC/AC can be translated into significant improvement in size of loads processed. Field experience indicates a minimum of 20-30% increase in load size replaces when a DC/AC process using conventional sine wave AC. Increases in productivity are attributed to electrical changes only, with colouring tank configuration and colouring bath chemistry remaining constant.

Conclusions

Summing up, in the absence of any other contribution, the alloy composition seemed to be colour determining, as happened in solution which were not complex forming electrolytes resistance part in parallel with the capacitance. The two-step colouring process for anodized aluminium has been shown to be a dynamic electrochemical process dependent upon the physical and electrical characteristics of the oxide layers. The deposition of metal within the porous layer is a result of the cathodic rectification of the current/voltage waveform by the barrier layer. Improved colouring speed can be achieved by cathodically offsetting the applied waveform. The extent to which colouring is enhanced independent upon the magnitude of the offset and the method by which the waveform is applied to the work. Colouring has been presented as a means of improving colour uniformity through the modification of the barrier oxide.

While DC/AC colouring does not necessarily improve colouring speed, use of DC/AC can improve productivity by increased load size.

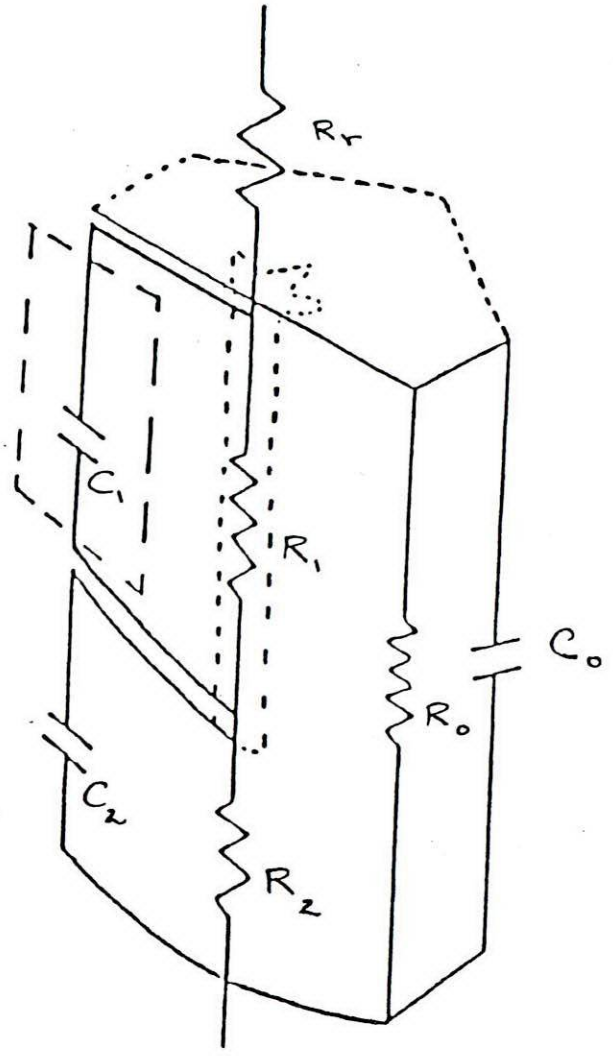


SIMPLIFIED CROSS SECTION - POROUS ALUMINUM OXIDE LAYER

A: Barrier Layer

B: Porous Outer Layer

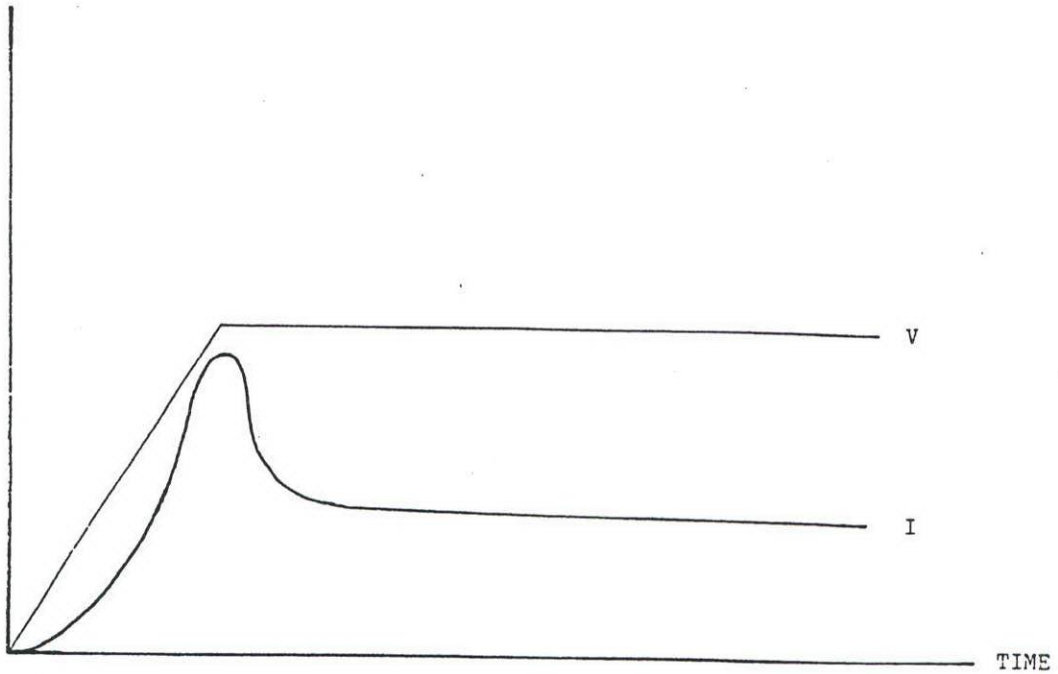
FIGURE 1



EQUIVALENT CIRCUIT

(Representing Porous Aluminum Oxide Layer)

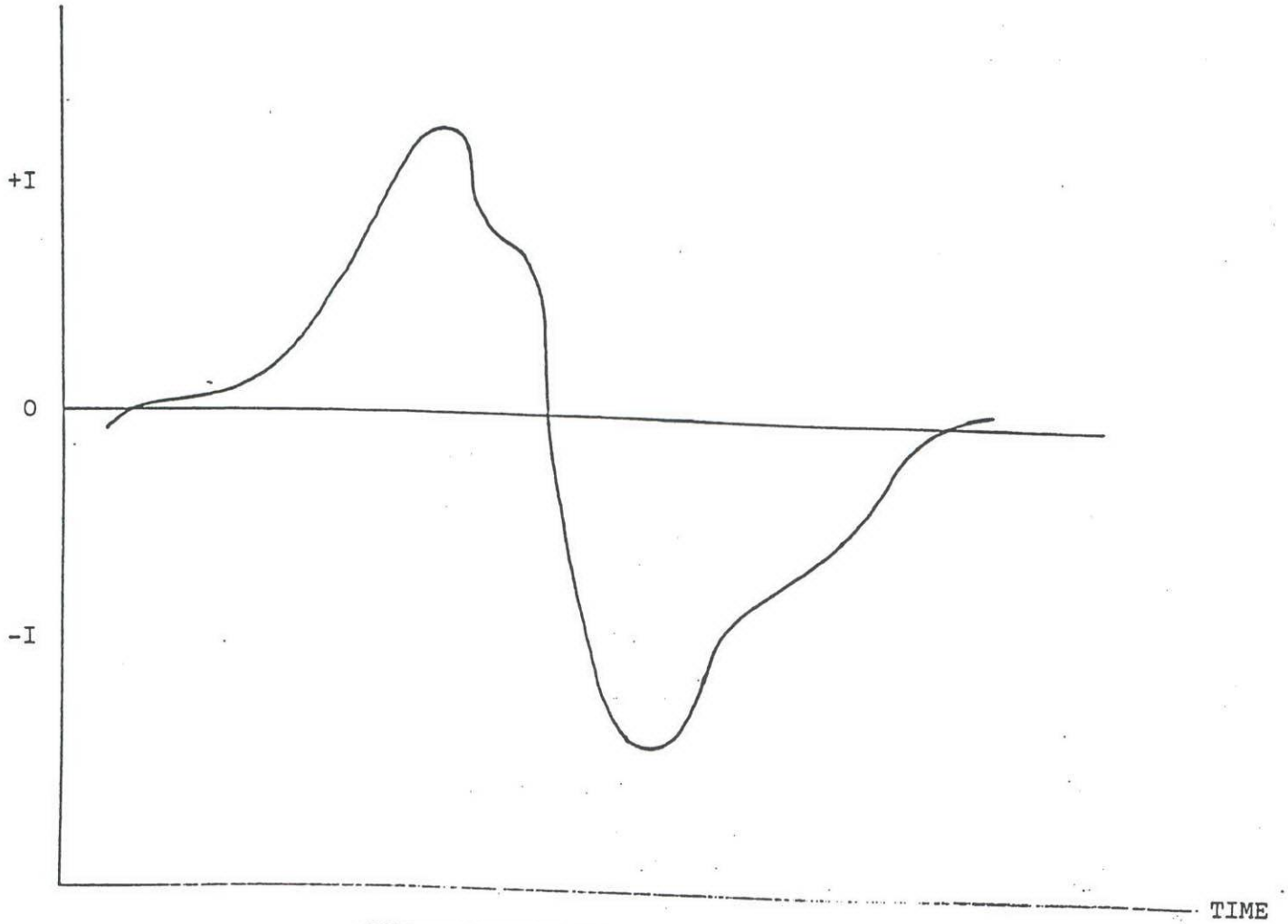
FIGURE 2



VOLTAGE-CURRENT PROFILE

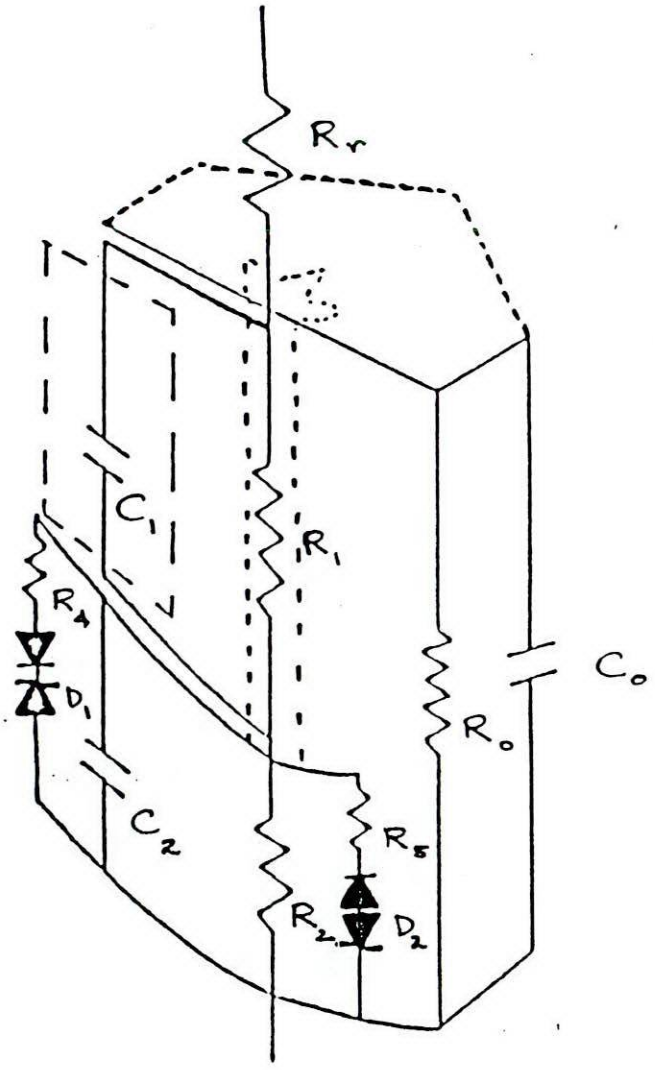
ELECTROLYTIC COLORING

FIGURE 3



CURRENT DURING ELECTROLYTIC COLORING

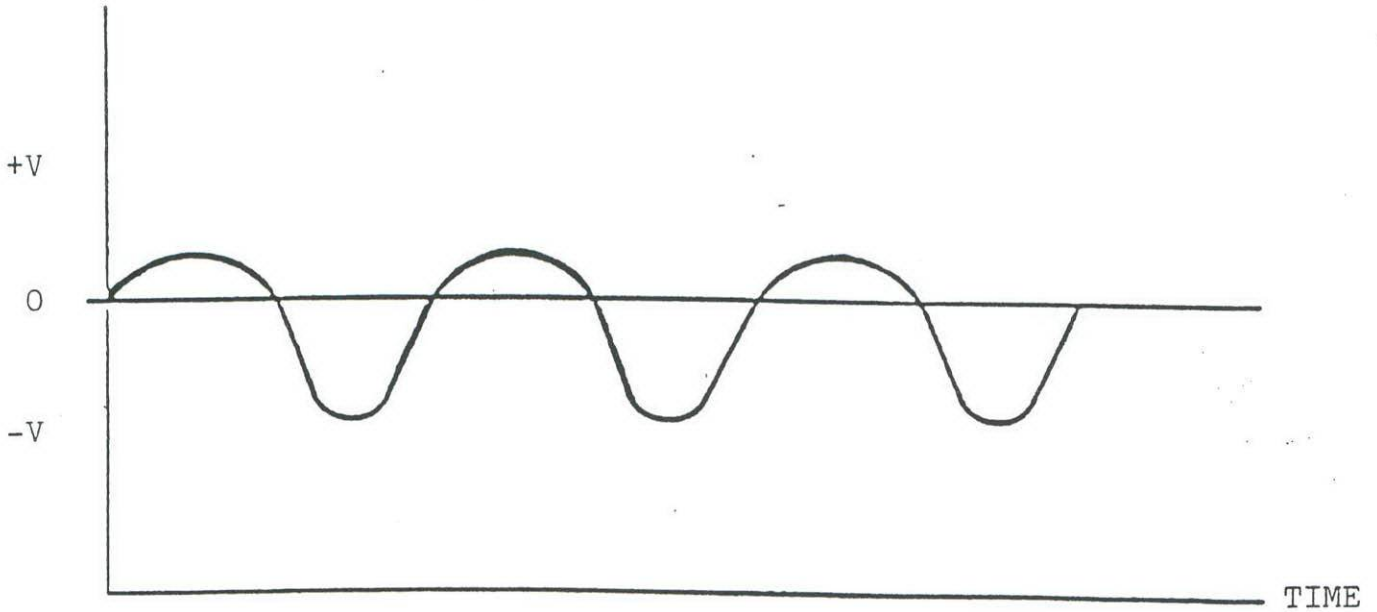
FIGURE 4



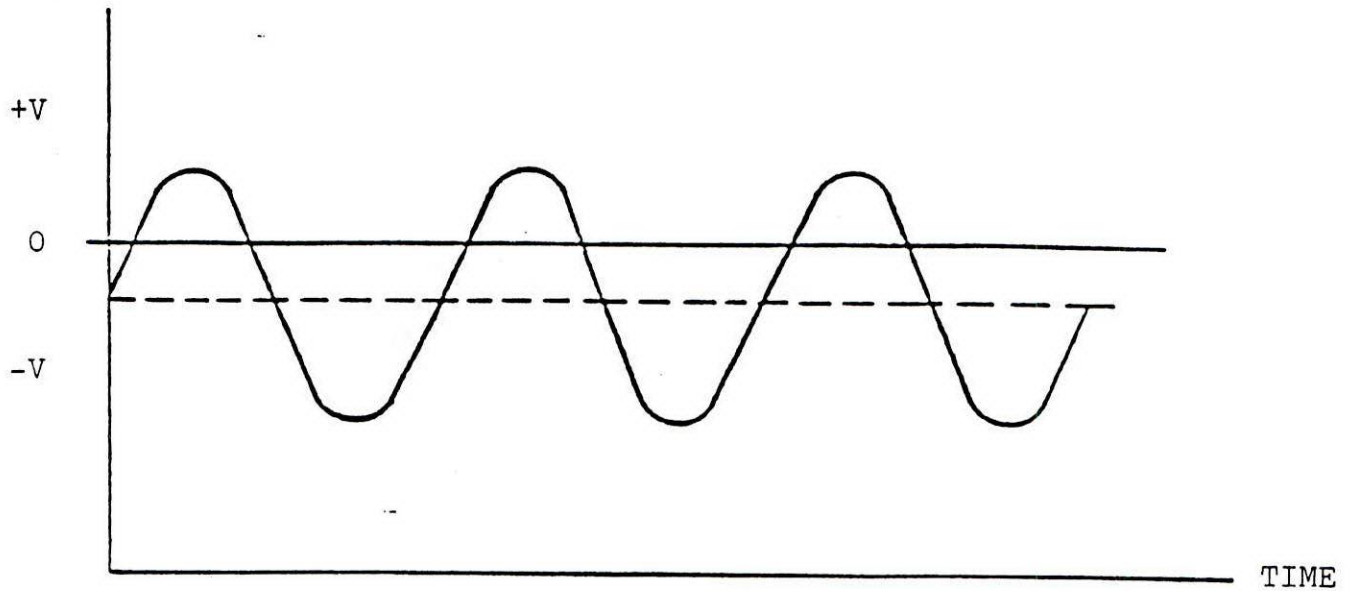
EQUIVALENT CIRCUIT

(Modified to Consider Rectification Characteristics of Barrier Layer)

FIGURE 5



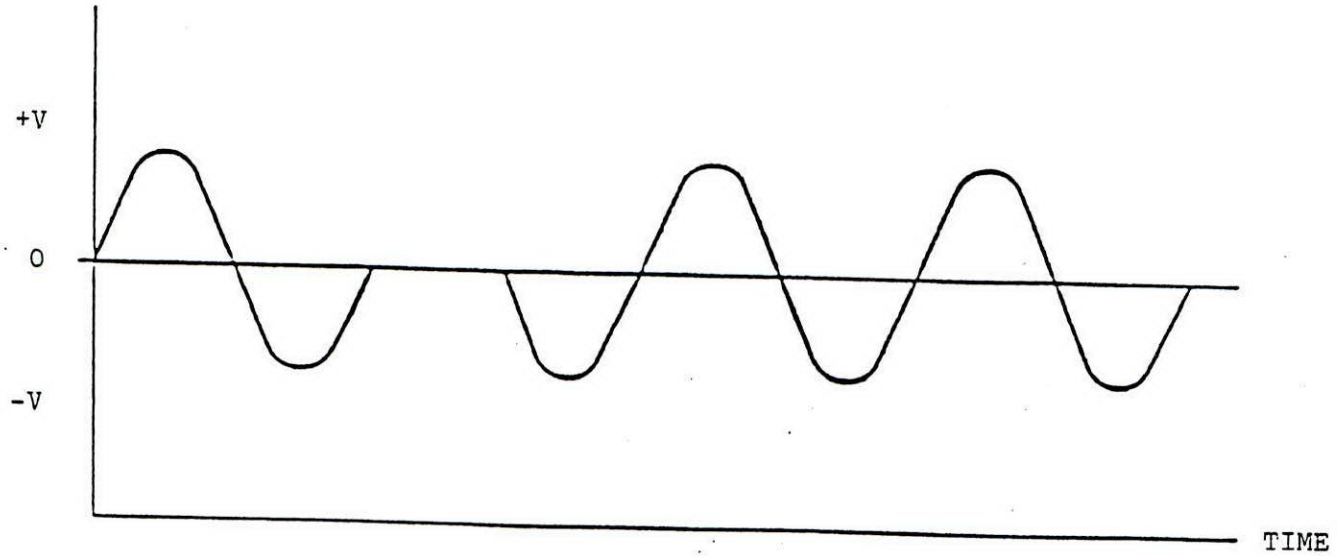
NON-SYMMETRIC AC



NON-SYMMETRIC AC

(DC OFFSET)

FIGURE 7



NON-SYMMETRIC AC

(OMITTED ANODIC PULSE)

FIGURE 8

Paper Not Available In Time For Publication

Sealing of Anodized Aluminum

Mores Basaly and Dr. Sam Massad, Novamax Technologies, Inc., Atlanta, GA

This paper will present an overview of the three sealing processes of anodized aluminum: Hot water sealing; nickel acetate-based, mid-temperature sealing; and nickel fluoride-based, low-temperature sealing. A comparative study of the sealing processes, as well as the advantages and disadvantages of each process, will be discussed. In light of promotion of a safe environment and the discouragement of using hazardous materials, environmentally friendly metallic salt-based seals will be discussed.

For copies of this paper please contact:

Mores Basaly
Novamax Technologies
1615 Johnson Road NW
Atlanta, GA 30313
404/799-1292
FAX: 404/799-1873

Paper Not Available In Time For Publication

Graffiti Resistance of Various Sealing Methods

Lee C. Branch, Melvin L. Todd, and Les C. Widmyer,
Albright & Wilson Americas, Surface Technologies Group, Ashland, VA

Vandalism of outdoor structures is becoming more of a problem, especially in urban areas. This paper will discuss the various sealing methods used by aluminum anodizers and evaluate the resistance of the seals to damage by graffiti following cleaning by commercial graffiti-removing solutions. A laboratory method will be discussed to evaluate graffiti resistance.

For copies of this paper please contact:

Lee Branch
Albright & Wilson
100 Lakeridge Pkwy.
Ashland, VA 23005
804/550-5507
FAX 804/550-4385

The Development of an Expert System using Neural Networks for the Identification of Process Defects in Anodizing

Arthur W Brace

Consultant - Stonehouse, Gloucestershire, GL10 3HH, England.

Summary:

The economic importance of defects and the difficulties faced in the correct identification of process defects is considered.. It is suggested that under present conditions there is a real danger of expertize on defects held in the informal structures of a company being lost with the movement of personnel and the general lack of written information. The paper then considers the contribution that information technology can make to the problem.

After critically reviewing some of the existing expert system programs, the author suggests that these have serious limitations as far as the identification of anodic process defects are concerned. The development of an identification method using a proprietary neural networks program is described and examples given of its ability to give appropriate classifications of defects, including situations where the information entered is incomplete, or there is more than one defect present.

The compilation of a reference/knowledge base on defects, using a card based hypertext program, giving a detailed description, advice on correction and avoidance, and relevant bibliography is described. Both the reference base and the neural network program can access a graphics file containing displays of many of the defects described.

In a previous paper [1]) the author attempted to develop a systematic approach to the identification of anodic coating process defects. In this paper the user of the algorithm developed is asked to first identify the probable origin of the defect. After this is established the user is asked further questions which are intended to allow him to identify most common defects. However, the collection of further data increased the number of defects identified from 65 to 107. These were later published in a book [2]) which also attempts to assist the reader in a systematic identification of the defects described.

The Economic Significance of Rejections due to Defects

Rejects by customers are always a cause for concern in an anodizing plant, since whether an in-house or trade anodizer operation, rejects cause friction between the parties concerned. Sometimes the cause may be attributed by the anodizer to the material, or as having arisen before the parts were received. Even if the anodizer believes this to be the case he has to convince either the customer or the material supplier that it is a manufacturing or material defect. Both parties may lack the expertize to draw the correct conclusions.

However, both parties sustain a loss in terms of the costs of such rejects. These costs are not simply the reprocessing costs, but include the following:

1. The cost of stripping the anodic coating and possibly the cost of repolishing or other preparatory operation.

2. The profit lost on work that could have been processed during the period the reject work is being reprocessed.

3. The time costs of the management and staff involved in investigating the causes of defective work.

4. The cost of delays to the customer's production line due to hold-up due to inability to complete operations on the whole of the batch.

It is therefore considered that rejections due to process defects represent a major area where costs are incurred that could be avoided, so that there is a need to deal with these. Experience suggests that the published literature is of limited value to plant personnel in identifying defects and providing guidelines to their correction. If a "trouble shooting" approach [3,4]) does not provide the answer, plant personnel often lack both the training and experience to approach systematically the problem of the identification of of defects.

Most anodizing plants operate on the basis of knowledge acquired by key personnel. This knowledge is rarely committed to paper, primarily due to the pressures of meeting the needs of production and, in some cases, because of a fear that such knowledge might reach competitors if recorded in an accessible form. Within larger companies, moves of personnel to other duties, retirement of experienced personnel and redundancy, can lead to a loss of valuable "know-how" which in the short term, at least, increases processing and operating costs.

The current situation suggests that the informal knowledge of defects which exists in an establishment is always in danger of being lost by movement and changes of personnel, unless incorporated into a formal system. This has important implications for a company wishing to retain existing and future expertize. It seems appropriate, therefore, to consider the contribution that recent developments in computer-based information technology has to offer in this situation.

The Potential Contribution of Computer-based Information Technology

Of course, there are barriers to the use of information technology in a number of plants, because many managers and technologists may not be computer literate. Personal experience indicates that there are only a limited number of plants using computer databases and information retrieval programs. On the other hand, many plants use computers for order processing and financial transactions.

However, there are a number of companies who have technical staff with computer skills. Some of these have developed large process information databases relevant to their operations and customers requirements. However, these are databases, which have significant limitations in their ability to identify process defects.

Expert Systems

In the information technology field much attention is being paid to the development of expert systems. These appear to be potentially relevant to the problem of defect identification. Essentially, expert systems represent an attempt, within the constraints of a computer, to provide the user with expertize in the particular topic which is the subject of the expert system.

An expert system usually incorporates a program, known as an expert system "shell", which interrogates the user as to the features of the problem and, based on "rules" developed by the compiler of the expert system, draws a conclusion as to the origin of the problem. Many such systems also provide a link to a database offering the user further information on the problem and advice as to suitable means of avoiding or correcting the problem.

This reference database (often referred to as a "knowledge-base" in the U.S.A.) may contain a high level of information and expertize on the subject area in question, including bibliographic references and, where appropriate, a graphics display to supplement the text matter.

Limitations to Expert Systems: If the level of computer literacy of the potential user of an expert system has not extended beyond the use of word processing programs, this can limit the value of an expert system, unless technologists are prepared to acquire a degree of computer literacy, or the company invest in training to this end.

Any expert system must be based on real expertize. This is not to deny the value of a program which guides a user through a diagnostic proceedure, since this is often used at the commencement of an expert system consultation, but real expertize is vital. If the expert system depends

upon a significant input from the user, this information must be cross-checked during the consultation procedure.

The problem for the expert compiling the system is that he cannot know the plant, equipment and operating conditions of every plant in which the system is used. He can only guide the user in the direction of probable solutions. Another factor is that In fault finding or defect analysis, the information available is often incomplete, so that an expert consultant may arrive at a partly intuitive, partly deductive conclusion, so that one is dealing with that area known as "fuzzy logic". In this situation the ultimata criterion is "will the expert system lead the user to a correct diagnosis ?"

Factors governing the Choice of Expert System

When this work was started, most expert systems shells available for use on a micro-computer were relatively expensive ($1,000-5,000), which was considered to be a likely deterrent to their use in the average anodizing plant. However, it was thought that it should be possible to develop an expert system at a lower price.

In the work subsequently carried out, the following were the objectives that it was hoped to meet in the construction of an expert system for the identification of anodic coating defects:

1. The cost of software should preferably not exceed $1000.
2. The final system should require only limited computer literacy.
3. The expert system should be capable of displaying graphics.
4. It should be comprehensive, covering defects of both process and material origin.

An Initial Evaluation of Expert System "Shells"

After consulting various computer journals and obtaining literature on programs available, several low cost "Shareware" expert system "shells" were obtained and examined [5,6,7]). These were written in various languages (Basic, Pascal and Turbo Prolog) and were formulated in the following type of basic structure:

Question to user

Answer - Yes/No

If "Yes ... then:

If "No" ... then:

Based on these answers the compiler will construct rules from which deductions would be made on the premise that:

If.... and .... and ..., then ....

An expert system based on this approach has been published in the U.S.A. for the identification of electroplating defects [8]).

Some so-called expert system "shell" programs available are often little more than a program that interrogates the user and diagnoses simple faults. It is important that expert system shells should be able to analyse defects which arise from possible complex interactions between the metal and the processes and sequence used.

They also need to take into account that there is usually an element of uncertainty in the answers given by the user during a consultation. This had been recognised in two of the programs examined [5,6]), where users have the ability to apply a probability weight to their answer, ranging from 0.90 for a high degree of certainty, down to 0.50 for a uncertain answer, with values diminishing down to 0.10 where the answer is one that it is almost certainly incorrect.

Even so, this brings a further difficulty, in that it requires a subjective judgement on the part of the user, effectively making him part of the expertize. Added to this, the features of the defect may have been changed during further processing, thereby being likely to give rise to uncertainty or erroneous answers to questions.

A problem inherent in most expert systems shells, as far as their use for defect identification is concerned, is that they can lead to a dead end. For example, assuming that the defect is due to a inadequate cleaning, a rule-based expert system usually poses the question:

Were the defective parts cleaned ?

If the answer is "Yes" the next questions will be along the lines:

Was the temperature as specified in the process schedule ?

Was the time as specified in the process schedule etc. ?

To each of these questions the user will invariably answer that the work was cleaned and the time and temperature were correct, although they may not definitely know that this is so. Yet a cleaning problem has occurred. Unless the problem is of material origin, the conclusion is either than the cleaning system is inadequate or that, despite the answers given by the user, the process laid down was not observed. The user now needs to identify which of these were responsible.

However, in this situation there is no certainty as to what occurred at the time of processing. The uncertainty can be made worse by the fact that there can be two defects occurring at the same time, such as a material defect and a process defect. It was felt that these considerations pointed to the need to a different approach.

Neural Networks as an Expert System Shell

Over recent years attention has been given in information technology

to the development of artificial intelligence. It is appreciated that human intelligence is a highly complex phenomena which cannot currently be represented in terms of a computer model. However, computers do have a capacity for storing and quickly retrieving knowledge, as well as identifying numerical and graphical patterns, and rapidly carrying out a series of sequential operations.

The development of neural networks represents an attempt to use the computer as a means of recognizing associations of digital or analog data stored in memory and comparing them with new data supplied by the user of a neural network program. The process of organising and storing this data in a form where its various associations can be recognised and compared with new data fed in is known as creating a neural network. It is sometimes claimed that such programs imitate the learning process and associations formed by the network of cells forming the brain. At best, neural networks are only a crude attempt to simulate the processes in the human brain.

Neural networks are capable of handling problems involving "fuzzy logic" and of recognizing patterns of association. They do not proceed on the rule-based structure of most expert system shells, but depend upon recognition of patterns of association and will accept "fuzzy logic", i.e. conclusions based on possibly incomplete data.

After a preliminary evaluation of several expert system shells, a review was seen in computer journals of a recently developed neural network program using back propagation [9]). This program provides for the input of data either in binary or in analogue format.

In binary mode, information relating to a particular problem, such as the identifying characteristics of a defect or a group of defects, can be entered in the upper half of the screen. Each line should normally only contain one identifying characteristic. Having entered one or more such characteristics, the classification of the problem (i.e. the name of the defect) is then entered in the lower half of the screen (below the dotted line appearing on the screen) and has to be confined to one line.

After preliminary trials it was considered that it seemed a promising approach to defect identification. However, this called for consideration of how the relevant information should be organised. The handbook supplied recommended the use of small files for speed of use. Since the display is confined to a 24-line display this factor reinforced the need for small files, since if more than 20 defect characteristics are entered they fill the screen, before the classifications are entered.

A further consideration was that the user would need to be given some guidance on the use of the program which would provide a logical step-by-step approach to defect identification. In a previous approach to the problem [3]), the author has used the following criteria for the primary identification of the problem:

Does the defect appear to be:

(a) Beneath the anodic coating ?

(b) Within the anodic coating ?

(c) Associated with sealing or surface deposits ?

(d) Associated with the material ?

This basis for the identification of defects has been retained when using the neural network program. The user is first advised to consult the file IDENTDFT which is intended to enable him to identify the origin of the defect and then for further analysis to consult one of the following files:

Beneath the anodic coating	*Within the anodic coating*	*Sealing or surface*	*Material related*
MECHDFTS	ANODFTS	SEALDFTS	CASTDFTS
BRITEDFT	COLORDFT		CORRDFTS
CLEANDFT			EXTRDFTS
ETCHDFTS			FABRDFTS
			SHEETDFT

The nature of the type of defects classified in each file should be recognisable to the user from the filename.

In constructing the IDENTDFT file a total of 52 cases were entered, i.e. combinations of characteristics and classifications. These utilised combinations of 17 primary characteristics and 12 classifications (corresponding to the above 12 files).

In preparing this and the other files in the system, the following are the steps involved:

1. The user enters a series of defining characteristics of the defect which are entered in the upper part of the screen and its classification entered in the lower half of the screen (i.e. below the dotted line on the screen). Only one defining characteristic or one classifying characteristic should be entered per line of the computer screen.

2. There may be more than one defining characteristic to each of the defects classified, but normally not more than three.

3. Having entered the defining and classifying characteristics the program requires the compiler of the expert system to check for defects by entering the appropriate instruction.

4. Having entered all the cases relating to one group of defects, the program requires these cases to be "learnt". This stage is only relevant when the file is being written.

5. Once this has been done, the user calls up the file and is presented with a screen on which the characteristics are portrayed in the upper portion of the screen and the primary classifications are in the lower part of the screen or hidden (see Fig. 1).

6. The user then places the cursor on the first line that contains a description of a characteristic of the defect and presses "Return", which then highlights the line. He then moves on to find the next line which contains a description of another characteristic of the defect and again positions the cursor on that line and presses return.

The following shows the commencement of the entry of the series of cases used to define and identify the primary classes of defects in the INDENTDFT file. It will be noted that there can be more than one defining characteristic for each of the classified in each file.

The first line entered for the identifying characteristics was:

The defect is beneath the anodic coating

Then the following classification characteristics are entered:

Cleaning defects defects are identified in the CLEANDFTS file
Defects arising in etching are classified in the ETCHDFTS file
Mechanical pretreatment defects are classified in the MECHDFTS file

Further defining and classifying characteristics are entered until the screen has the display shown on page 8:

When all the defining and classifying characteristics have been entered the compiler enters the instruction for the model to be "learnt". This creates the neural network incorporating the above characteristics. The file thus created is ready for use.

To classify the main type of defect and to obtain the name of the file to be called up for its identification the user places the cursor on the line of the screen that gives a description relevant to the defect and presses "RETURN". This highlights that lines selected and an example of a two line entry made to identify a defect is now shown:

The defect is within the anodic coating
The thickness of the anodic coating is incorrect

When this step is completed the user presses the F3 function key and a line in the lower display giving the defect classification is highlighted, together with a number less than 1.0, which will normally lie between 0.1 and 0.9. If the value displayed is greater than 0.5, this indicates that the expert system assesses this as the probability that the defect being displayed is correct. However, a lower value indicates that the data entered is not sufficient for the user to be certain that it has correctly identified the defect.

In the case of the example above, pressing the F3 key produces the following line highlighted in the lower half of the screen:

Anodic coating defects are identified in the ANODFTS file 0.91

It will be seen that with these identifying characteristics entered, the probability of the answer being correct is 0.91.

Fig. 1: The Defining and Classifying Characteristics entered in IDENTDFT File for Primary Identification of Anodic Process Defects

```
-------------------------------------------------------------------
The defect is beneath the anodic coating
The defect is within the anodic coating
The defect is associated with sealing or the anodic coating surface
The defect appears to be of material origin
There is evidence of pitting, white spots or other possible corrosion
The component has been made from a defective casting
The component is an extrusion with an uneven appearance
Unsatisfactory appearance possibly due to brazing, forming or welding
The component has been made from sheet which may be of poor quality
Mechanically pretreated parts have an unsatisfactory appearance
Chemically polished (brightened) work has an unsatisfactory appearance
The work has a patchy appearance possibly due to poor cleaning
After etching the components have an unsatisfactory appearance
The appearance of the work after anodizing is unsatisfactory
The thickness of the anodic coating is incorrect
The properties of the anodic coating are incorrect
The anodic coating has been dyed or electrolytically coloured
After dyeing or colouring the appearance is unsatisfactory
The coating has failed sealing tests
After sealing the coating is discoloured
There is surface bloom present after sealing
-------------------------------------------------------------------
Anodic coating defects are classified in the ANODFTS file
For defects in chemical polishing/brightening - see BRITEDFTS file
To identify defects originating in casting - see CASTDFTS file
Cleaning defects are in the CLEANDFTS file
Dyeing and colouring defects are in the COLORDFT file
Defects due to corrosion are classified in the CORRDFTS file
Defects arising in etching are classified in the ETCHDFTS file
To identify defects originating in extrusion - see EXTRDFTS file
To identify defects arising in fabrication - see FABRDFTS file
For defects resulting from mechanical pretreatment - see MECHDFTS file
For defect arising from sheet manufacture - see SHEETDFT file
For classification of sealing defects - see SEALDFTS file
-------------------------------------------------------------------
```

The file is also capable of pointing the user in the right direction if there is more than one type of defect present. The user may examine a defective component and enter the following defining characteristics:

```
The defect is within the anodic coating
The appearance of the work after anodizing is unsatisfactory
The anodic coating has been dyed or electrolytically coloured
After dyeing or colouring the appearance is unsatisfactory
-----------------------------------------------------------
```

On pressing the F3 classifying key the following highlighted display appears on the screen:

Anodic coating defects are classified in the ANODFTS file 0.80
Dyeing/colouring defects are evaluated in the COLORDFT file 0.91

In this way the user is provided with a means of primary identification of the defect being investigated. Once the primary classification of the defect has been made using the IDENTDFT file the program will advise the user which file relates to the process stage at which the defects probably occur. If it is an anodic coating defect, then it will be the ANODFTS file that will be indicated as being relevant.

Following this procedure, we can now illustrate what happens when the user calls up the ANODFTS file.

Fig. 2: The Defining and Classifying Characteristics entered in the ANODFTS File for the Classification of Anodic Coating Defects

The work has been sulphuric acid anodized	
The work has been chromic acid anodized	
The work has been hard anodized	
There are one or more rough areas associated with metal dissolution	
In these areas there is little or no anodic coating	
These areas may also be associated with holes in the metal	
The film produced in chromic acid is clear	
There are fine pits present and chloride is found in the electrolyte	
When viewed at a glancing angle to the light, fine lines (cracks) appear	
The coating is duller than normal after anodizing	
The dulling increases with film thickness and current density	
The electrolyte contains more than 50 p.p.m. of heavy metals	
The sulphuric acid electrolyte contains more than 20 g/l aluminium	
The voltage required is higher than normal under standard conditions	
There are small irregular pits in the coating after hard anodizing	
When viewed at a glancing angle to light a rainbow effect is seen	
There is pattern of patchiness associated with the draining direction	
The coating has a powdery surface which can be removed by rubbing	
The powderiness is heavier in some areas than in others	
The coating is soft and fails abrasion test if tested	
Some/all of the parts do not meet the expected or specified thickness	
This defect is due to "burning" of the anodic coating	
This defect is "chloride pitting"	
See reference book for causes of a "clear chromic coating"	
This is characteristic of a "crazed/cracked anodic film"	
This is classified as "dull appearance"	
This is classified as "dull appearance"	
This is classified as "dulling - contamination	
This is associated with "excessive aluminium content"	
This arises as a result of "galvanic pitting"	
This is inter-metallic dissolution" during hard anodizing	
This feature is known as "iridescence"	
Tis is classified as "patchiness - poor rinsing"	
See reference book for causes of a "powdery anodic coating"	
See reference book for origins of a "soft coating"	
See reference book for causes of "wrong film thickness"	

The identifying characteristics of anodizing defects shown in Fig. 2 represent the characteristics of all the defects noted in compiling this file. To use this file the identifying characterisitcs of any particular defect may now be entered. When using a file to identify a specific defect, the user should only enter those defining characteristics relating to that defect (usually between 2 and 4 characteristics only).

As an example we may consider the defect where there is dulling of the anodic coating on anodizing. This can be due to different causes:

1. Dulling of the coating from use of a high current density.
2. Metallurgical factors such as precipitation of intermetallics.
3. Contamination of the electrolyte with heavy metals.

We can now examine how the program handles such defects.

If the user enters the following identifying characteristics, the program classifies the defect as follows:

```
The work has been sulphuric acid anodized
The coating becomes duller than normal after anodizing
The dulling increases with thickness and current density
-------------------------------------------------------
This is classified as "Dull appearance"  0.90.
```

Alternatively, if the use enters the following identifying characteristics, the classification will be as shown:

```
The work has been sulphuric acid anodized
The coating becomes duller than normal after anodizing
The electrolyte contains more than 50 p.p.m. heavy metals
---------------------------------------------------------
This is classified as "Dulling - contamination"  0.90.
```

One of the advantages of the neural network is that it will provide an assessment of a problem even if incomplete data is entered. If too little data, or partially incorrect data is entered by the user, the probability factor indicated for the correctness of the answer will diminish, at worst to below the 0.50 significance level. This is illustrated by the following example where the user has entered incomplete data:

```
The work has been sulphuric acid anodized
The coating becomes duller than normal after anodizing
------------------------------------------------------
This is classified as dull appearance  0.51
```

In other words, the program recognizes the defect but with incomplete information it only gives an 0.51 probability of the defect being "dull appearance". However, the following line is also displayed:

```
This is classified as "Dulling - contamination"  0.33
```

All the other classifications show probabilities around 0.10. This shows that

whilst it is likely that the defect is "dull appearance" there is a also some probability that it could also be due to contamination.

The program provides classifications if two defects are present. Suppose the user enters the following identifying characteristics:

```
The work has been sulphuric acid anodized
When viewed at a glancing angle to light, fine cracks appear
The electrolyte contains more than 50 p.p.m. of heavy metals
-------------------------------------------------------------
```

On pressing the F3 classifying key the following appears:

```
This is classified as a "Crazed/cracked anodic coating"  0.91
The is classified as "Dulling - contamination"  0.57
```

This indicates that the program has correctly assessed the likely defects.

In all, a total of 111 defects have been described and classified, divided between the 12 files listed on page 6 and checked with numerous test cases to verify the correctness of the data entered.

Compiling the Reference Base

The neural networks, whose construction has been described above, are believed to be an effective means of identifying most defects. Having achieved this it leaves the user without information on the steps to be taken to correct the defect. To do this a Reference Base has to be created which it was considered should provide for the following:

1. A more detailed description of the defect, such that an experienced user could call up the appropriate Reference Base file and identify the defect from the description.

2. Advice on how to correct or avoid the defect in the future.

3. References to published literature on the specific defect.

4. The ability to illustrate the defect as a graphic.

Possible Programs for Use as a Reference Base

From a user viewpoint, clarity of presentation of information is important, so that a card-based system appeared to be a logical choice. The author has used previously commercial programs [10,11,12]) to summarize and retrieve information which were card-based, which have quite sophisticated search facilities. Two of them have the ability to incorporate graphics. One of these [12]) has a simple hypertext facility.

The Advantages of Hypertext for Information Bases

Hypertext is a means of obtaining a very rapid appearance of data on the screen. Programs with a hypertext facility enable information to be stored in

a form in which is can be rapidly retrieved and linked to other parts of an information base by means of specially designated symbols known as hypertext links, which provide rapid links to display other related information within the same file or in a separate file. Such programs are either card based or text based. With a card based system the information appears on the screen in a card index form, requiring a separate card for each topic. Cards can be grouped together in a single file.

In principle, all the data comprising the information base could be stored in a single file, but this tends to slow up speed of retrieval when using the hyperlink. Usually, the information base is split into a series of files for speed of access.

The advantages of such hyperlinks are that they enable immediate cross-referencing to be made between topics, thus avoiding the necessity of exiting to other programs or having to consult reference books to obtain additional information. Card based programs were considered to be a more manageable way of displaying the information.

After reviewing descriptive information on hypertext programs, one was obtained [14]) which appeared to meet current needs for the following reasons:

1. It has the option of a card-based or text-based format.
2. It provides for "windows" with hypertext links, in which bibliographic information or graphics could be displayed.
3. It is capable of forward and backward chaining.
4. The cost of the program is below $100.

In terms of its hypertext capability it was able to offer the following:

1. Links to any card in the current file.
2. Links to cards in other of the defect files.
3. A link to a bibliographic database for each card.
4. A graphics link, but limited in its capability.
5. Provision to call another program whilst the hypertext program remains memory resident.

Structure of the Hypertext Reference Base

For ease of retrieval the files in the hypertext database have the same filenames as those used in the neural networks program. The file AN-INTRO was also added to provide the following:

(i) On-line information on the structure and use of the hypertext reference base, as part of the expert system.

(ii) Information on the neural networks defect identification program and its relation to the hypertext reference base.

(iii) The basic layout of the hypertext reference card.

(iv) Some notes concerning the bibliographic references provided.

Apart from the AN-INTRO introductory file, when defect files are opened, the screen display has the general format of the ANODFTS file shown in Fig. 3 overleaf. It consists of a title giving the filename, followed by a card display, with each card being identified with a letter and number which is the same as the number appearing on the corresponding neural networks file which identifies the defect. This is intended to assist rapid access to the relevant card in the database.

In addition to the card number there is also the corresponding descriptive name of the defect. By use of a pointer controlled by a "mouse" placed between the <.....> hypertext links it is possible to make a hypertext jump to the relevant card. In addition, the card index display provides a list of other defect files.

Fig. 3: Layout of the Hypertext Reference Card for Anodizing Defects

List of Cards in the Anodic Coating Defects File (ANODFTS)

Card no.	Description	Card no.	Description
A1	<"Burning">	A8	<Galvanic pitting>
A2	<Chloride pitting>	A9	<Inter-metallic dissolution>
A3	<Clear chromic film>	A10	<Iridescence>
A4	<Crazed anodic film>	A11	<Patchiness - poor rinsing>
A5	<Dull appearance>	A12	<Powdery anodic coating>
A6	<Dull - contamination>	A13	<Soft anodic coating>
A7	<Excessive Al content>	A14	<Wrong film thickness>

Files for Other Main Classes of Defect

Arising in Processing	Arising from the Material
Mechanical pretreatment	Corrosion
Chemical polishing	Casting
Cleaning	Extrusion
Etching	Fabrication
Dyeing and Colouring	Sheet and strip
Sealing and Surface	

As far as the cards are concerned that are accessed from the above, a typical card from the ANODFTS file is displayed in Fig. 4. It will be seen that is has a title centred which is the name of the defect as identified by the neural network. Below and to the left is an alternative name for the defect. The text that follows explains the nature of the defect. This is followed by a heading "Remedy" in which advice is given for correcting or avoiding the defect in the future.

It will be noted that in this text there are hyperlinks which provide for immediate access to other pitting defects, so that the user can compare the characteristics of defects having a basic similarity. After a hyperlink has been activated the user presses the "ESC" key to return to the original screen.

Fig. 4: Example of the layout of an ANODFTS Hypercard

GALVANIC PITTING

Alternative description: Pitted coating

For a number of reasons, work may be held in a rinse tank after anodizing and before dyeing and sealing. If the tank is made of steel there is a potential difference between the steel and the aluminium. Rinse residues, such as sulphuric acid, have high conductivity, so that if the workbar carrying the anodized parts is in direct contact with the wet rim of the rinse tank, pitting of the anodic coating can occur. This defect may prove difficult to identify as to its origin, since it will have some resemblance to rinse water corrosion after etching, especially since the metal is pitted in both cases. The origin of the pitting can only be established by observation. It is necessary to check whether the pitting is present before or after anodizing, or rinsing after dyeing. See <Card E7> for rinse water corrosion, or Card C3 for pitting in dyeing.

Remedy

The essential remedy is to make sure that the workbars and racks are electrically insulated from the tank. This is normally done by putting insulating rubber or plastic strips on the tank rims where the workbars would come into contact. Pitting can also be caused by stray current, so that earthing of the tanks is advisable.

A7 <Next card> <Previous card> <File list> <Bibliography>

Fig. 5: The Bibliographic Reference Card linked to the above Card A7.

This defect was described and illustrated by E P Short and P G Sheasby (Trans. Inst. Metal Finishing 1975,53,169-173). It is firther considered by A W Brace "Anodic Coating Defects" p.68; Technicopy Books, Stonehouse, Glos., GL10 2NA, England 1992.

Graphics Display.

In addition to the text hyperlink features, the program makes it possible to provide a graphic link to display the defect on the screen, but there are limitations to the graphic formats that can be accepted. Since some users may wish to view a graphic of the defect after the defect has been classified using the neural network program, it appears preferable to use a separate program (for example [15]) for this purpose without the using the hypertext link facility of the hypercard.

Summary

The above paper has attempted to demonstrate how recent developments in information technology can be used by the anodizing technologist and researcher. The advantages of neural networks over rule-based expert systems for process defect identification have been clearly shown.

The cost objective of restricting the cost of software to less than $1000 was also attained, since the cost of the three programs used was less than $500.

The advantages of a card-based hypertext program for the Reference/ Knowledge Base has also been demonstrated, especially in terms of clarity of display of information, ease of use and rapidity in making cross-references to related defects.

Acknowledgements:

This work has been carried out as part of a research project on the development of and expert system for anodic coating defect identification. It forms part of a Ph.D. Thesis being submitted shortly to Aston University, Birmingham, England. I am indebted to Dr J K Dennis and to Mr L W Crane of the Department of Mechanical and Electrical Engineering for helpful discussions on this project.

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APPENDIX

The Nature of Neural Networks

Neural networks is a tool developed for artificial intelligence inspired by the concept of trying to simulate on a computer the processes of the human brain. The concept is that the human brain consists of neurons which accept stimuli and pass them on to other centres of the brain which respond to these stimuli and produce human activity, either of movement, speech or intellectual analysis.

The principle of the neural network programs (Fig. i) is that they accept a series of inputs of data - the input function - and process them to produce outputs (the output function). The process in its simplest form can be represented as follows:

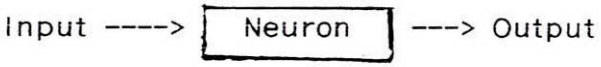

Fig. i: Principle of the use of neurons

The process by which the neuron processes the inputs to arrive at an output is a summation of inputs followed by a linear function applied to this sum, and called an output function.

However, this model represents individual independent neurons which have no practical value until they are interconnected into a network of neurons, where they are called nodes as depicted in the diagram below:

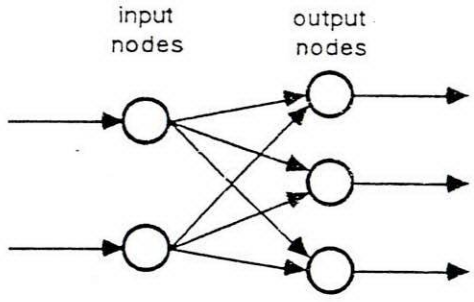

Fig. ii: Diagrammatic representation of a Network of Neurons

Each of the input nodes passes its data to each of the output nodes for final processing, but as this first layer passes its values to the second layer, the values are weighted to represent connection strengths. To reinforce a connection positively, the weight is increased, whilst negative weights inhibit a connection.

In binary mode data is processed by accepting input values between 0 and 1 into the input nodes. The NeuroShell program calls these input patterns Defining Characteristics. The network produces output patterns which the program call Classifying Characteristics. The program allows the weight to be varied by the user of the program so as to reinforce particular connections, where this is judged to be appropriate. Feedback is produced when patterns to be learned are presented to the input nodes, with each input pattern having an output pattern referred to as a sample case.

The error between the predicted and actual outputs for a given output node is measured and then the weights leading to this output node are modified slightly in the direction needed to produce a smaller error the next time the pattern is presented. The process of repeated presentation of patterns and weight modification from the feedback is referred as "learning". Once the learning process has been completed the network should be capable of reproducing the correct output pattern when presented with one of the input patterns it has learnt, which is called classification in NeuroShell terminology.

Back Propagation

The neural network model described above is a simple two layer network which is limited in its capacity to learn more complex patterns. Neuroshell™ provides back propagation by means of which one or more layers of hidden nodes (or layers) between the input nodes and the output nodes, although one extra layer is adequate for most problems as long as sufficient nodes are used.

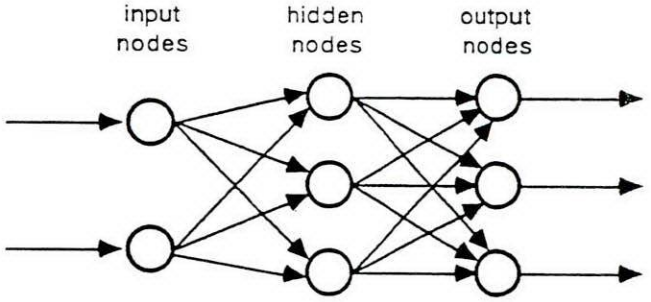

Fig. iii: Diagram of a Neural Network with Hidden Nodes

With a three layer neural network the weight modifications must not only be made between the second and third layers, but must be propagated right back between the first and second layers. Learning improves up to a point with an increase in hidden nodes, but only up to a point, but too few hidden nodes may prevent the learning of all the unique samples cases in the input. Two other factors also affect learning - the learning rate and momentum. The program, defaults to a learning rate factor of 0.6 and a momentum factor of 0.9 respectively. It has not been found necessary to adjust these.

The Neuroshell™ Handbook contains an Appendix giving a more detailed description of the neural network used. The handbook also draws attention to a book which gives a detailed and technical account of the underlying principles of neural networks [50]

*__Note:__ Since this work was carried a "Windows™" based version ("NeuroWindows"™) has also become available.

A Quality Approach to Troubleshooting Your Anodize Line

By

Mark Spencer
Sandoz Chemicals Corporation

The economic sign of the times is that our customers produce the part today and want it anodized yesterday. Since anodizing usually is the last stage of the product manufacturing process, we don't have much time to finish the parts in our plant. The anodizer that can turn the product around the quickest without producing rejects will get their lions share of the market. With these challenging conditions in mind and our anodizing line starts producing rework loads we have to be quick to respond and fix the problem.

Clear anodizing will not show the flaws in the anodic coating as greatly as colored anodizing. There is a frequent tendency to blame the dyeing process or even the dyestuff for color faults that lead to rejection of the product. Even though in the majority of such cases it has been proved that undetected deviations in the prior or post treatments are responsible for the faults.

It is the goal of this paper to provide you with techniques and strategies that will reduce the amount of time required to correct a problem in the coloring of anodized aluminum.

We believe there are 5 steps to the troubleshooting process:

I Define the problem
II Fix
III Identify the root cause
IV Take corrective action
V Evaluate and follow up

Let's take a closer look at these 5 steps, and see how we can use these procedures to decrease the amount of time it takes us to solve problems generated in the anodizing process.

I. Define the problem:

This is the most important step in any troubleshooting practice. If we do not clearly describe the problem accurately, we will be wasting a lot of time and energy. We need to define what the problem really is, not what it seems to be. It is a good idea to get everyone's input.

II. Fix:

This is a temporary step to keep the anodizing process going. A fix can be: longer anodize time, wiping the smut off the part, or dumping the tank. It is important to note that this step in the troubleshooting process is not a permanent solution.

III. Identify the root cause:

After we have established a quick fix, we now have time to establish exactly what the root cause of our problem is. The first step of identifying the root cause is to make sure we have a clear understanding of the anodizing process. This includes how the customer manufactures the product, how we (the anodizer) process the product, and how the final customer uses the product. There are a number of tools we can use to help us identify the root cause:

Process Model Work sheet
Threads of Similarity
Cause and effect diagram (fishbone)
Parieto Analysis (80/20 rule).

IV. Take corrective action:

Once we have determined the root cause, it is now time to implement the changes required and inform all parties of the action that is needed to prevent this problem from arising again.

V. Evaluate and Follow up:

Once all the changes have been made and all parties are properly trained, we should plan a follow up session to ensure the change did work, that the change did not create any other problems, and that we are still following the necessary guidelines.

Let's examine how we can use this process using real life examples:

I. Our line is producing color variations from rack to rack, one problem could be a gradual decrease in color intensity.

Possible root cause	**Corrective action**
A) Drop in dye concentration through consumption	- extend dye time - Add dye to correct deficiency

B) Accumulation of deactivating contaminants in dyebath	- prevent drag in of other contaminants by thorough rinsing - Extend dye time - Increase dye concen. - Decant dye tank - Replace dye bath
C) Decomposition of dye by reaction with non-resistant metal parts	- Check for metal objects that have fallen into tank - Decant dye tank - Replace dye bath
D) Different alloys	- Adjust operating parameters for alloy type
E) Variation in time between anodizing & dyeing	- Do not allow parts to stand in rinse water - Maintain uniform processing routine
F) Color loss in seal	- Check seal and rinses for phosphates - Increase dye temp. and/or immersion time - Dye at higher temperature or for a longer time at lower dye concentration - Use cleanest possible water for sealing - Immerse at highest practicable sealing temperature - Use of nickel seals
G) Variations in dyebath pH	- Buffer dye solution with sodium acetate - Growth of micro-organisms in solution
H) Anodic coating variation	- Correct anode/cathode ratio
I) Uneven depletion of dye mixture components	- Use homogeneous dyes - Select dye mixture with uniform exhaustion rates - Make periodic additions of individual mixture components

J) Chemical instability of dye solution	- Select more stable dye(s) - Maintain dye pH at high end of pH range - Keep dye solution at reduced temperature - Replace dye solution at more frequent intervals

Another problem could be color differences within the same rack.

Possible root cause	**Corrective action**
A) Poor rack contact	- Make sure racks are properly stripped - Check rack tips for burning - Avoid starting anodize cycle at full voltage or high current density
B) Presence of different alloys	- Do not mix alloys
C) Temperature variation in anodizing due to poor agitation	- Improve agitation in anodizing tank
D) Excess current density	- Reduce current density - Increase distance to cathode - Reduced cathode area
E) Irregular dye take up	- Increase agitation - Reduce dye temperature and increase dye immersion time - Raise pH of dye solution - Better rinsing - Similar pH in rinse tank before dye tank - Nitric acid rinse before dye tank
F) Difference in immersion time due to short dye time and slow acting overhead hoist	- Immersion time should be a minimum of two minutes - Adjust other parameters to increase dye time
H) pH of dye solution too low	- Raise pH and buffer solution at proper value

I) Dark color on edges of of stamping	- Galvanic problem - exposed substrate on sharp edges - Current density too high
J) Variable light & dark patches	- Cleaning problem - Oily film on dye surface - Contamination in air supply
K) Chalky or Sooty dyeing	- Poor rack contact causing loss of current flow

Finally we can see a <u>color difference on an individual part.</u>

Possible root cause	**Corrective action**
A) Poor temperature distribution in anodize tank	- Increase agitation throughout anodize tank
B) Excessive current density	- Keep between 12.5 & 15 amps per square foot
C) Poor cleaning	- Check cleaner for excess soil build up
D) Oily contamination in anodize, rinse, or dye solutions	- Make sure agitation is oil-free - Skim tank to remove
E) Hydrolized aluminum present in coating	- Improve rinsing facilities - Lower aluminum content in anodizing solution - Add nitric acid dip between anodizing and dyeing
F) Excessive heating during polishing	- Improve polishing techniques or abrasive compound

G) Electrolyte entrapment in recessed areas; i.e., riveted areas, spot welds, blind holes	- Nitric acid dip - Immersion in neutralizing solution, i.e., sodium bicarbonate - Redesign parts to provide drainage - Blow out with clean air and rinse well - Plug blind holes
H) Concentration or dry on of dye solution during transfer	- Shorten transfer cycle - Reduce dye temperature
I) Galvanic pitting corrosion	- Poor quality coating - Alloy not suitable for processing on titanium i.e., 2xxx series - Rack in electrical contact with metallic tank - Significant difference between alloy composition of parts and rack
J) Undissolved dye particles	- Boil up, agitate, and filter dye bath
K) Superficial precipitation of dye at surface of coating	- Raise pH to proper value
L) Coating degraded	- Make sure pH of dyestuff is a minimum of 4.0

Besides examining root causes and possible corrective actions it is important that we understand the different variables regarding the dyeing of aluminum and how they affect the dyeing process.

> Concentration of Dye bath - this can be monitored using a spectrophotometer, which will provide us with the total (nominal) dye content. Another measurement is to do actual dyeings, comparing how our bath dyes against the standard. This will provide us with the effective dye content. It is important to keep track of the nominal vs. effective dye content. Differences between the two will cause longer dye times, reduced color repeatability, and higher processing cost.

> pH - pH values can be checked with a pH meter and should be maintained within the dyestuff manufacturers specifications. When the pH is out of specification the following can occur: poor dye ability, insufficient color tone, and uneven dyeing. pH adjustment is usually carried out with the following reagents:

Raise pH: diluted caustic soda
Lower pH: diluted acetic acid.

> Aluminum - dissolved aluminum is carried into the dye bath solution as a form of Al2(SO4)3 Aluminum Sulfate. Certain dyestuffs are affected by the accumulation of aluminum sulfate more so than others. When we have higher concentrations of aluminum we generally see reduced activity of the dyebath. Good rinsing practices will help reduce the amount of aluminum build up in the dye baths.

> Mold - Mold will be grown in the dye bath due to the organic compound if the dye tank remains at low temperatures for long periods of time. The mold decomposes the dyestuff and will cause the pH to vary which in turn will lead to insufficient dyeing. It is recommended that the dye tank be covered during periods of in operation.

The most important aspect of troubleshooting is to resolve the problems before they become a problem. We do this by establishing controls, such as: tank titration, spectro analysis of the dye baths, actual dyeings of the production bath compared to lab standards, and regular decanting of process tanks. Establishing Statistical Process Control (SPC) charts will provide us with a map of how our line is running. And training your employees on how to use cause and effect diagrams will greatly enhance your ability to minimize down time. The small amount of time we invest daily on controlling our anodizing tanks will save us lost profit dollars later.

ACCELERATED CORROSION TESTING

By Amiel G. Forshee, PE, CQE
Boeing Commercial Airplane Group, Seattle, WA

Salt spray testing is the metal finishing industry standard for corrosion resistance of finishes. Salt spray limitations have been thoroughly documented,[1] leading one to the conclusion that an accelerated corrosion test is highly desirable. This article considers 20 accelerated corrosion tests for correlation with long-term salt spray. Three of the tests were evaluated, using chromic acid anodize. The Cathodic Breakdown Test (CBT) correlated well with long-term salt spray, is quantitative, inexpensive, and takes ten minutes. CBT is now a standard test procedure and is in use at several Boeing locations. Work with an ASTM subcommittee is underway to make this test an ASTM and ISO standard. This article is based on a series of three published articles.[2-4]

Discussion Of Possible Accelerated Corrosion Tests

The objective of these efforts was not to replace salt spray testing. Salt spray tests are considered the reference, regardless of their limitations. Many military specifications require salt spray testing even though it is slow, expensive and subjective. Alternative tests which are quick, inexpensive and objective are needed for: (1) frequent monitoring for process changes, (2) troubleshooting and (3) research and development. Alternative tests must relate to salt spray test results because, in the end, salt spray is the ultimate criteria.

Twenty possible accelerated corrosion tests are placed into 11 categories and listed in Table 1. An evaluation of these tests was made with respect to capital cost, type of data (quantitative or other), possibility for correlation with salt spray tests and test time requirements. The latter consideration was given a high weighting because an acceptable test must be fast enough to enable making process changes before any substantial amount of hardware has been processed. Considering our processes and costs an arbitrary limit of 60 minutes was required of any candidate for further consideration. After evaluating these twenty tests, it was decided to evaluate three test methods in detail: (1) Tafel Plot Extrapolation, (2) Cathodic Breakdown Test, and (3) AC Impedance.

Tafel Plot Extrapolation

Test Description

Tafel Plot extrapolation involves plotting voltage versus log current density, passing through the open circuit potential. At about 50 mV from the open circuit potential, the anodic and cathodic curves exhibit linear behavior (Tafel slopes). Figure 1, from ASTM G 3, shows a hypothetical cathodic and anodic polarization diagram. The intersection of these Tafel Plot lines defines the corrosion current density for the system.

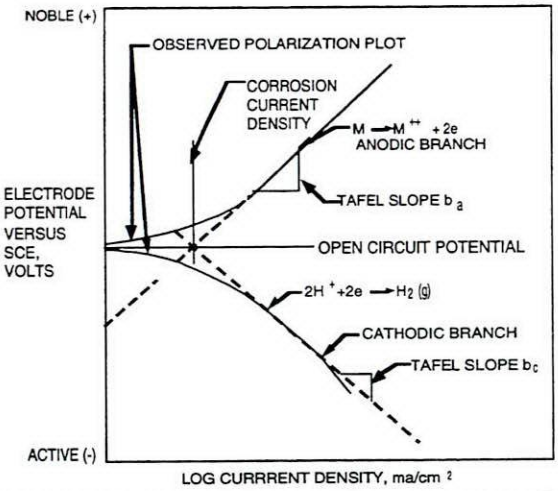

FIGURE 1. HYPOTHETICAL CATHODIC AND ANODIC POLARIZATION DIAGRAM

Test Procedure

A preliminary evaluation of Tafel Plot Extrapolation (TPE) was performed to evaluate the ability to discern between specimens with widely varying salt spray resistance. Test specimens were prepared by varying anodize time, anodize free chromic acid concentration and seal time. Two salt spray chambers were used to test specimens processed concurrently with the TPE test specimens. An article by Yousri[5] describing good correlation between Tafel Plot data and long-term salt spray testing formed the basis for the test procedure and equipment used. The test cell and counter electrodes were purchased from Yousri and used according to his test procedures.[6] Figure 2 shows a test cell schematic. Equipment specifications and test procedures follow.

TABLE 1. ACCELERATED CORROSION TESTS

DESCRIPTION	ASTM SPECIFICATION	ESTIMATED TEST TIME	ESTIMATED EQUIPMENT TEST COST ($)	CHANCE OF SUCCESS	LIMITATIONS/OTHER
A. Use Salt Spray Test - accelerate seeing corrosion	B 117	12 to 48 hrs.	$100K TO $500K	very poor	Use magnetic sensors for corrosion sites. Unproven.
B. Use a Fog Cabinet and Accelerate:					
(1) Corrodkote	B 380	> 24 hrs.	$20K	very poor	Used on Ni/Cr, etc. Mechanism different. Humidity chamber used.
(2) Modified salt spray	G 85	> 24 hrs.	$30K	poor	Acetic acid, sea water acidified, SO_2. Mechanisms different. Aluminum resistant to some of above.
(3) CASS test	B 368	> 24 hrs.	$30K	poor	Used on decorative coatings, etc. (Copper accelerated acetic acid salt spray)
C. Immersion Tests					
(1) Exfoliation Test	G 31 G 34	1 to 4 hrs.	nil	poor, but possible with other electrolyte	NaCl, KNO_3, HNO_3 to pH 0.4. Not normally used for control.
(2) $CuSO_4$	—	—	nil	poor	Recommended by Jack Snodgrass of Reynolds Aluminum. Look for Cu deposition.
D. Gas Pressure	—	< 30 min.	$5K	poor	Boeing work. Attack by weak NaOH; measure pressure due to H_2 evolution.
E. Make Standard Specimens	—	vary with test used	vary with test used	fair to poor	Use pure aluminum specimen and doctor with elements at known sites. Run through process. Preserve mechanism.
F. Galvanic Cell	G 71	minutes to hours	low	fair to poor	Make a cell with test specimen and graphite (or ?) in an appropriate solution.
G. Galvanostatic Tests					
(1) PASS Test	—	< 30 mins.	$2K	fair with modifications	Used on painted metal. Cathodic current. Not highly quantitative.
(2) Electrolytic Oxalic Acid Etching	—	minutes	$2k	doubt if mechanism applies to aluminum	Used on stainless steel (replaces ASTM A 262). Anodic current. Not highly quantitative.
H. Galvanodynamic Tests					
(1) Galvanostaircase	G 100	< 60 mins.	$15k +	if time available, worth trying	Work done on 1 cm^2 specimen. Stan Hirozawa (BASF Corp.) has done most work on this.
I. Potentiostatic Tests					
(1) EC (Electrolytic Corrosion)	B 627	< 30 mins.	> $10K	poor	Used for decorative coatings (Cu/Ni/Cr). Does not duplicate corrosion mechanism. Specimen anode.
(2) FACT Test	B 538	< 10 mins.	$10K	variation possible	Small test area. Specimen cathode.
(3) Cathodic Breakdown Test	—	< 10 mins.	$3K	worth evaluating	Glenn Gholson (Boeing Everett) has used. Specimen cathode.
(4) Impedance Test (Aztac Test)	B 457	< 10 mins.	$15K	poor - need entire curve (see K)	1 V RMS, 1000 Hz, 3.5% NaCl neutral. Commercial equipment available, Not considered promising. No service correlation. Small specimen area. Leakage can give low readings.
J. Potentiodynamic Tests					
(1) Polarization Resistance (Linear Polarization)	G 59 D 2776	< 10 mins.	$10K to $20K	use Tafel Plot (J.(2))	Must know Tafel slopes (see J.(2)). Small test area. Scan ± 10 mv of E_{corr} Assumptions must be made.
(2) Tafel Plot Extrapolation	G 3 G 5	< 45 mins.	$10K to $20K	worth evaluating	Must have linear Tafel regions. Pratt & Whitney using. Assumptions must be made. ASTM specification may be written in future.
(3) Cyclic Polarization	G 61	< 60 mins.	$20K	poor	Used for susceptibility to localized corrosion for Fe, Ni, or Co based alloys in chloride environment. Not applicable to aluminum in present form.
K. AC Impedance	—	< 60 mins.	>$30K	worth evaluating	Can be excellent R&D tool. Can differentiate between parts of anodized layer. ASTM specification may be written in future.

A. Electrolyte (two evaluated)
   (1) 5% NaCl meeting ASTM B 117
   (2) 16.67 g/L NaCl + 0.207 g/L H_3BO_3, pH 10.5
B. Electrolyte Quantity: 125 ml
C. Counter Electrodes (two evaluated)
   (1) Platinum ring, approximately 1.5" diameter
   (2) Inconel 625, 0.020" sheet with 300 3/64" holes
D. Cell Size: 2.00" diameter by 2.9" high
E. Cell Material: Organic
F. Preparation of Inconel 625: 2 minutes in 1% HF + 15% HNO3 solution, then water rinse
G. Counter Electrode Position: 1.0" above specimen
H. Reference Electrode: Standard Calomel Electrode
I. Reference Electrode Position: 0.25" above specimen
J. Agitation: 0.75 ft^3/hr airflow through a fritted glass located between counter electrode and specimen
K. Pre-Conditioning: 5 minutes to obtain stable E_{corr} (open circuit potential), then 30 seconds at -1.0 V versus Ecorr, then a 60 second minimum wait until stable E_{corr}
L. Tafel Plot Direction: + 200 mV to - 400 mV versus SCE
M. Scan Rate: 0.5 mv/sec
N. Equipment Used: EG&G Princeton Applied Research Model 273 Potentiostat with EG&G software

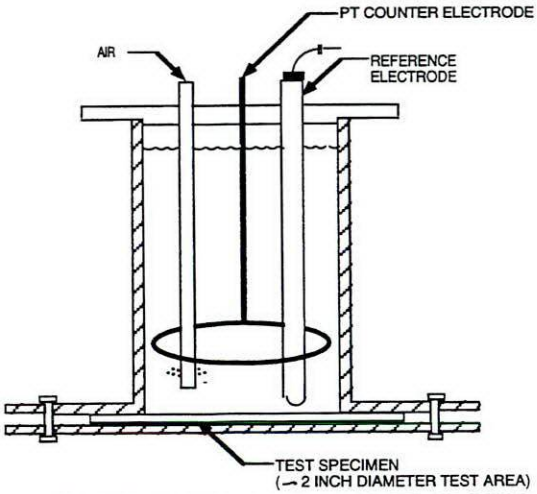

FIGURE 2. TAFEL PLOT TEST CELL

Test Results/Discussion

Table 2 shows the results of the TPE-salt spray correlation. From this table, it is noted that the TPE data spread is very narrow even though there is a wide range of salt spray results. TPE was, therefore, eliminated from further evaluation. The author has no explanation for the difference between results herein and those published by Yousri. With a different Tafel Plot procedure, the results may have been different. The Tafel Plot procedure used in this evaluation has not been adopted by other laboratories.[7] The pre-conditioning step used herein will affect test results by removing oxygen at the surface.[8] Also, the Tafel Plot direction used in this evaluation (from anodic branch to cathodic branch) differs from EG&G recommended procedures.[9] EG&G recommends: (1) going from E_{corr} negative to obtain the cathodic slope, then (2) going from E_{corr} positive to obtain the anodic slope. If this EG&G procedure had been followed, the anodic influence on the cathodic slope would have been eliminated. No attempt was made by the author to use other Tafel Plot procedures because the Cathodic Breakdown Test was promising and equipment cost was lower than that for Tafel Plot Extrapolation testing.

Cathodic Breakdown Test

Test Description

Figures 3 and 4 show a test schematic and test cell details of the Cathodic Breakdown Test (CBT).[10] To use the CBT with the Reference 10 test procedure, it is only necessary to call out: (1) test voltage, (2) polarity, (3) media, (4) counter electrode and (5) time. No separate reference electrode is used. For chromic acid anodize testing, the voltage was -950 mV with the specimen being cathodic (electron donor). The media was 5% NaCl meeting the requirements of ASTM B 117. The counter electrode was 0.030" diameter, 99.7% minimum purity aluminum wire. Test time was 10 minutes or the time to reach 3,000 microamperes, whichever came first. During the CBT test, current versus time is recorded. The parameters used to correlate CBT data with salt spray results were: (1) the time to rapid current increase and (2) the time to reach 250 microamperes. Figure 5 shows examples of how the time to rapid current increase is determined.

TABLE 2. TAFAEL PLOT DATA ON CHROMIC ACID ANODIZE

	TAFEL PLOT RESULTS, M.P.Y.			SALT SPRAY RESULTS (30 IN ^{2})	
TEST NUMBER	INCONEL 625 E* P&W SOLUTION	INCONEL 625 E* 5% NaCl	PLATINUM E* 5% NaCl	RECEIVING CHAMBER HRS : PITS	BMT CHAMBER HRS : PITS
2	0.04	0.02	0.04	500 : 0	336 : 0 500 : 3
3	0.02	0.00	0.07	336 : 0 500 : ~50	336 : 0 500 : 1
4	0.02	0.00	0.02	500 : 0	500 : 0
5	0.02	0.00	0.02	500 : 0	500 : 0
6	0.04	0.01	0.02	500 : ~60	500 : ~5
7	0.02	0.00	0.05	500 : ~35	500 : ~10
8	0.02	0.00	0.00	368 : 0 500 : >100	368 : 0 500 : >100
9	0.02	0.02	0.03	400 : >70	400 : >75
10	0.06	0.01	0.01	240 : >100	168 : >100

E* = ELECTRODE

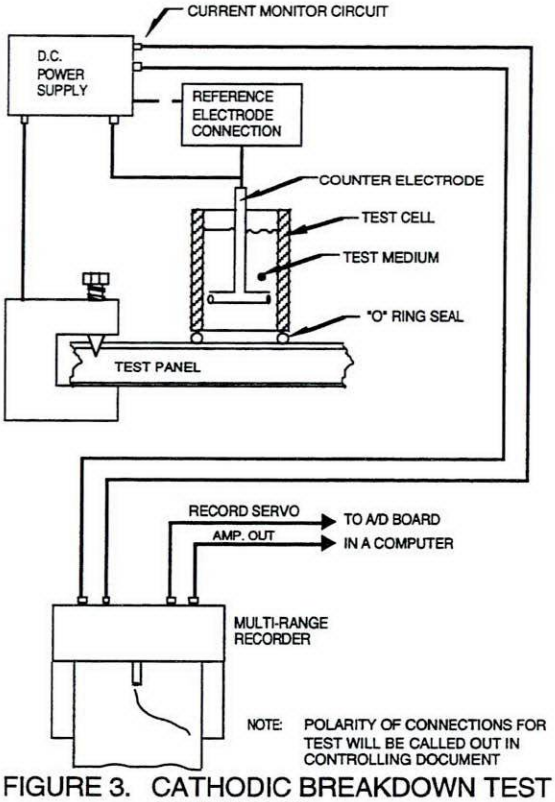

FIGURE 3. CATHODIC BREAKDOWN TEST SCHEMATIC

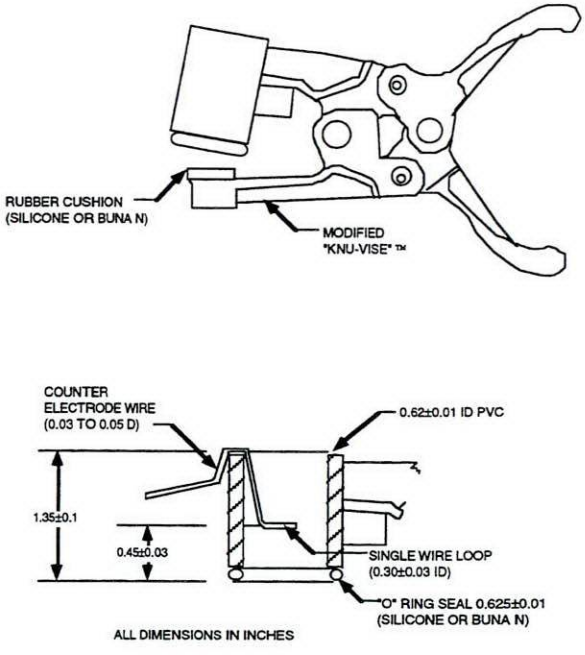

FIGURE 4. CATHODIC BREAKDOWN TEST CELL

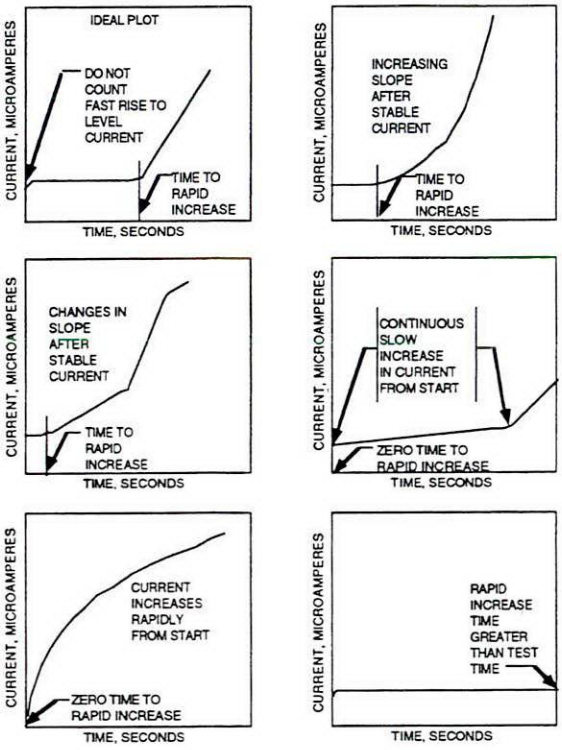

FIGURE 5. DETERMINATION OF TIME TO RAPID CURRENT INCREASE

Test Procedure

The Cathodic Breakdown Test (CBT) has been shown to correlate with salt spray tests on a pass/fail basis.[11] To identify any sources of inconsistency in this correlation, a designed experiment was completed using all major variables in a typical chromic acid anodize process. Sixteen variables were identified (Table 3) and arranged in a 2^{16-11} fractional factorial experiment. No alkaline cleaner bath parameters were varied. Preliminary tests indicated the alkaline cleaning step had no effect on response variables. The chromic acid anodize temperature was held at 95° F. Including preliminary testing, a total of 63 tests were used in the CBT-salt spray correlation.

Four 3" x 10" x 0.040" 2024-T3 aluminum test panels were salt spray tested (ASTM B 117, six degree incline) at each design point of the experiment. One salt spray chamber was used for all panel testing to avoid variations between chambers.[12] The test panels were put in salt spray and checked every four days by removing them, rinsing with deionized water, and counting the pits. Panels which had not failed were returned to the test chamber. The criteria for failure was five pits or more on a 3" x 10" test panel. The salt spray score for a particular design point was the average failure time of the four panels. The salt spray score was compared to the CBT data to determine whether CBT correlated with salt spray pass/fail results. The basic test procedure with the CBT is to file a specimen corner to bare metal, clamp the test cell to the specimen, make the electrical connections to the counter electrode and to the bare specimen corner, pipette 5 ml of 5 % NaCl solution into the test cell, and then start the test. Tests were conducted at ambient laboratory conditions.

TABLE 3. PROCESS VARIABLES AND EXPERIMENTAL LEVELS

DEOXIDIZER BATH		
Copper	0;	250 ppm
Nitric Acid	10;	20 oz/gal
Amchem	0.6;	1.4 oz/gal
Aluminum	0;	2.3 oz/gal
Time	5;	18 minutes
Temperature	65;	90 F
ANODIZE BATH		
Free Cr^{+6}	30.5;	52.0 g/L
Aluminum	0;	6.5 g/L
Time	35;	60 minutes
NaCl	0;	200 ppm
Sulfate	0;	500 ppm
SEAL BATH		
Cr^{+6}	45;	80 ppm
pH	3.2;	3.8 pH units
Temperature	190;	200 F
Time	23;	28 minutes
Silicate	0;	10 ppm

Correlation With Salt Spray

Figure 6 shows the correlation between salt spray days to failure and the two CBT parameters: (1) time to 250 microamperes (T_{250}) and (2) time to rapid current increase (break time, B_T). Numbers are the average time to failure (days) of four salt spray test specimens. The chromic acid anodize specification requires passing a 14 day test. However, specimens were evaluated every four days, so a salt spray failure is considered any time of 16 days or less. From Figure 6, all salt spray failures can be identified if two conditions are met: (1) T_{250} is less than 55 seconds and (2) B_T is less than 15 seconds. There is approximately a 4 to 1 ratio

between 55 seconds and 15 seconds, so a single number has been calculated to account for these two parameters:

Combined CBT (seconds) = 0.2 T_{250} + 0.8 B_T

If the Combined CBT is less than 15, the CBT test predicts a salt spray failure. As an example, if T_{250} is 30 seconds and B_T is 10 seconds, the calculation shows: 0.2 (30) + 0.8 (10) = 6 + 8 = 14 seconds. This would be marginal for passing salt spray. The Combined CBT does not correlate exactly with the described two parameters, but does come close.

From Figure 6, using the above B_T and T_{250} criteria, one can see that out of 63 tests, 10 of 10 salt spray failures were correctly identified, and 50 of 53 salt spray passes were correctly identified. Three salt spray passes were identified as failures while no salt spray failures were identified as passes. Figure 6 data were obtained from specimens tested from one to six days after duplicate specimens went into salt spray. To compare test data, all T_{250} times were corrected to day zero (day of processing). This was done by using the average rate of change of T_{250} with time, which was found to be an

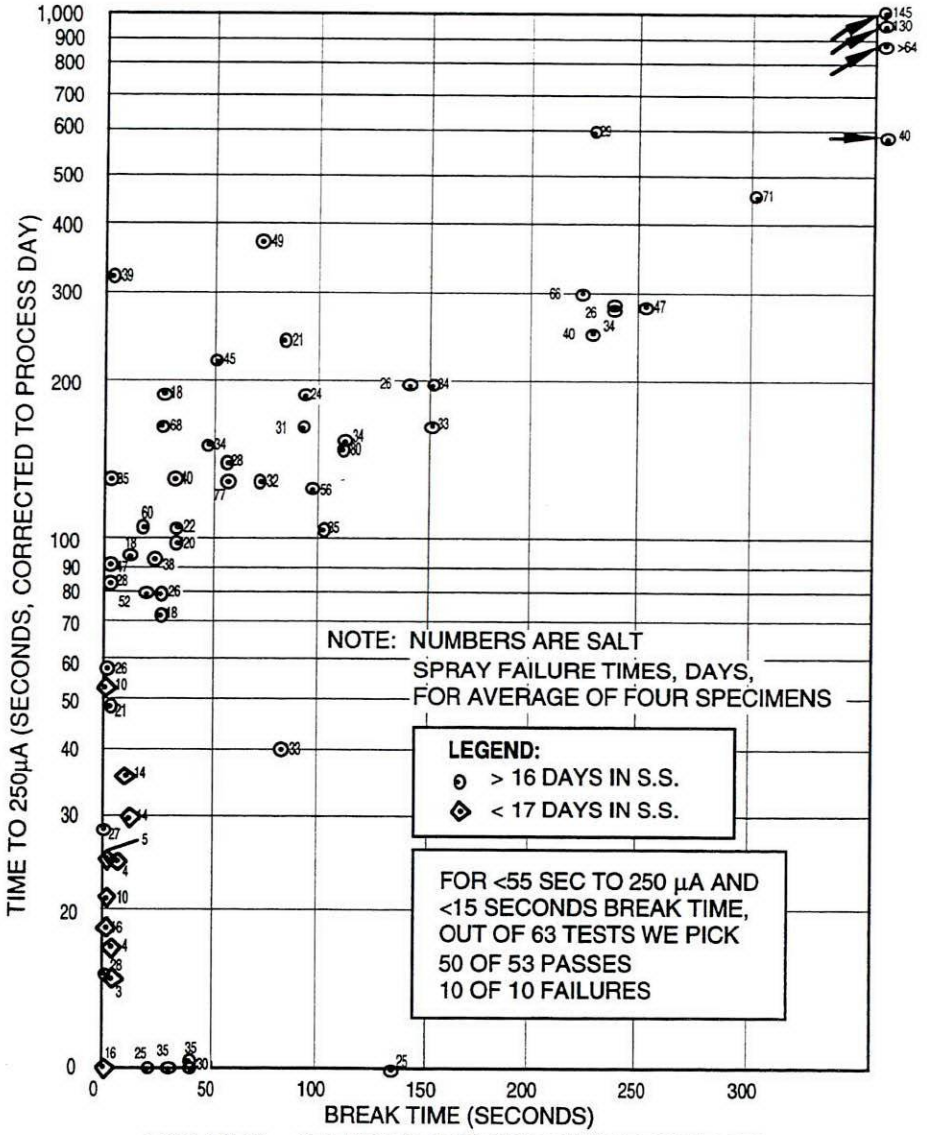

FIGURE 6. CATHODIC BREAKDOWN TEST DATA

increase of 5.5%/day. If it were possible to consistently run tests the same day specimens went into salt spray, T_{250} data might be better relative to salt spray correlation. B_T values did not change significantly with time, thus requiring no correction for the time frame up to six days. In an effort to understand the three cases where salt spray passes would be identified as failures by B_T and T_{250} criteria, scanning electron microscope (SEM) cross-sections were obtained from selected specimens. The SEM photos did not help explain why one low time (B_T under 15 seconds and T_{250} under 55 seconds) specimen passed and the other failed salt spray.

AC Impedance

Test Description

AC Impedance testing is based on the principle that electrode surfaces generally behave as a network of resistive and capacitive elements from which an electrical impedance can be measured and analyzed. Therefore, application of an impressed alternating current on a specimen can yield information on the state of the surface of the specimen, and thereby yield information relating to the corrosion resistance of the specimen. Various models of an equivalent circuit have been used to explain the Bode plots (impedance versus frequency and phase angle versus frequency) commonly used in AC Impedance.

After data collection, the results may be plotted in a number of formats. The impedance portion of an idealized Bode plot, shown in Figure 7, is most convenient for extracting polarization resistance information.[13] The log-log Bode plot displays the absolute impedance, - Z- , versus the frequency ω. In a simple system, the solution resistance R_Ω may be obtained from the high frequency data by extrapolation to the y-axis, as shown in Figure 7. At middle frequencies, the coating displays its capacitive behavior. Combined polarization resistance and solution resistance $R_p + R_\Omega$ can be estimated by low frequency extrapolation, as shown in Figure 7. Polarization resistance data was used for the salt spray correlation and is obtained by subtracting the solution resistance from the combined polarization and solution resistance. The polarization resistance is inversely related to the corrosion current in accordance with the Stern-Geary relationship[14,15]

$$i_{corr} = \beta_a \beta_c / 2.303\, R_p(\beta_a + \beta_c)$$

where i_{corr} is the corrosion current, β_a and β_c are the Tafel coefficients for the anodic and cathodic partial reactions, respectfully, and R_p is the polarization resistance. As the above relationship shows, the corrosion rate of the substrate decreases as the polarization resistance increases.

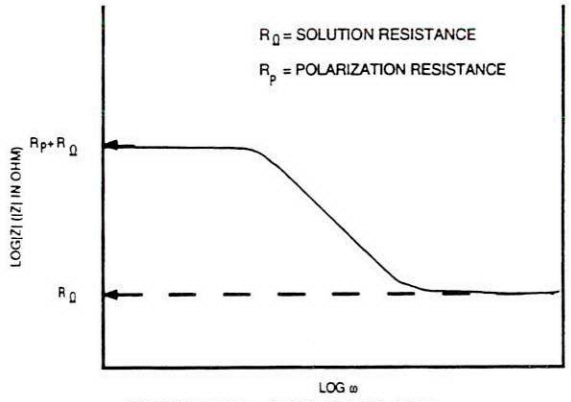

FIGURE 7. BODE PLOT

Test Procedure

AC Impedance equipment was not available when the chromic acid anodize designed experiment was initiated. AC Impedance equipment is much more expensive than Cathodic Breakdown Test (CBT) equipment. Therefore, there was no economic incentive to pursue AC Impedance after CBT was shown to correlate well with salt spray pass/fail tests. AC Impedance data was obtained on selected specimens after-the-fact, recognizing there was a time variable effect on the test specimens.

AC Impedance data was obtained using an EG&G Model 273 Potentiostat with Model 5301A lock-in amplifier.[16] An EG&G flat cell, Model K0235, was used, which fixes the position of the electrodes and size of the specimen area exposed. The specimen area was 1 cm^2. A platinum counter electrode, a standard calomel reference electrode and three hundred ml of 5% sodium chloride solution meeting ASTM B 117 were used. The solution was not stirred and the test was conducted at ambient laboratory conditions.

The specimen was loaded into the flat cell and the salt solution added. Data collection began after the instrument read a steady state open circuit potential. A frequency range from 100 kHz to 6.5 mHz was scanned. More information at the lower frequency range would be useful, but the long measurement times associated with these low frequencies made more data collection impractical. To accurately

measure response, the system was perturbed by a 10 mV waveform. If too large an AC amplitude is applied, the electrode may be altered. However, 10 mV was large enough to give an accurate response without altering the system.

AC Impedance-CBT Correlation

Due to the lack of test equipment when the designed experiment was run, AC Impedance data was obtained months later on selected specimens which had been previously run by CBT. Figure 8 shows a plot of AC Impedance and Combined CBT values. From Figure 8, there is a reasonably good correlation between AC Impedance and CBT tests. If the AC Impedance test had been run concurrently with CBT, the correlation may have been better. AC Impedance data was separately obtained on the three specimens which passed salt spray, but were identified by CBT as salt spray failures in Figure 6. As with the CBT, AC Impedance data indicated poor salt spray results would be expected, which means both test methods came to the same conclusion.

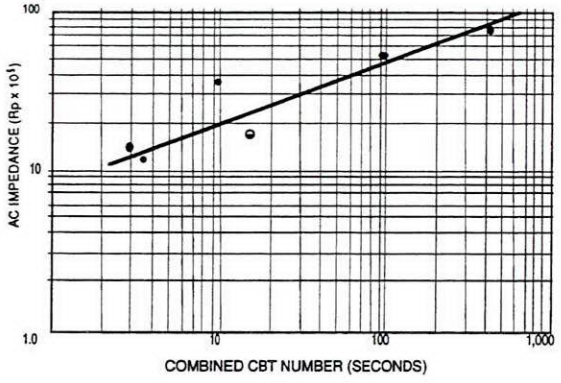

FIGURE 8. CATHODIC BREAKDOWN TEST - AC IMPEDANCE CORRELATION

CBT Test Discussion/Applications

CBT Data Discussion

Why do we have a good usable correlation between salt spray and the CBT when we use both B_T and T_{250} when the use of either of these parameters by themselves would not show this correlation? Figure 9 explains this. There are four possible B_T and T_{250} acceptable or unacceptable salt spray values, i.e., B_T greater and less than 15 seconds and T_{250} greater and less than 55 seconds. Values of T_{250} indicate the severity of the corrosive attack, with higher values meaning the attack is less severe. Values of B_T indicate the increase in the rate of corrosive attack, with higher values meaning a smaller rate of increase. In other words, if T_{250} is the velocity, B_T is the acceleration, with higher values indicating better corrosion resistance.

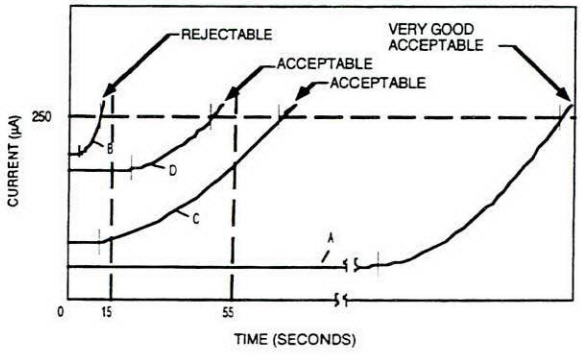

FIGURE 9. CATHODIC BREAKDOWN TEST POSSIBILITIES

Curve A in Figure 9 represents a test specimen with good resistance to attack (high T_{250} value) and a very slow increase in rate of attack (high B_T value). This coating has a T_{250} much greater than 55 seconds and a B_T much greater than 15 seconds. A coating with these values might hold up in salt spray for over 100 days.

On the opposite extreme, Curve B in Figure 9 shows an example of a poor coating, with both poor resistance to attack (low T_{250} value) and a fast increase in rate of attack (low B_T value). This coating has both a T_{250} under 55 seconds and a B_T under 15 seconds. A coating with these characteristics would probably not pass a 14 day salt spray test.

Curves C and D in Figure 9 represent acceptable coatings which pass one CBT parameter and fail the other. Curve C illustrates a coating which has good resistance to corrosive attack combined with a relatively fast increase in rate of attack. This is an example of an acceptable coating, with a T_{250} over 55 seconds but a B_T under 15 seconds. Curve D represents a coating which has relatively poor resistance to attack combined with a slow increase in rate of attack. This is an example of an acceptable coating, with a T_{250} under 55 seconds and a B_T over 15 seconds. Curves such as C and D might represent coatings which are anything from marginal to holding up well in salt spray. As shown in Figure 6, an exact failure time cannot be predicted.

Use of the CBT Test

There are three identified uses for the CBT test: 1) routine process control, 2) troubleshooting process failures and problems and 3) research and development. For routine process control it is recommended the CBT be run one or two times per week. CBT tests should be run before and after a planned major process control event (bath dump/remake, major bath chemical additions, etc.), and run immediately after an accidental process event (wrong chemical additions, etc.). CBT quantitative data will enable rapid determination of whether a process is the same, improving or deteriorating relative to corrosion resistance. This information will enable corrective action to be taken before salt spray failures can occur.

Troubleshooting a process is generally the same as described in Reference 17 with one difference: one can now find causes of poor corrosion resistance in hours instead of weeks or months or perhaps never finding the causes. A number of process changes can be combined to more rapidly determine causes of poor salt spray results. One Boeing chromic acid anodize line was running salt spray panels daily due to frequent failures. Since incorporating a weekly CBT test, there hasn't been a salt spray failure in four months[18] and the frequency of salt spray tests have been reduced to once a month. Implementation of the CBT enabled the Boeing shop to: 1) see changes occurring in the deoxidizer bath and dilute chromate seal bath, and to dump/remake these baths before salt spray tests were jeopardized, 2) optimize the time in the deoxidizer bath and the dilute chromate seal bath, and 3) prevent production hardware impact due to salt spray failures.

With the CBT, research and development can be dramatically improved over that using salt spray panels. The CBT was recently used on anodized panels from a study of non-chrome deoxidizers. In about two hours quantitative data was obtained to show relative corrosion resistance differences between two non-chrome deoxidizers and the chrome-containing deoxidizer run as a control. The CBT data correlated well with salt spray results obtained two weeks later. Presently, salt spray will remain the ultimate criteria for new process baths, however, the CBT will enable rapid determination of relative differences between baths and bath chemistries. Thus, the CBT delivers great time savings and provides objective quantitative data.

Boeing Applications to Chromic Acid Anodize Process Control

As of this article, CBT is in the process of being accepted as an option for salt spray, and if accepted, the CBT will be included in the Boeing Chromic Acid Anodize Specification.[19] Boeing and subcontractor locations may then choose to incorporate this CBT test as an option to salt spray, within specified guidelines. It is assumed that CBT will never be a requirement nor a total replacement for salt spray. The most likely scenario will be weekly CBT run with normal salt spray testing for six months. After this time, if all goes well, weekly CBT would be run with the salt spray test intervals increased to every six months. If the process deteriorates to where specified CBT values for T_{250} and B_T are obtained, a salt spray test would be required immediately. Salt spray tests would thereafter be run on a specified schedule until CBT values exceed the point where there is any real risk of salt spray failure.

When CBT process control is implemented at multiple locations the feedback will be of great value. Quantitative data from multiple sources, which indicates the change in corrosion resistance due to process variables, will enable optimizing this anodize process or any other process the CBT is used on.

Other Applications for the CBT

The CBT can be used for any surface finish, whether on aluminum or other conductive substrate, after the test parameters (voltage, test media, counter electrode, etc.) have been determined. The data obtained may not be as conducive to interpretation as that shown herein for chromic acid anodize. It is recommended that anyone evaluating this test on another finish run a designed experiment which incorporates all critical process variables to ensure valid results.

At Boeing, a Boric-Sulfuric Acid Anodize (BSAA)[20] designed experiment with 16 variables was recently run using the CBT (-850 mv, all other test parameters were the same as for chromic acid anodize). Correlation with salt spray was poor. Due to surface conductivity which is inherent in BSAA coatings the current normally goes up from the start of testing, therefore, the B_T value is always zero. The best CBT test output was determined to be the current at the end of 10 minutes. Despite CBT data not being able to to predict whether BSAA salt spray specimens passed or failed, the CBT still yields valuable information. The CBT can indicate relative changes in corrosion resistance,

thus enabling use in routine process control, troubleshooting salt spray failures, evaluating changes in process baths, and in evaluating new process baths.

Summary
This article on accelerated corrosion testing: 1) evaluated 20 possible accelerated corrosion tests, 2) evaluated three tests for correlation with long-term salt spray, using chromic acid anodize, and 3) presented use of one test, the Cathodic Breakdown Test (CBT), in detail. The CBT correlates well with salt spray, gives quantitative data, takes ten minutes and costs under $2,000 (excluding a computer). CBT use at several Boeing locations indicates it works well in routine process control, troubleshooting and in research/development applications. The CBT is currently being evaluated to allow the reduction of salt spray testing for chromic acid anodize process control. CBT use for other applications is being evaluated. Work with an ASTM subcommittee is underway to make this test an ASTM and ISO standard.

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QUALITY
The Spark of Life for Anodizing

Author: Richard W. Mahn
Southern Industrial Chemicals, Inc.
Atlanta, Georgia

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ABSTRACT

The most difficult production issues are: what is quality, what determines how we can achieve it, and what determines that we have achieved it. This paper discusses these quality issues in general terms, and then looks more specifically at Quality in relation to the Anodizing Process.

Webster's New World Dictionary provides two basic definitions for **Quality**. One is: *"the degree of excellence of a particular item"*. Usually this is what comes to mind when quality is discussed. The problem with this is that one person's idea of what is excellence will differ from another person's. This difficulty arises from the **Subjective** nature of excellence. When different criteria are used to evaluate the same thing, or when the same criteria are given different degrees of importance, then the same conclusions can not be drawn as to the excellence of the thing, and it becomes difficult to agree on the product's quality.

The other definition is: *"that which makes something what it is"*. This definition focuses on the functionality or practicality of a thing. It either fulfills the basic need or it doesn't. This allows an **Objective** means of determining a product's quality and results in agreement as to acceptability.

Let's look at an example of how these two taken together can influence productivity. At the turn of the century the horseless carriage was developed as the latest revolution in the transportation industry. The invention and further development of vehicles powered by internal combustion engines must rank as one of the very top things that has significantly impacted our society in this century. Henry Ford saw the value and importance of automobiles as a primary source of transportation for everyone. His simple philosophy was to offer a practical vehicle at an affordable cost which would carry one from point A to point B. This resulted in the Model "T" Ford. Mr. Ford's philosophy allowed that the car would be a standard, one-color black vehicle, and that in all other aspects of serviceability each would be identical. Practical, functional, and serviceable were the words that could be applied to this product. This made quality an easy thing to measure and control because each car was identical and any variance would show up immediately.

The car was a success and a failure at the same time. While the Model "T" provided reliable, functional transportation - a measurable objective quality - Mr. Ford had not counted on the other factor - perceived excellence - a highly subjective quality. People wanted dependable transportation, but they didn't want to have the same car as everyone else. They wanted options and variety which had less to do with functionality and more to do with comfort and status. Determination of quality now had the added element of being subjective; that is, what did people **"like"**. As a consequence, he introduced the Model "A", which was a "grander" vehicle. In time many other models were added, and the rest, as "they say", is history.

When it comes to providing a product to the public or private sector of the economy, you can not just take into consideration its functionality, but you must also take into account the enjoyment factor. This holds true in almost

everything that is manufactured today, including ANODIZED PRODUCTS.

Therefore, we are must determine a set of values that makes a product what it is - both objectively and subjectively. If we were to combine both definitions, our ultimate definition of quality would read as follows: "The degree to which a thing has the characteristics that make it what it is corresponds to the degree of excellence that is ascribed to that thing." In other words, the more we fulfill **all** of the requirements the higher is the quality. Let's see how this works for anodizing.

The first characteristic of most "active" metals is that they do not occur as metal in nature. They are generally combined with other materials as salts or oxides. When we isolate the basic metal we find the second characteristic which ties to the first - the pure metal does not "like" to remain uncombined. It will react, with differing degrees of activity, to form at least some product of oxygen and/or water. After we have gone to the trouble of isolating the metal for use we must now put our efforts into preventing this recombining activity from taking place. The whole of the metal finishing industry is designed around this simple principal of restricting the metal from returning to its original state.

In the list of several useful metals that have this characteristic is Aluminum. The characteristics of Aluminum that make it so useful are:

1. It is abundant in nature.
2. Although not a simple process, it can be isolated from the materials with which it is combined.
3. It can be isolated in a very pure form.
4. It can be mixed with other metals (alloyed).
5. It is plastic in the following ways:
   a. Castable - when fluid it will take the shape of its container and solidify to retain that shape.
   b. Ductile - In its solid state it can be drawn.
   c. Malleable - In its solid state it can be extruded or flattened.
   d. Heat treatable - The crystal structure of the aluminum and its alloys can be manipulated to produce different characteristics of the solid metal.
6. It is strong, yet light weight (density).
7. The surface of the aluminum metal is chemically active which will allow it to be chemically altered to produce various protective and decorative coatings.

All of the above attributes have made Aluminum important in the construction industry where it is widely used both functionally and aesthetically. However, to produce such products requires several steps and considerable care.

Remembering that isolated and formed Aluminum left to itself, in time, will corrode (moisture) and oxidize (air), it is necessary to provide a surface that will prevent this from occurring. Anodizing is the process used to produce a controlled form of oxidation (Al_2O_3) which can protect the base metal from deterioration due to its natural reactivity - the practical or objective side of anodizing. At the same time other processes used in conjunction with anodizing are capable of producing an aesthetically pleasing product - the subjective side of anodizing. However, if the aluminum is not prepared properly and the anodizing is not done properly, then the aesthetic result of the coloring processes has little added value to the product because deterioration of the protective coating will lead to a deterioration of the appearance of the product.

In order to achieve an excellently (high quality) anodized part, we must determine the qualities that we want it to have as is appropriate to its end use. Then we must determine what it takes to obtain those qualities. The qualities that we need (objective) and want (subjective) are:

1. Structural strength
2. Anodizability resulting in:
   a. Protection against abrasive forces
   b. Protection against corrosion
   c. Protection against oxidation
3. Color
   a. Enhanced attractiveness

The Anodizing Step does not stand alone in the overall production process, but is dependent on the production steps before and after it. A look at each production step will help us understand how all these steps work together to form the total anodizing process and a total quality product.

METAL PREPARATION

1. Mining

Bauxite (Aluminum Ore) - The idea that the quality of anodizing has its beginning in the earth, I suspect would be met with "sure it does", with little believability. However, the evidence speaks for itself that we are facing more and more of a challenge starting with this first step. The U.S.A. used to be one of the largest miners and refiners of bauxite in the world. While there is still some mining done in the U.S., most has gone to other countries, because of the depletion of high quality bauxite ore in the U.S. The supply of bauxite being in other countries has lead to refining and reduction processes going to other countries. This has resulted in a world-wide Aluminum economy - meaning that whatever aluminum is used may have its source in any number of countries, and the quality of the subsequent metal may vary according to the care of its production. At one time the majority of the world's supply of aluminum metal was produced by three U.S. producers, but not anymore.

2. Refining

a. Purification of the Ore to produce alumina (Al_2O_3) - This is a very sophisticated process whose goal is to remove other mineral oxides from the aluminum oxide. As the quality of bauxite changes according to the source or location, the technology must adapt itself to the removal of impurities present at each location. When there were a few centrally located refining plants in which alumina was generated, the consistency of the resulting alumina was assured through reproducible, single-location production. Now that each location has its own alumina refinery, that means that the number of sources of alumina has increased accordingly. The quality of the primary aluminum is directly dependent upon the quality of the alumina used to prepare it.

3. Reduction

a. Isolation of Aluminum Metal - The reduction step electrochemically converts the aluminum oxide - which is dissolved in molten cryolite in contact with carbon electrodes through which is passed a direct current - to aluminum metal and carbon dioxide. The result is Primary Aluminum, sometimes referred to as Virgin Aluminum.

b. Purity of the Aluminum - The reduction step is non-specific; that is, it does not selectively reduce Al_2O_3 to aluminum and leave the rest behind. Any metal oxides present after alumina refining - silicon, iron, copper, zinc, etc. - that can be reduced will also be converted and end up in the aluminum. The concentrations of these other metals determine the purity, and hence useability, of the aluminum for subsequent alloys. Many alloys have strict limitations as to the quantities of these other metals that can be present.

4. Alloying (Primary Metal)

a. Structural properties - As stated earlier, aluminum has many properties that make it a highly desirable metal to work with and results in a great variety of aluminum products. However, "plain, raw aluminum" is too soft to have very many practical uses. But, if it is combined with other metals in very controlled amounts, the aluminum crystal structure will

take on modifications of its basic properties that result in stronger structural properties with a greater variety of uses. As a consequence of this capability to change characteristics with the presence of other dissolved metals, a tremendous variety of alloys have been developed over the years and new ones continue to be developed. The biggest challenge to the anodizer is that these alloys also vary in their response to the anodizing process.

b. Anodizing properties - It is important to note that "ALL aluminum alloys can be anodized". Of course, this statement must be modified to say "but not with identical results". The problem is not in the conversion of the aluminum present. If it were possible to utilize 100% purity aluminum this would diminish our difficulties significantly. However, every time a material is introduced into the aluminum matrix it has a direct effect on the amount and form of aluminum being converted during anodizing and on the subsequent integrity of the aluminum oxide film generated.

5. Recycling (Secondary Metal)

a. Structural properties - Just when we thought we had all the variables under control for virgin aluminum products, along comes recycling. This is a very helpful process in saving energy and conserving on metal wastes, but it has created a new set of parameters that, while they may be satisfactory from the structural sense, have increased the difficulty of obtaining a desired anodize response.

b. Anodizing properties - The principle difficulty with recycling is that the aluminum product is a mixture of virgin aluminum and previously-alloyed aluminum. The recycled aluminum has already formed a fixed crystal pattern, plus some of the individual metallics have formed discreet combined particles - such as, magnesium silicide. Having a crystalline structure different from that of the virgin alloy leaves these particles suspended within the metal matrix but not fully a part of it. The consequence of this is that these particles, in addition to the other alloy ingredients, affect the uniformity and integrity of the metal surface and subsequently the anodic coating.

6. Casting

a. Billet - Importance is given to the effect of proper casting of billet, because whatever crystal structure or distribution of alloying ingredients exists at this point may not be suitably altered in subsequent steps. The outer layer of the billet log and the inner crystalline structure must be of a certain size and homogeneity to be compatible with the extrusion process and the final extruded product. A certain amount of uniformity will be achieved in the subsequent heat treat process (step 7.), but only if the ingredients are properly dispersed initially and the crystal structure is within certain tolerances.

b. Ingot - What is good for the billet is also good for the ingot. Similar requirements prevail and although ingots are generally much larger and are rolled flat instead of being extruded, they still require the same finesse of casting as the billet.

7. Solution Heat Treat (Homogenization)

a. Billet and Ingot - This is probably one of the most interesting characteristics of aluminum alloys. Once the billet log or rolling ingot has been cast and cooled, it is reheated to just below its melting point. In this condition it is a solid, but it will act like a liquid in that the dissolved metallic elements will begin to migrate and disperse themselves more uniformly within the semi-solid billet. This includes the combined forms such as the magnesium silicide mentioned before. Once the homogenization cycle is finished and the billet or ingot allowed to cool, the position of those dispersed materials will become fixed into a final pattern of uniformity. If the crystalline structure prior to homogenization is too coarse, then the proper uniformity will not be achieved.

8. Forming

a. Extruded shapes - Proper control of the extrusion process centers around the billet temperature entering the press, type of profile die, extrusion speed, and exit quench temperature. These elements comprise the conditions that will give the resulting aluminum shape the structural and anodizable properties it will need.

b. Sheet - Rolling the ingot down to very fine thicknesses of aluminum changes the internal grain structure of the sheet tremendously. Also the condition of the rollers and the lubricants used can affect the outer surface characteristics.

c. Molded (Recast) Products - This process often remelts pre-alloyed ingots or pigs which molten metal is then poured into sand or permanent molds or is die cast. The other possibility is that a foundry is available to melt unalloyed aluminum and add the particular ingredients needed to produce the desired casting alloy. The principal factors that influence cast quality are the temperature of the mold at the time of filling and the rate of cooling of the cast aluminum metal. Both are critical to porosity and grain structure of the part.

9. Heat Treatment

a. Temper - This process is similar to that of homogenization (step 7.). Temper as it relates to iron requires heating the iron to a special temperature, beating on it to arrange the alloying ingredients, and then submerging it in cold water to "fix" those ingredients in place. But not so with Aluminum. The temperature of the aluminum to which it is elevated is important, but the greater influence is the time it is left at that temperature. The degree to which the dissolved alloying ingredients in the semi-solid state react with each other and migrate into a specific pattern will determine the temper upon cooling of the aluminum, which is not a quick water quench, but a slow air cooling.

b. Structural strength - The resulting temper will determine structural strength and anodizability. The higher the temper number the harder the aluminum and the finer the crystalline structure of the part. However, if the crystalline structure is too coarse after the extrusion process, this can not be overcome in the heat treat cycle.

c. Anodizing Process Response - The crystalline structure of the aluminum alloy at this point, which will have been determined by the accumulation of all the steps (1 - 9) discussed so far, will determine the final uniformity of the anodized metal surface that will be exposed during the anodizing process. Therefore, any one of or combination of the previous steps will directly influence the degree of success of the anodizing process.

ANODIZING

10. Cleaning

a. Surface cleaning - Cleaning of the metal surface is a two-fold process: (1) removal of any oils and general soils deposited ON the surface during one of the metal preparation steps; and (2) removal of oxide films and any ground-in materials. The second requires a slight "bite" to the cleaner that will remove a minute layer of metal through a light etching action. The purpose is to "scour" the surface clean for the subsequent bright dip or etching step. This can be accomplished by a single alkaline or acid cleaner, but sometimes requires both alkaline and acid cleaners to attack specific problem soils or oxides separately.

The controlling parameters for cleaners will include temperature, agitation, cleaner concentration, pH, and time in the solution.

11. Bright Dip

a. Surface smoothing - This procedure acts to remove surface metal in a highly selective manner. The action of the solution dissolves the rough "micro-peaks" of the metal surface, cutting them down, but leaving the "valleys"

alone. The result is a very micro smooth surface. The acid balance, temperature, and time in the bright dip are extremely critical to the degree and uniformity of the smoothing action.

b. Gloss enhancement - The result of the action of the previous step can be a bright almost mirror-like finish, but only on certain alloys. Many alloys can be prepared to have a bright surface prior to anodizing, but during the anodizing step will become "rough" again, due to the crystal structure and/or metallics present, and lose their brightness (reflectivity), although they may otherwise appear smooth. Therefore alloy selection is very important to achieving the desired result.

12. Etch

a. Sub-surface cleaning - This procedure operates to remove surface metal also, but it performs a function opposite to the bright dip. The etch solution is a highly caustic material which is designed to dissolve aluminum in order to remove both deeper ground-in soils and to remove die lines that come from extrusion or roll marks that come from flattening.

b. Gloss reduction - This action roughens the surface and gives it a "matte" appearance that is not reflective. It also exposes the underlying metallic crystalline structure that is the result of the previous Metal Preparation steps. Control parameters for this bath are primarily the caustic concentration and the temperature. Chelators are used to help hold the etched aluminum in solution, and sometimes special grain refiners are added to enhance the matteness of the surface.

13. Desmut

a. Surface particle removal - Caustic will readily dissolve aluminum, but many metals are not dissolved. Therefore, during the etching step the other metals that are present as a consequence of the alloying step **and** their form (crystal structure) as a result of the heat treatment step (temper) will remain on the surface after etching. These will include silicon, iron, and copper. This powdery, gray-to-black material is referred to as smut and must be removed prior to anodizing.

The desmut solution is a strongly acidic material capable of dissolving the metallic smut (without attacking the aluminum). Usually this can be achieved at "room temperature", given that the warmer the solution the faster will be the reaction. Temperature is not a critical control parameter. Acid concentration is important but can operate effectively in a broad range, especially if it is accelerated with one of a variety of additives that react with the metals to speed up there conversion to a soluble metal ion.

14. Anodic Coating[1,2]

a. Specialized surface protection - As discussed previously, an aluminum oxide film is not unique to the surface of aluminum. What makes it special is how it is achieved. The anodizing step consists of placing the thoroughly cleaned part into a conductive solution (usually acidic), connecting it to an electrical source (usually DC), and passing a current through this system. It is very simple in its principle.

The controlling factors are: (1) the electrical current source to flow through the aluminum part, (2) the oxygen source to react with the aluminum to convert it to Al_2O_3, (3) the temperature of the solution, and (4) time. The aluminum oxide, when formed properly, will exist as interlocking cellular molecules which form an uninterrupted, but porous, film over the entire surface of the aluminum that has been exposed to the reaction process. Using these four factors several kinds of film can be generated for different purposes.

b. Industrial and Aerospace - This type of coating has the toughest specifications - usually requiring thick (2 mil and up) and/or highly abrasion resistant coatings. Corrosion/oxidation protection may or may not be important depending on the specific application. These

properties are achieved through high current density, reduced bath temperature, and long cycle times.

c. Architectural and Commercial - This type of coating has moderately tough specifications - usually requiring moderately thick (0.4 to 1.0 mil) and/or moderately abrasion and corrosion/ oxidation resistant coatings. These are achieved through moderate current density, closely controlled ambient bath temperature, and moderate cycle times.

d. Residential and Automotive - This type of coating has modest specifications - usually requiring moderately thick (0.3 to 0.7 mil) coatings. Corrosion/oxidation resistance is important, while high abrasion resistance is not. These are achieved through low to medium current density, ambient bath temperature, and moderate cycle times.

e. Decorative - This type of coating has the lowest specifications - usually allowing for thin (0.1 to 0.4 mil) coating and minimal abrasion and corrosion/oxidation resistance. These are achieved through low to moderate current density, ambient bath temperature, and short cycle times.

15. Color

a. Enhanced attractiveness - Color is usually present to enhance the appearance of the final product. Colors are much more attractive than the "silvery" color of anodized aluminum.

Color does not enhance protection of the aluminum, but it is often associated with the fact that a film must be present in order to obtain color. However, sometimes the amount of color may be considered to indicate the amount of coating present. This is not necessarily valid.

Color does not cover the aluminum surface to hide any anomalies associated with the pre-treatment steps up to this point. The anodic coating is transparent and, when it is colored, at best it is translucent, thereby letting the exposed aluminum surface show through. That is why metal preparation and pretreatment are so important.

Presently there are in the industry three primary ways to achieve color:

a. Integral Color - This process uses a special-acid anodizing solution which has limited solubility to the aluminum and its alloying ingredients. While the anodizing reaction is generating the anodic coating, it is also incorporating undissolved metal particulate into the film which causes light to be dispersed through the translucent coating in such a way as to create a range of colors from light bronze to black. The color intensity depends on the film thickness, and the anodizing conditions of temperature and chemical concentration. One other condition that controlled the color shade and intensity was the alloy of the aluminum. For many years special alloys were produced that would give specific color results, but they became expensive to produce against the "generic" anodizing alloys. As a result the process had to adapt itself to using the standard alloys available and has been able to continue successfully.

b. Dyeing - This technique takes advantage of the porous nature of the anodic film. As the aluminum oxide cellular matrix is generated, part of the aluminum is dissolved by the acid of the clear anodizing solution. This leaves a series of openings in the surface of the film which can be filled with various materials. One of those is an organic dye. There is a very large variety of dyes that are suitable for this purpose. However, because they are organic they may not be stable when exposed to fairly intense sunlight, which can bleach out the color. Therefore, most applications of dyeing are used inside, in locations of moderate sunlight intensity, or with a limited selection of dyes which are resistant to fading. It is important to select colors carefully for the particular application.

The principle parameters that require

control during the immersion of the anodic coating (uniformly produced) into the dye solution are: (1) concentration of the dye; (2) pH of the dye solution; and (3) temperature of the solution. Contamination can be a problem, since bath life is extended as long as possible. Therefore, it is critical to control what goes into the dye bath.

c. Electrolytic Color - The electrolytic coloring process also takes advantage of the porous nature of the anodic film. The difference between dyeing and electrolytic coloring is that the dyes are absorbed by the pores and adsorbed onto the pore walls near the surface of the film, while the electrolytic medium is deposited at the base of the pore nearer the metal surface. The means of doing this has its basis in plating through the process of converting a metal ion into metal particles within the pore of the anodic film by the passage of an electric current. The principle colors used in this fashion are similar to those of the integral color process - light bronze to black. Because the electrical requirements and, hence, costs associated with clear anodizing followed by electrolytic coloring are much less than those for integral coloring, this process has taken over the architectural industry in the U.S. With other metal salts or other power technologies it is possible to create other electrolytic colors.

The primary control requirements for the electrolytic color process are: (1) a uniform anodic coating (in porosity and thickness); (2) chemistry of the color solution; (3) electric current (AC or modified AC); (4) temperature of the bath; and (5) time. Uniformity of color from one load to the other can be achieved by close tolerance of these conditions.[1]

16. Sealing

a. Closing the Pores - While hardness and abrasion resistance are directly related to porosity and thickness, corrosion and oxidation resistance are related to how well the pores are sealed after all the steps have been completed - clear anodizing, integral color, dyeing, or electrolytic color.

b. Hot water - The principle method used for years for sealing anodic pores was a boiling water seal. Water forms a particular hydrate with the aluminum that is greater in volume than the original aluminum oxide after anodize. This expanded, hydrated form fills the pores of the film essentially closing the holes, preventing penetration of any materials that would cause corrosion or oxidation. The critical factors are: (1)the temperature (at or near boiling); (2)water quality of the highest purity - distilled or deionized - and discarded as soon as it is contaminated with dissolved solids that result in any degree of electrical conductivity; (3)a pH of 5.5 ± 0.3; (4) a suitable antismutting agent; and (5) time (requiring a minimum of 3 minutes per micron) to achieve thorough sealing.

c. Mid-temperature with Nickel - The energy intensity and sensitivity of the hot water seal is obvious from the control parameters. A new process was developed which has similar parameters for control, but a greater latitude in its operation. The temperature is not as high (80-85°C); the bath concentration of the active nickel, which is formulated with a suitable antismut agent, is variable; the pH still requires careful monitoring; and the bath, once prepared in bulk with deionized water, will last much longer, with care, as it is not as sensitive to contamination. Besides the lower-temperature cost savings, the seal time can be cut to 1 minute per micron or less depending upon the anodic film requirements. This process combines the actions of aluminum oxide hydration with nickel hydroxide precipitation within the pore. This combination seals the pores and is very resistant to corrosion and oxidation.

d. Room-temperature with Nickel - The latest technology allows for sealing to take place almost at room temperature (32-34°C). The

energy cost benefits are significant so it has become very popular. Its mechanism of action is still being investigated and discussed[3,4,5], but basic agreement centers around the idea that when the porous aluminum oxide film is immersed in the "cold" seal bath the nickel fluoride chemicals enter the film pore and react with the active inner surface of the aluminum oxide to form a primordial liquid mush of nickel and aluminum salts. When removed and rinsed the mush begins to set up, eventually cementing the pores closed. Some hydration may occur, but is not the principle sealing ingredient as with the other seals. Once set up, the "cement" is very resistant to corrosion and oxidation. However, there is a curing time that must pass before the sealing action is complete. The sealing time needed is between 0.8 and 1.2 minutes per micron with an upper limit of 15 minutes beyond which time there seems to be little benefit.[6] However, too short of times can lead to inadequate sealing. The other parameter, chemistry of the bath, is critical in its range of control and more sensitive to contamination than the mid-temperature seal. The bath does not evaporate much so make up water contamination is not a serious problem, but drag-in from prior processes and displacement of chemicals within the anodic film can eventually interfere with its operation. The bath will not last indefinitely although with care there are some baths that have been running for a year or more.

It is interesting to note that even with significantly diminished seal time and energy costs in recent years, the pressure continues to cut time and chemical concentrations even further. The seal bath is viewed as a necessary evil instead of realizing that it is a **NECESSARY GOOD** which adds the final element of protection to all the work that has gone into bringing the aluminum this far.

e. Non-nickel metal base - Nickel is an interesting metal in the fact that it is so compatible with aluminum. Many different metals have been investigated over the years to find an alternative that would be considered environmentally safer. Other metals may be substituted but not with the same degree of effectiveness and efficiency as nickel. If nickel is going to be replaced, then proper sealing conditions are going to have to revert to some extent to the older more aggressive times, temperatures, and concentrations.

17. Rinsing

a. Good - Proper rinsing is important in preventing cross contamination in baths that would jeopardize pH, concentration, insolubles content, and chemical reactivity. Contamination is a serious threat in many of the process baths, as in all of the types of seal baths. Proper rinsing is primarily needed for rinsing the metal surfaces prior to the next step. For example, after the anodize step the surface is like a micro-sponge retaining what is in the pores from anodizing or picking up something else that is available to it in another rinse. Good rinsing helps remove some of the materials from the pore by the process of solution migration from a higher concentration in the pores to the lower concentration in the rinse. This only works if indeed the rinse is cleaner than the solution in the pore. The importance of proper rinsing can not be over-stressed.

"Good" rinsing requires at least two tanks after each step. Recognizing the difficulty of this, there are some alternatives that can conserve without compromise. Another parameter in rinse tanks is temperature. Most rinse tanks are not controlled at a steady state of temperature. This presents a serious problem of variability from the cold season to the hot season. One of the basic principles of chemistry is that warm water will dissolve chemicals more quickly than cold water and that it will hold more chemicals in solution. However, rinse time is often the same whether the incoming temperature is 5°C or 25°C. It is important to realize that the efficiency of the

rinse is proportional to its temperature.

b. Conserving - The pressure that is being put on the chemical processing industry to cut down on effluent, chemicals, and wastes being put out into the environment has continued to increase. One of the best ways to accomplish rinse conservation is to use cascading rinses to get the greatest solubility benefit of the incoming water supply. By getting multiple use of the water better rinsing is achieved and less water is going out the exit. The main consideration is that we can not cut rinsing down below practical limits and expect good results.

SUMMARY

Having defined the quality of a product as that which makes something what it is - Anodized - and having looked at the many steps involved in arriving at an anodized product and their importance to each other, we have determined how we would be able to achieve a quality product. In order to maintain quality we simply determine which of the previous steps can be short cut. The answer is none of them.

In an effort to control this situation many architectural plants have included as many of the steps under their control as possible, starting with step 4. - the alloying of high purity virgin aluminum - and then controlling all subsequent steps. Job shops are not able to exercise such control, but can be aware of the importance of each step and require their sources to provide quality products.

All process steps have ranges of operation which provide for flexibility of control yet still produce a suitable product, assuming that the process will be run in the middle to upper regions of the operating range.

Another reason for operating ranges is to provide for different requirements of the final product. A product that may be used under relatively non-aggressive conditions can be prepared less vigorously than a product requiring service under severe conditions. The conditions to generate a product for use under severe conditions requires higher production standards. However, the temptation is to use the same production conditions as for the lesser product. Therefore it is important to remember that the quality - both functional and aesthetic - of the product is directly proportional to the procedures used to produce it. If we do that we can also have confidence that we have achieved the desired quality.

CONCLUSION

In industry the pressure is on to do or pay less and less without sacrificing the desired quality or qualities of a particular product, but this cannot be done as a regular practice. When the lower limits of control are breached, the product can not be expected to perform as well. Therefore, "The Spark of Life for Anodizing Aluminum" must be to recognize what it takes to produce the "Qualities" that are needed to meet the service and/or aesthetic requirements and then be sure that all of the metal forming and anodizing steps are performed under the best of conditions to achieve those requirements. This will then result in the "QUALITY" of the product fulfilling the degree of excellence expected.

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Abstract...

AUTOMATED CHEMICAL PROCESS CONTROL IN ALUMINUM FINISHING

Implementation of automated process systems like hoist controls are essential in our market place. The ability to control costs, reduce overhead and still put out a quality product allows business' to maintain and spread their margins which is the real challenge in today's globally competitive atmosphere.

One difficulty in realizing the full benefits of these types of systems is that the automation is hampered by the manual, laborious task of process control. Manual monitoring, analyzation and adjustment of the various chemical and physical parameters of process tanks and baths detracts from the automated process. An unacceptable rejection or scrap rate may become present due to fewer eyes following the product(s) through each step of the process.

Another problem is in the increased use of products such as long-life etch baths, anodizing additives, electrolytic coloring, low temperature seals and nonchromate conversion coatings. Although they provide improved finishes, a cleaner environment and in some cases, lower production costs...they also generally require much tighter control of operating parameters in order to achieve consistency and quality.

Automated chemical process control is the crucial link between automation and profitability. It is the "Watch Dog" of automation and the key ingredient to higher quality out put and the reduction of waste and scrap...

AUTOMATED CHEMICAL PROCESS CONTROL

IN METAL FINISHING

INTRODUCTION

The metal finishing industry has adopted many technological advancements over the past ten (10) years. Automated systems such as programmable hoist controls have given way to increased production, reduced labor costs and improved control over a few of the process variables i.e., tank times and temperatures. With the realization of these automated process systems and their benefits, industry leaders such as yourselves look to take the finishing process to the next level...Automated Chemical Control.

Implementation of automated systems like hoist controls are essential in our market place. The ability to control costs, reduce overhead and still put out a quality product allows business' to maintain and spread their margins which is the real challenge in today's globally competitive atmosphere.

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Automated chemical control is the crucial link between automation and profitability. It is the "Watch Dog" of automation and the key ingredient to higher quality out put and the reduction of waste and scrap. Some of the benefits of these systems include:

- ***Increased analytical frequency, offering tighter control of process baths and product consistency.***
- ***Greater accuracy over manual analytical procedures.***
- ***Improved utilization of labor acquainted with manual monitoring, analyzing and adjusting.***
- ***Reduction in product and chemical handling eliminating further room for error and securing worker safety.***

These generalized benefits lend themselves to such numerous quantifiable advantageous that Return On Investment (ROI) calculations consistently show an approximate 1 YEAR PAYBACK. With this type of return, monthly savings from operating expenses could pay for the system if it were purchased via some type of short term financing.

AUTOMATED CHEMICAL PROCESS CONTROL SYSTEMS

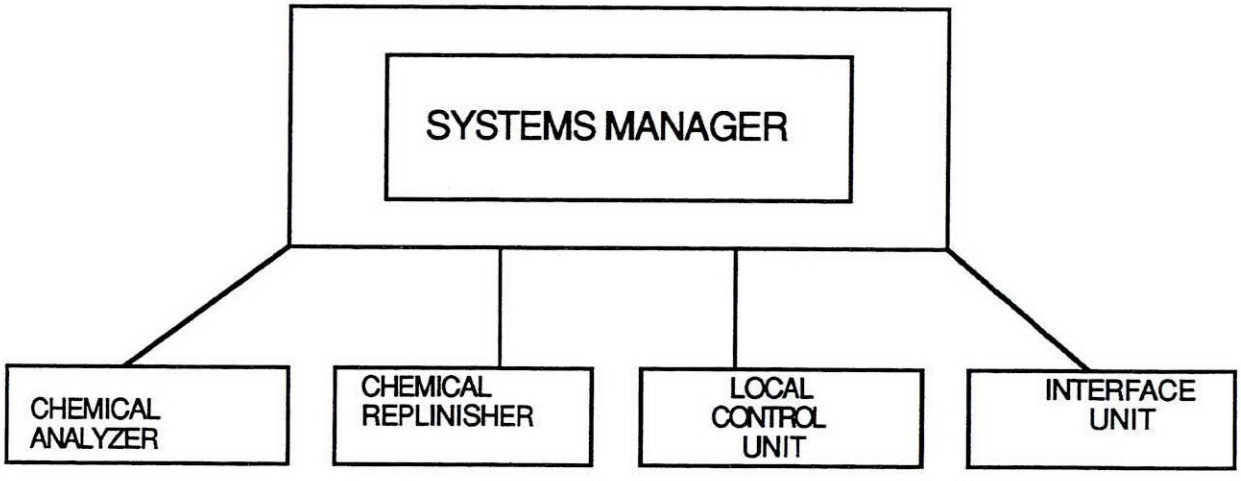
There are several models of process control systems available. The main areas which set these units apart are:

Capacity	***User Friendly (ness)***
Accuracy	***Flexibility***
Consistency	***Expandablity***
Repeatability	

Regardless of their differences, these systems work toward the same goal...control over the chemical and physical parameters of various tank solutions.

For example, one particular unit is a fully integrated system capable of monitoring and controlling any number of chemical and physical parameters regardless of the number of chemicals involved. This sytem is modular in design allowing the customer to address the most critical and or cost justifiable areas first and add additional controls some time in the future.

The system is comprized of essentially four (4) parts or modules and a computerized "Manager" for parameter settings data logging and operator control.



CHEMICAL ANALYZER

The analyzer is responsible for performing automatic sampling and chemical analysis of the process baths or streams being monitored. It is extremely flexible, can sample any number of process tanks, and can automate a variety of analytical procedures. These procedures are replicated several times on each sample and then compared to historical trends to ensure accuracy and repeatability.

This system can automate a wide variety of analytical procedures including wet chemical analysis techniques as well as sophisticated instrumentation methods. The main analyzer functions include...

Sample Retrieval
Sample Aliquot/Preparation
Chemical Analysis:
- ***Direct - pH, Etch Rate, Specific Gravity***
- ***Titration - pH, ISE, ORP, Turbidity***
- ***Colourimetry***
- ***X-Ray Fluorescence***

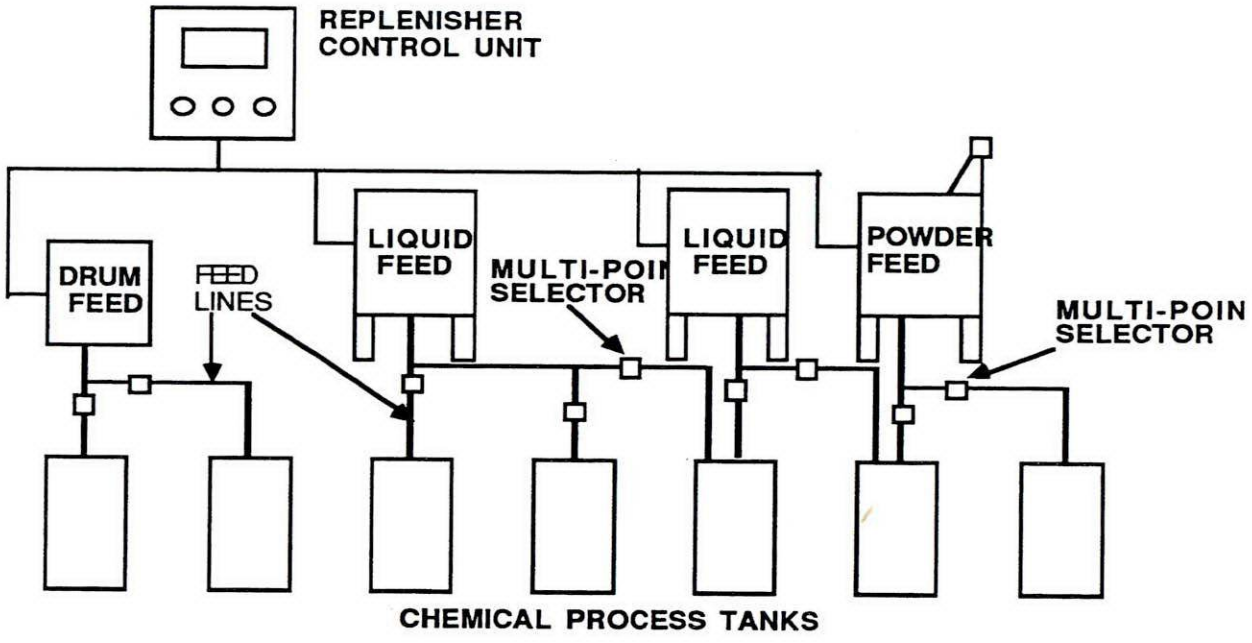
Voltammetry
Auto-Calibration, Diagnostics and Cleanup

Once the system has completed the analysis it will either: 1)Communicate with the Automatic Replenisher which will feed necessary chemical concentrates to the appropriate tanks; (2)Post the results and the recommended replenishment procedures on the Manager screen or Work Order print out or; (3)Alert the operator that the results are not within acceptable ranges indicating a possible problem in the sampling procedure.

If the operator is alerted that the results of the analysis are not within acceptable ranges he/she may run the on-screen "Self Diagnostics" to quickly determine if the problem lies within the analyzer configuration.

CHEMICAL REPLENISHER

The Replenishment Module provides automated control of chemical replenishment. The unit is capable of executing chemical feed instructions either from its own external keypad or from the Systems Manager. The Replenisher is programmed to understand feed instructions such as ***chemical to be fed, quantity to be fed and process tank to be fed***. The unit can simultaneously control the delivery of multiple feedstocks to any number of different chemical process tanks. The Replenisher automatically monitors the total flow of the additions and shuts off when the requested quantity of chemical has been delivered.



A record of chemical feedstock inventories is maintained by the Replenisher. This information is available to the operator and is used by the system to activate low level alert lights on the front of the unit as well as signals on the Manager screen which notify the operator to refill the chemical holding tanks or replace chemical drums.

Once the Systems Manager informs the Replenisher which chemical, what quantity and which tank should receive the addition, the Replenisher automates the addition or draw-off and reports back to the Manager when the request has been completed so the information can be recorded into the Manager data files. Chemical inventories, pump status, feed status, level status and delivered feedstock volume are all available to the operator from the Manager.

THE LOCAL CONTROL UNIT (LCU)

The LCU is used to monitor and control the physical process parameters such as:

Temperature	***Level***
pH	***Conductivity***
Flow Rates	***Amperes***
Voltages	

Specialized equipment has also been developed to monitor chemical etch rate on aluminum and chemical milling rate on titanium.

The unit is programmed to constantly monitor the electrical signal inputs it receives from the various types of tank mounted sensors located throughout the process line(s). The information is then sent to the Manager and compared to the operator defined setpoints for activating alert and alarm functions. If required, the Manager will alert the LCU to transmit the necessary output signals to return the parameter to its target value.

From the Manager, the operator can view the status of all the physical parameters controlled by the LCU from any given tank. The display is shown on the same screen as that of the chemical parameters monitored and controlled by the Analyzer. This allows the operator to select only one display screen and be provided with all of the available information for every parameter in that particular process bath.

THE SYSTEMS MANAGER

The Manager in this chemical control system coordinates the operation of the other components into a fully integrated network capable of providing total control of any chemical process. The Manager records the process information it receives into a database that maintains historical records on each individual process parameter. The current parameter values are compared to established setpoint limits.

These comparisons are used by the Manager as a means of providing alert and alarm indications as well as activating control response signals. The system module *(analyzer, replenisher or local control unit)* responsible for controlling the parameter under consideration, activates the necessary control equipment to return the parameter to its optimum value.

The Manager provides the operator with a graphic, full color, menu driven display of all process information being accumulated by the other modules. The operator simply accesses the desired information by selecting the appropriate display screen on the system terminal.

Graphic display screens allow for the *1) Selection, 2) Examination, 3) Alteration and/or 4) Printing* of the following areas...

Process Line Status

Tank/Stream Parameter Status

Parameter History ***(in tabular, graphical and SPC formats)***

Parameter Setpoints

Parameter Data Accumulation Schedule

Parameter Replenishment Information

Status Display for Individual Modules

CONCLUSION

As our world becomes smaller and global competition becomes more prevalent in our respective demographic areas, the relationship between quality and consistency and the ability to spread profit margins continues to become more direct. These types of chemical process control systems are the future and are being implemented into companies in the Metal Finishing Industry as we speak. Cost justification analysis can be completed with relative ease and considering the many benefits which can be derived, it is a worth while exercise.

The question is not usually, *"Should I make this investment?"* It is, *"When should I make this investment?"* One either begins the investigative procedure of viability today, with the objective of maintaining and increasing market share or...waits for competition and or customers to force the decision resulting in an objective of regaining lost market share.

SUMMARY

features	***benefits***
ANALYZER	•Increase the frequency of analysis for tighter process control. •Eliminate laborious, manual analytical procedures. •Eliminate error and variations associated with manual procedures. •Improve employee productivity by utilizing gained work time in other necessary areas.
REPLENISHER	•Increase the accuracy of chemical replenishment. •Increase the consistency of process solutions. •Eliminate the chemical waste associated with manual procedures. •Further secure worker safety.

LOCAL CONTROL UNIT	•Centralize control of physical parameters on all desired tanks and baths. •Eliminate the inefficiencies of manually spot reading process baths. •Improve production quality by tightening the tolerances beyond those practically possible with less sophisticated equipment (individual, stand-alone controllers).
MANAGER	•Monitor, analyze and automatically make adjustments to any of the parameters on any of the desired process baths from one centralized location. •Immediately alerts operator of any parameter(s) which has gone beyond the tolerance limits and allows instant diagnostics and correction. •Keeps a history file of all process parameters and activities offering comprehensive records of all goods processed through the line.

Aluminum Finishing for the Lighting Industry

Aluminum plays a big role in the lighting industry. Today's specifiers, builders and owners demand cost effective installations, energy savings and aesthetic design. Aluminum is called on to perform in lamp and electrical components, housings and mounting hardware, poles, and reflectors. In most cases it is the optical system, including the aluminum reflector, that is called upon to deliver the long term operational economies and customer eye appeal. The formed aluminum reflector and the selected finishing processes are key to providing these qualities.

Today's reflectors must:

-- Shield the user from the direct glare of the light source.

-- Direct and control the light energy to its place of use.

-- Have a quality fit and finish; an appearance that complements the surrounding architecture.

Reflector finishes vary according to application and performance requirement and include:

Reflector Finishes

Painted

Anodized

Metalized

Plated

While painted reflectors may shield the light source and offer a desired appearance, anodized aluminum reflectors are the predominate choice in general lighting applications, when the light energy must also be directed and controlled effectively. Metalized and plated reflectors have specialized application such as automotive, aerospace, etc.

Whether the aluminum is finished before or after the primary forming operation, the final result must provide function and decorative appeal.

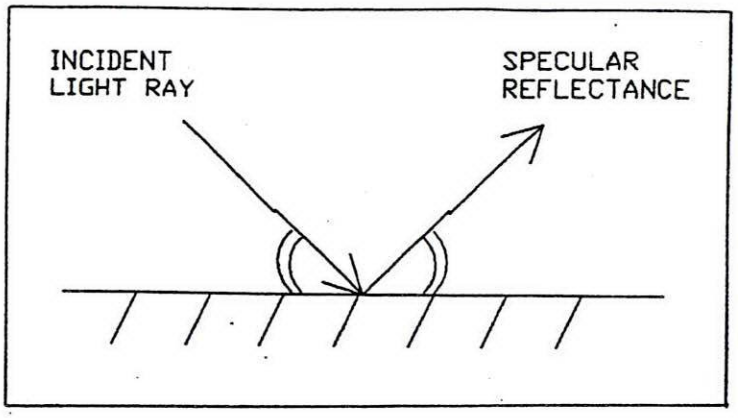
Function

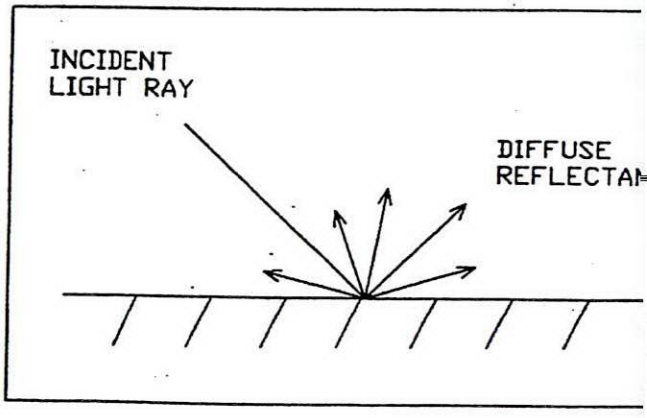
Photometric performance
- Total reflectivity
- Specular reflectance
- Diffuseness

Surface Protection
- Corrosion protection
- Abrasion resistance
- Cleanability

Decorative Appeal

Image Clarity
Color
Freedom from visual defects





Depending on the reflector's design, aluminum can be pre-anodized as coiled sheet and post-formed into the reflector's shape or aluminum can be pre-formed into the required shape and then post-anodized. In both cases, the anodizing process along with the attendant finishing precursors serves to enhance and protect the aluminum surface.

Pre-anodizing is done on coil anodizing equipment while the post-anodized reflectors are finished in batches on crane, both manual and programmable, and hand dip lines. While the desired resultant reflector finish might be similar, the materials and processes employed are usually quite different.

Reflector manufacturing typically starts with the selection of the appropriate aluminum alloy and temper:

Desired Finish	Coil Anodized	Batch Anodized
Specular	5657 - H25	3002 - 0
Semi-specular	5005 - H25	
Diffuse	5005 - H25 1100 - H14	1100 - 0

To provide the desired finish for directing and controlling light, the surface finish provided by the aluminum mill and the subsequent surface finishing processes employed by the anodizer combine to yield the final appearance. As an example, coil and batch anodizers use different methods of achieving a specular finish [one with high image clarity and a high percentage of incident light reflected off at the angle of incidence]:

Reflector Manufacture: Specular Finish Process

	Coil Anodize Method	Batch Anodize Method
Aluminum		
Form Supplied	Coiled Sheet	Circle
Finish Supplied	Rolled Bright (one side)	Mill Finish
Reflector Production Sequence		
	Clean	Fabricate Reflector
	Bright Dip	Cut Down Buff
	Anodize	Color Buff
	Color (optional)	Clean
	Seal	Bright Dip
	Fabricate Reflector	Anodize
		Color (optional)
		Seal

The following process sequence comparison is for providing chemical brightening and anodize surface protection for a specular reflector:

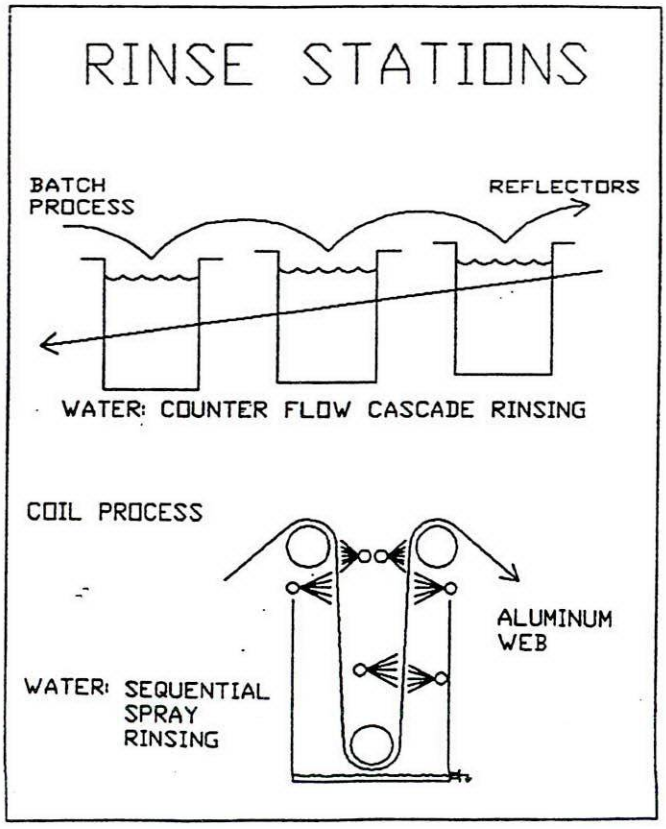
Process Sequence

Step #	Coil Anodize Method	Batch Anodize Method
1	Acid Cleaner	Buffing Compound Cleaner
2	Spray rinse	Soak rinse
3	Bright Dip	Alkaline Cleaner
4	35% Recovery rinse	Soak rinse
5	Soak rinse	Soak rinse
6	Soak rinse	Acid Cleaner
7	Spray rinse	Soak rinse
8	Deox/desmutt	Soak rinse
9	Spray rinse	Soak rinse
10	Anodize	Bright Dip
11	Spray rinse	35% Recovery rinse
12	Color dye (optional)	Soak rinse
13	Spray rinse	Soak rinse
14	Seal	Deox/desmutt
15	Spray rinse	Soak rinse
16	Dry	Soak rinse
17		Anodize
18		Soak rinse
19		Soak rinse
20		Soak rinse
21		Soak rinse
22		Color dye (optional)
23		Soak rinse
24		Hot rinse
25		Seal
26		Final soak rinse
27		Dry

There are two major causes for the difference in process steps necessary to provide a bright, specular anodized finish on aluminum reflector surfaces using the above methods.

1. **Soil Removal:** The coil anodizing process uses bright rolled aluminum from the mill with only a light mill oil on the surface to prevent scratching and corrosion. The batch anodized reflector has forming lubricants and buffing compounds on the surface requiring a much more sophisticated removal procedure.

2. **Process Mechanics:** The coil anodizing process can make much greater use of spray processing, particularly for rinsing. The aluminum web moving through the coil anodizing machine is much easier to drain and rinse than its formed reflector counterpart in the batch process. In fact, a single spray rinse station can be set up to give three or more rinse passes in a single chamber or station.



Although the basic processes of cleaning, brightening, anodizing and sealing used by both the coil and batch anodizer for finishing reflectors are similar, some operating conditions differ significantly. The following table depicts some of these differences:

Typical Operating Parameters

Process Step	Coil Anodized	Batch Anodized
Clean		
Time	40 sec	600 sec
Temp	160°F	180-200°F
Bright Dip		
Time	30 sec	150 sec
Temp	235°F	215°F
Anodize		
Time	180 sec	720 sec
Temp	90°F	75°F
DC Volts	20-24 vdc	16-18 vdc
Current Density	30-50 asf	12 asf
Seal		
Time	150 sec	720 sec
Temp	210°F	210°F

The operating conditions vary because:

-- Different soils must be removed.

-- Transfer time between tanks.

-- DC current transfer from rack to part limitations.

-- Anodic coating density affects seal.

Finally, with the coil anodized reflector material, a wide variety of simple photometric tests can be conducted since the material is flat after finishing. These tests can determine total reflectivity, image clarity, diffuseness, and specular reflectance. These tests can predict the reflector's performance in directing and controlling light as well as its appearance. Generally the curved surface of reflectors anodized after forming do not lend themselves to photometric testing except when installed and tested as a complete luminaire. This is a cumbersome procedure and not suitable for conventional quality control.

Reflector Quality Tests

Test	Typical Result	
Total Reflectivity[1]	70-86%	
Image Clarity[2]	Specular	80 min.
	Semi-Specular	60-80
Diffuseness at 15 deg.	Specular	0.05 max.
	Semi-Specular	0.08-0.20
Gloss at 85 deg.	Diffuse	35-75
Anodic Film Thickness	0.000125", 3 microns	
ASTM B-136 Modified Stain Test (seal)	Pass (no discoloration)	
L*a*b* color	Within 4 color difference units	

1. TR2 Total reflectometer by Technidyne Corporation, New Albany, IN
2. Dorigon D-47 Glossmeter by Hunter Associates Laboratory, Fairfax, VA

Both the coil and batch anodized aluminum reflectors can be checked for adequate anodize protection. The anodic film thickness and seal completeness can be measured. Colored reflectors can be visually and/or instrumentally checked for proper color.

Limitations:

Coil Process Method: When reflectors are fabricated out of pre-finished anodized aluminum, the sheared edges around holes and edges will not be anodized. Severe forming and bending will result in the crazing of the anodized surface near the deformation. Crazing is the formation of very fine cracks due to the relatively low elasticity of the aluminum oxide anodic layer. Coil anodizing is cost effective for long runs of standard finishes.

Batch Process Method: When reflectors are fabricated and then post-finished with an anodizing process there tends to be more variation in the resultant finish. This affects both film thickness and color. Since there is more handling, costs tend to be higher but this is offset in some cases by the ability to do smaller runs. Many reflector shapes cannot be pre-finished however, so the batch process can accommodate a much wider range of product.

ENVIRONMENTALLY OPTIMIZED ALUMINUM FINISHING LINE

Paul W. Fecsik, CEF and Bruce T. Miller
Hughes Missile Systems Company
Tucson, Arizona

This paper discusses the development and implementation of a waste minimization strategy for an automated Aluminum Finishing Line to meet the requirements of an environmentally optimized factory concept in use at Hughes Missile Systems Company in Tucson, Arizona. The line is utilized for a variety of anodize, chromate conversion coat and cleaning processes on aluminum alloy hardware supporting a dozen missile programs. Specific topics include: 1) Rinse Waters - Controlled Water Rinsing, Elimination of Chromium via Ion Exchange with Water Recycling; 2) Chemistries - Chrome Free Deoxidizers, Aqueous Cleaning in place of 1-1-1 Trichloroethane, Bath Life Extension through use of Statistical Process Control; and 3) Plating Line Software Control Upgrades - Process Mixing Capability.

INTRODUCTION

A new Aluminum Finishing Line "Plating System 3" was installed in 1985 at Hughes Missiles Systems Company in Tucson for the chemical cleaning, anodizing and chromate conversion coating of a wide range of aluminum alloys. Figure 1 is a computerized overview of a 42 station "u-shaped" line having fully automated hoist, rectifier, temperature and pH controls. Operation has been the traditional "timeway" mode for fifteen different processes.

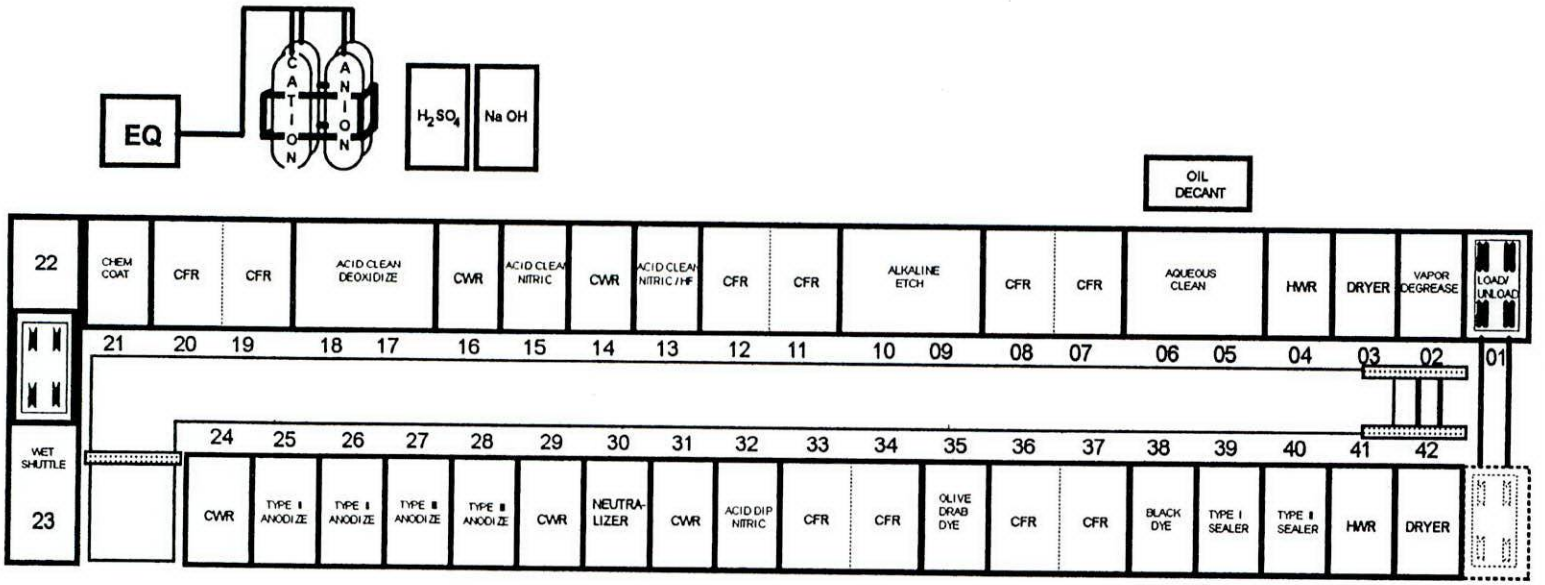
After successfully developing and implementing a waste minimization strategy for two Acid Copper and Solder Plating Lines in our Printed Wiring Board Shop (Ref: Galvanotechnika 1993 "Implementing A Waste Minimization Strategy On Your Copper/Solder Line" by Fecsik & Miller), attention was directed toward the Plating and Surface Finishing Shop.

Since our Corporate Environmental Technology Committee had already done much research into the areas of plating rinse water reduction & recycling, chromium reduction & elimination and ozone depleting chemical elimination, our task was to practically apply knowledge gained in the areas of water rinsing, chemistry usage and plating line control for maximum environmental optimization.

FIGURE 1. LINE OVERVIEW OF PLATING SYSTEM NO. 3

February 21, 1994

ALUMINUM ANODIZE LINE



F1	F2	F3	F4	F5	F6	F7
INPUT SCREEN	RACK SCREEN	ALARM SCREEN	ANCILLARY SCREEN	TANK SCREEN	TREND SCREEN	SPC SCREEN

RINSE WATERS

1. Controlled Water Rinsing. Because of the requirement for fully automated and multiple process (one at a time) capability on the Plating System 3, the original rinse water strategy was to activate water flow solenoids for only those rinse tanks utilized in the process timeway selected. An example Chromate Conversion Coat Process Timeway 304 for wrought stock aluminum alloys would activate rinse tanks 7-8, 19-20, 22-23 and 41 as shown in Table I. The actual flow rates were regulated via manually preset flow meters. Significantly, the other nine rinse tanks remained off for a substantial decrease in water flow.

Today we are cutting the flow down even further while still utilizing timeways. The rinses that are activated during the process cycle need only be on for a fraction of the run time. Once the water has reached an acceptable level of cleanliness (residual concentration), an automatic shutoff of the solenoid valve can occur. So far, activating the water flow as the workload enters the rinse tank and deactivating it at some point after the workload has exited has been working well. Utilizing a sequential line controller, substantial additional programming has been required putting the completion of this project on hold pending software upgrades.

TABLE I
RINSE TANK UTILIZATION VERSUS TIMEWAY

TIMEWAY SELECTED	RINSE TANK UTILIZED												
	4	7	11	14	16	19	22	24	29	31	33	36	41
301	x	x	x	x	x								
302		x	x			x	x	x		x	x	x	x
303		x		x	x		x						x
304		x				x	x						x
305		x	x			x	x						x
306		x		x	x		x	x		x	x		x
307		x				x	x	x		x	x		x
308		x	x			x	x	x		x	x	x	x
309		x		x	x		x	x		x	x	x	x
310		x	x			x	x	x		x	x	x	x
311			x			x	x		x	x			x
312		x		x	x		x		x	x	x		x
313		x				x	x		x	x	x		x
314		x					x						x
315		x	x	x	x		x						x

2. Elimination of Chromium Via Ion Exchange with Water Recycling.

A decision was made in 1993 to remove all chrome from plating line rinse waters. It was determined that routing all chrome into the concentrated acid and alkaline waste stream would result in a more efficient operation at our waste treatment facility. The use of ion exchange offered the best means to accomplish this.

On Plating System 3, there were originally two sources of chrome - the deoxidizer tank and the chromate conversion coat tank. Implementing a non chromated deoxidizer solution is covered later in this paper. The closing of a California production site made available three ion exchange units that were quickly relocated to Tucson to avoid a major capital outlay. One of these units had been utilized for the removal of Cr^{+3}, Cr^{+6} and water recycling. Of course, there was still a cost for installation, equipment overhaul by the original manufacturer and a renewal of the resins.

Figure 2 depicts the flow of water between the post deoxidizer counterflow rinse tank 19-20, the post chromate conversion coat overflow rinse tank 22-23 and the ion exchange unit. The loaded rinse waters first flow into an equalization (EQ) tank that helps maintain the rinse tanks in an overflow condition. The ion exchange unit becomes the only source of water to the rinse tanks via recycling. Makeup water is automatically added to the EQ tank to offset evaporation and rack drag out losses. Upon exit from the EQ tank, the rinse waters first pass through the cation exchange column containing a strong acid resin primarily for removal of Cr^{+3} then through an anion exchange column containing a weak base resin for removal of Cr^{+6}. At this point, water is recycled back to the original rinse tanks at a water quality level tolerable within the process (about 200K Ohm). Although not required, the water could be purified further or be directly discharged to the local Publicly Owned Treatment Works. Maximum allowable discharge levels for chrome and other metals vary from place to place.

There are duplex cation and anion columns that are PC controlled for continuous automated operation and regeneration. The electroplater periodically replenishes the day tanks with 40% technical grade sulfuric acid for cation regeneration and 50% rayon grade sodium hydroxide for anion regeneration. Low level backup alarms are also installed on each day tank with all pertinent signals monitored at our waste treatment plant.

FIGURE 2. RINSE WATER RECYCLING SYSTEM

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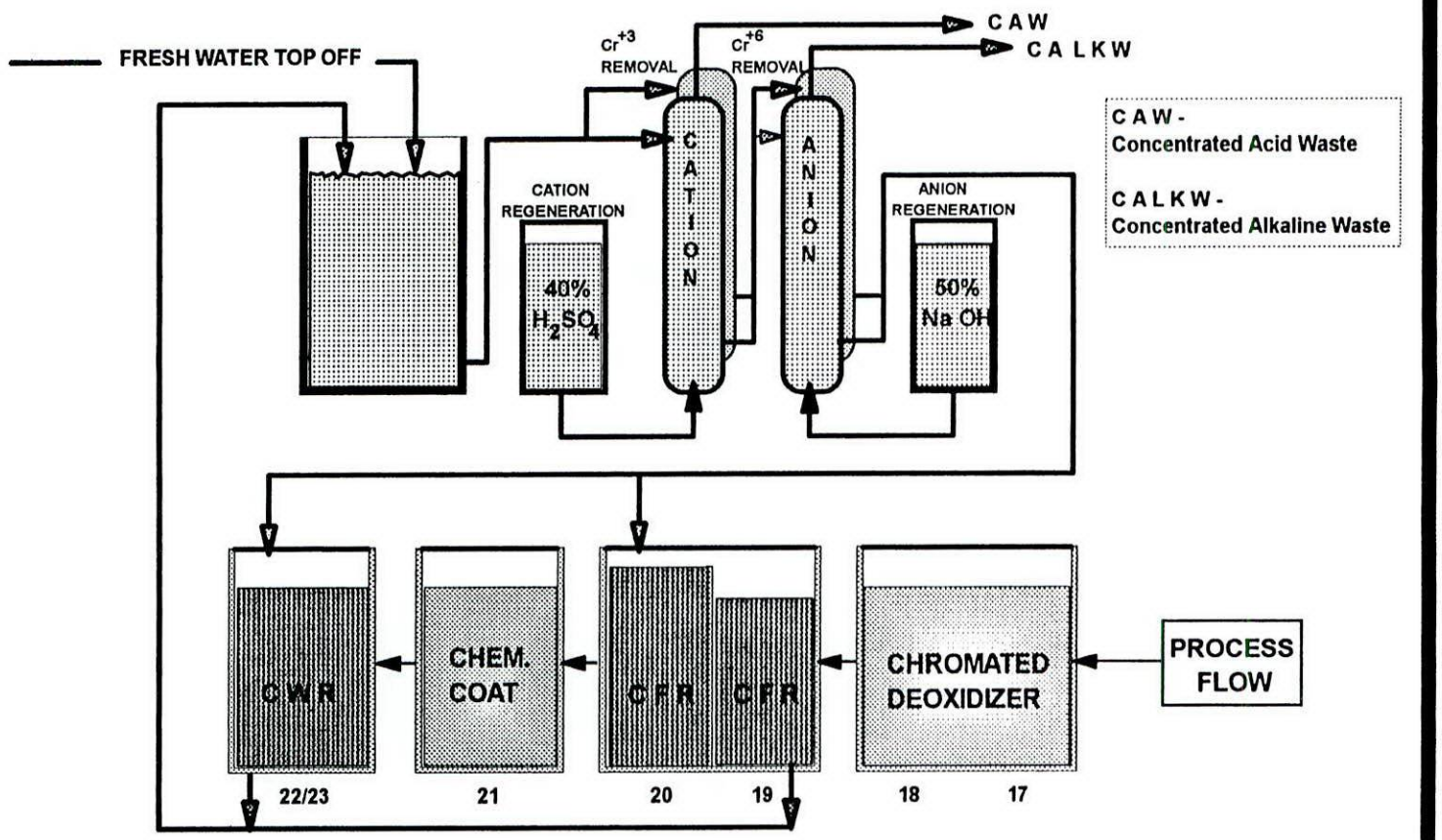


CHEMISTRIES

The use of drag out tanks had not been included in the original design and, while worth consideration, were not addressed in this study. However, spray bars have been incorporated on numerous tanks and drip times have been extended to their maximum.

1. Non Chromated Deoxidizers. It was found that our current supplier of chromated deoxidizer solutions already had two non chromium replacements available. The actual one selected was especially formulated for use on 6061-T6 alloys. While a fairly easy conversion, some up front testing is required to verify that the existing automated dwell times will not etch the aluminum. This was particularly important at Tucson as the deoxidizer frequently had a long dwell time as part of timeway optimization.

So far, the Chromate Conversion Coat solution has no replacement with respect to meeting MIL-C-5541. However, the Hughes Environmental Technology Group has conducted research into suitable replacements.

2. Aqueous Cleaning. Plating System Three was designed and built with an in line and fully automated vapor degreaser utilizing 1-1-1 trichloroethane with semi automated trichlor supply and return system installed for ease of operation. However, efforts taken over the past few years to eliminate ODCs (ozone depleting chemicals) had eventually targeted our Plating System 3 for shutdown of the vapor degreaser. Three alternatives were considered:

1) Converting the existing degreaser into an aqueous cleaner.
2) Converting the existing alkaline cleaner into an aqueous cleaner.
3) Performing all degreasing ff line.

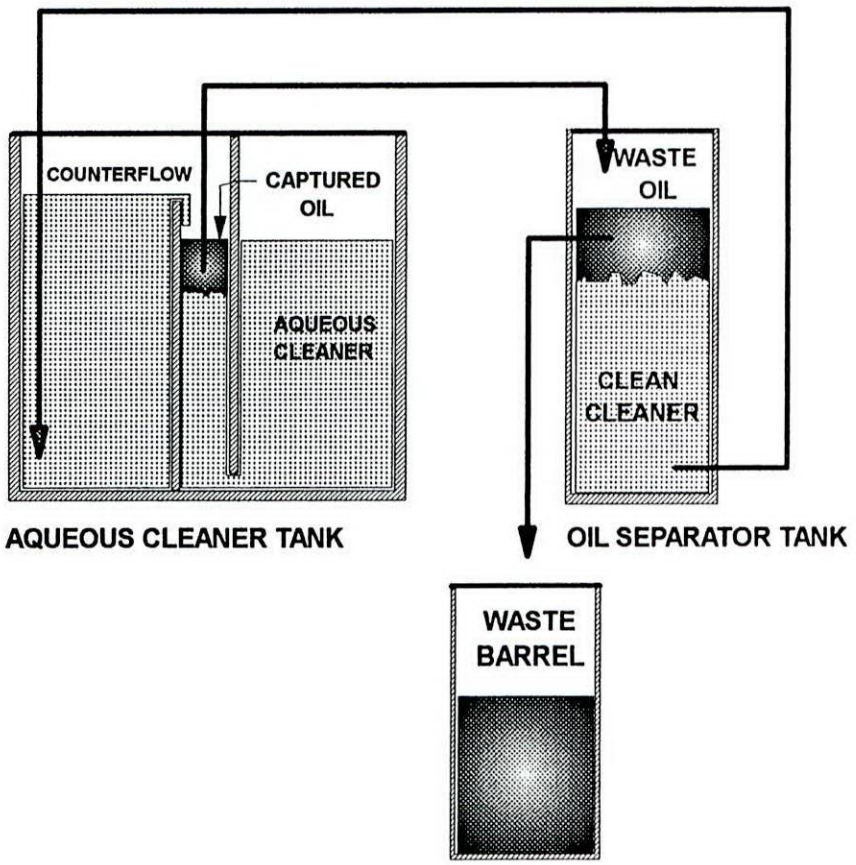
Several companies have been successful at converting existing degreasers into aqueous cleaners. We decided against this to avoid interfering with production in case we had problems. Off line degreasing was highly undesirable since the on line method was cheaper, offered quicker turnaround and provided better quality control of the overall plating process.

The conversion of the existing alkaline cleaner tank 5-6 required a new cleaning solution, a method to move oils to a trap and some form of oil decanter. Figure 3 shows the final results. Oil is separated in the decanter via gravity flow, collected in a small container and sent to the waste treatment facility.

FIGURE 3. AQUEOUS CLEANER

February 21, 1994

OIL SEPARATION SYSTEM



3. Statistical Process Control (SPC) of MIL-A-8625 Type II and III Anodize Thicknesses. The prime motivation for implementing SPC on Plating System 3 was to eliminate a formal laboratory submittal for thickness measurement, to improve plating shop turnaround times and to set up a plater driven process control plan. It is well documented that a good process control plan can result in an overall reduction in chemical usage through bath life extension and a decrease in plating wastes requiring treatment.

Figure 4 shows the SPC Data Entry Screen that is selectable from the Line Overview Screen shown in Figure 1. Thickness measurements are made while the parts are still on their racks with a hand held eddy current device (available from several manufacturers). Data is entered for Types II or III Anodize thickness in mils (thousandths of an inch). The plater enters in date, five thickness readings and pushes F5 update. Everything else is automated. Pushing F3, for example, pulls up the X Bar and R Charts for Type III Anodize. Figure 5 shows a typical X Bar Chart. Notice that average thickness readings that are out of the statistically generated control limits automatically get identified by number (circled 7 and 8) with a cause and corrective action entry required by the plater on another screen.

PLATING LINE SOFTWARE CONTROL UPGRADES

This task is currently underway and may hopefully be complete by Summer 1994. The anticipated use of a computer controlled, random loading system resulted in a decision to salvage a major process line "Plating System 4" during current lower production rates. When rates go back up, the decreased water usage, chemical consumption and waste treatment requirements will easily offset the cost for controller upgrades to meet our Customer's needs. Additionally, the control of rinse tanks mentioned earlier now becomes a simple, user friendly task. More on this effort in a later paper.

SUMMARY / FUTURE WORK

The changes that are being made to Plating System 3 at Hughes-Tucson have been required to remain competitive and environmentally compliant. As for the future, it is an ongoing optimization. Acid purification is under serious consideration as is the expanded use of ion exchange for rejuvenating chromate conversion coat and anodize solutions.

About the Authors

Paul Fecsik and Bruce Miller are Senior Process Engineers with Hughes Missile Systems Company (a Subsidiary of General Motors Corporation) in Tucson, Arizona (USA). They provide process and environmental engineering support to a variety of production plating and surface finishing operations for printed wiring boards and other missile components. Both are members of the American Electroplaters and Surface Finishers Society (AESF).

FIGURE 4. SPC DATA ENTRY SCREEN

HMSC - TUCSON ANODIZE OPERATION

ANODIZE II THICKNESS READING (mils)

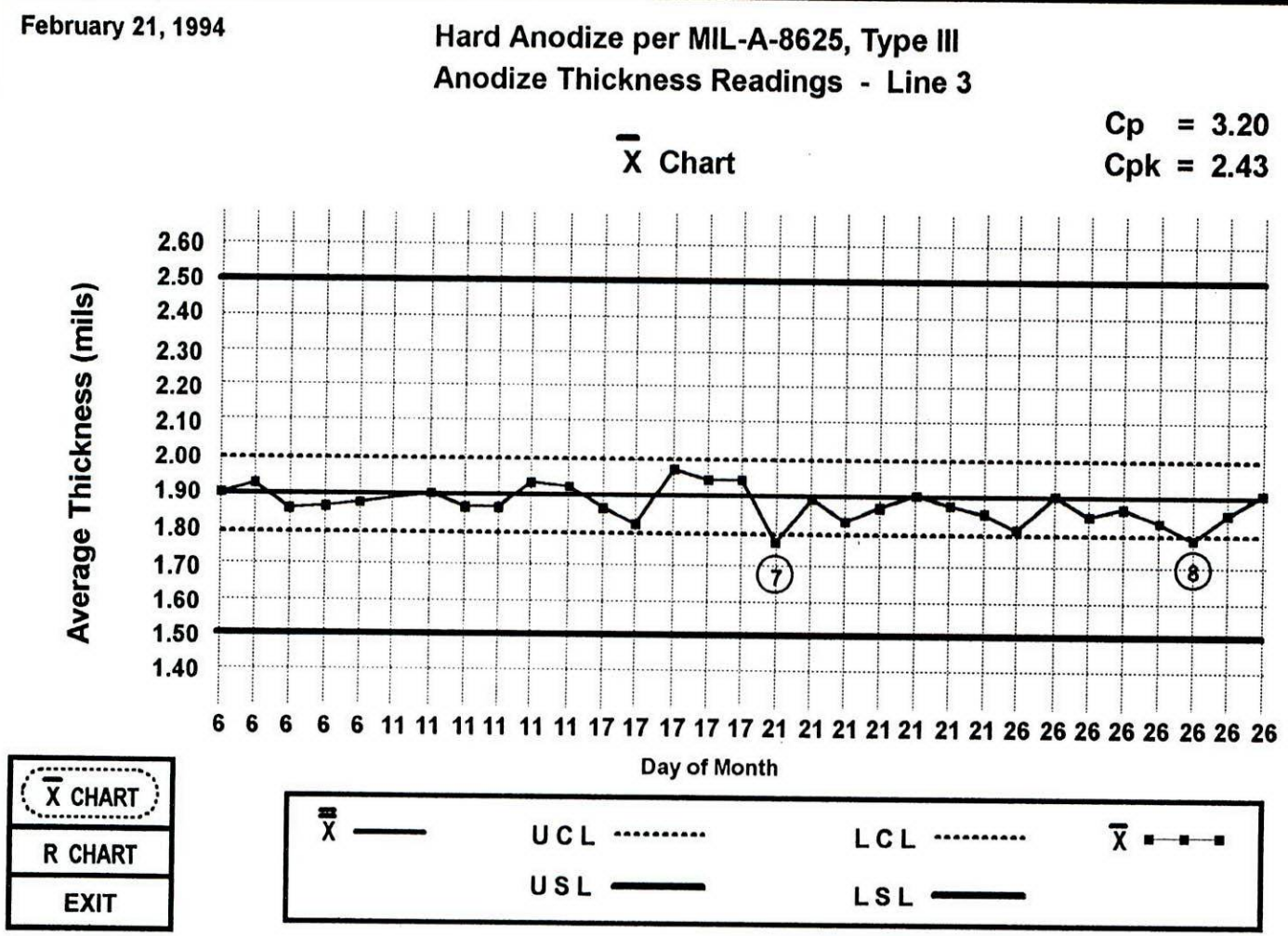
DAY	READING 01	READING 02	READING 03	READING 04	READING 05	$\bar{X}$	R
17	0.00	0.00	0.00	0.00	0.00	0.00	0.00

ANODIZE III THICKNESS READING (mils)

DAY	READING 01	READING 02	READING 03	READING 04	READING 05	$\bar{X}$	R
17	1.91	1.85	1.87	1.94	1.82	1.88	0.12

F1 EXIT	F2 TYPE II	F3 TYPE III	F4 NEW	F5 UPDATE

FIGURE 5. $\bar{X}$ CHART FOR ANODIZE THICKNESS



Preserving Solderability on High Density Printed Circuits Boards

James P. Langan

Abstract

The increased use of surface mount components has focused attention on processes capable of preserving solderability during multi-heat cycles. Proper placement of fine pitch components on printed wiring boards requires coatings which are free of "bumps" and are of uniform thickness. This is difficult to achieve with hot air leveling.

Coatings to satisfy these requirements are detailed. These include fused solder paste, non fused tin and tin/lead electrodeposits, chemical deposited tin/lead, nickel/gold and organic coatings. Cost considerations and limitations of present technology are analyzed.

The impact of global competition predicates a demand for a procedure which is economical, uniform, and reliable. Particular emphasis will be placed on the process controls required for organic coatings to satisfy all three criteria. Focus will center on applications where preflux or inhibitor coatings are best suited.

This paper will outline equipment and processing costs which the P.C. fabricator can expect as organic coatings replace HASL.

Fine Pitch SMT Limitation of HASL

During the last decade, hot air solder leveled coatings (HASL) have replaced reflowed tin/lead electrodeposits as the preferred coating for preserving solderability. SMT's need for solder mask over bare copper (SMOBC) was a major contributing factor. As packaging density increased, SMT uncovered a shortcoming of HASL.

When a copper pad/trace is hot coated or electroplated and fused, the tin/lead coating forms a meniscus. The center of the pad or trace is much thicker than the edges. Thus, when a specification calls for 12.7 microns (0.0005"), it is measured at the center of the pad.

With leaded technology, a heavier coating did not present a problem as long as the holes had sufficient clearance for components. Fine pitch SMC's have created a need for a flatter and more uniform thickness of the tin/lead coating. To achieve this, the thickness must be reduced to lessen the height of the meniscus in the center of the pad. By so doing, it increases the danger of some pads being too thin. This causes solderability problems.

With narrow leads inherent to fine pitch components, the amount of solder in a fillet is also crucial. The fillet is composed of tin/lead from the lead, pad and solder paste. The volume of solder paste and component plating thickness can be controlled but solder leveling presents a dilemma.

The multi-heat cycles required for SMT processing causes the intermetallic layer to grow - resulting in loss of solderability in thin coatings < 2.54 microns (0.0001"). The variations in P.C boards make it difficult to uniformly coat a complex board to a thickness of 5 +/- 2.5 microns (0.0002" +/- 0.0001").

This limitation of HASL is a concern which has fostered investigation into alternative methodology for preserving solderability. These include fused solder paste, Optipad and Sipad process, electroless tin/lead, electroless gold over nickel, preflux, inhibitor coatings, and combination inhibitor/preflux. Most of these approaches were tried and abandoned for technical reasons. The need for flat pads has prompted investigators to explore modes to overcome acknowledged deficiencies. The most promising are the organic coatings due to low cost and ease of application. They also have a long history of success in the Far East.

A Uniform Tin/lead

Since both fused tin/lead plating and HASL have preeminence for reliability, numerous procedures for enhancing thickness uniformity are under investigation. All have had limited success albeit inhibited by severe limitations.

Inhibitor Coatings

An inhibitor coating is usually a benzotriazole or an imidazol (nitrogen compounds). These inhibitor coatings are extremely thin and virtually invisible on a copper surface. They protect the copper by chemically bonding to it thus preventing a copper-oxygen reaction. This type of coating requires careful handling since finger prints and similar soils will adversely affect it. It would be applied after the rinse cycle following the mild acid cleaning. It is normally applied by spray but it can be dip coated. After application, it is rinsed and air dried. This type of coating by itself is not recommended for multi-heat cycles processing.

It may be possible to use inhibitor coatings for multi-heat cycle applications if all thermal processing is performed in an inert atmosphere. This is of great importance because inhibitor coatings are so easy to apply.

Recent Developments in Inhibitor Coatings

Most benzotriazole and imidozol coatings are in the 50 to 100 angstrom range causing them to be fragile when subjected to handling and an environment with temperature/humidity variations. There are new processes under development which claim the ability to produce coatings with substituted imidozoles that can be deposited in the 0.2 to 0.5 micron range. The initial layer is formed through a complexing reaction with copper followed by a build-up of the benzimidozole to the required thickness.

This process has been lab-proven to produce coatings capable of withstanding multiple heat cycles. The question now is whether it can produce continuous quaranteed results in high volume production.

Resin/Rosin Coatings Air Dried

Coatings of this type have long been utilized. They served their purpose on print and etch boards but are not capable of preserving solderability for the multi-heat cycle manufacturing procedures required for SMT. Requiring solvents with low flash points and fast evaporation rates, they create safety and air pollution problems.

Multiheat Cycle Coatings

These coatings dictate oven drying and closely controlled preparation of the copper surface prior to application of the organic coating. The key to success is applying the heat stable preflux over a clean dry copper surface treated with an inhibitor coating, viz., benzotriazole or imidazol. Methods of application include brush, spray, dip, or roller coating. Recommended is a uniform film between one and three microns (after drying). Thickness is controlled by solids concentration of the preflux. The solids content will vary with the method of application.

The multiheat cycle preflux most often contains a heat stable resin, solvents with flash points over 38°C (100°F), and antioxidents. It is preferred that the solvents have low evaporation rates to simplify control of the solids content and to lessen emission into the work environment. The antioxidents prevent copper from being oxidized and also the heat stable resin from being polymerized so that it remains soluble with the solvents in the flux.

It is important that the P.C. board be completely dried so that a uniform adherent film will coat the surface. The preferred thickness is one to two microns. For added protection, a benzotriazol or imidazol can be applied post rinse following the mild acid cleaning. If an inhibitor coating is used, then the importance of an immediate application of the preflux is decreased. However, if possible, the entire cleaning: inhibitor coating/organic preflux coating should be in rapid sequence to assure maximum protection.

The need for flat pads and the multiheat cycles inherent in SMT assembly has increased the use of copper P.C. boards which are protected by a heat stable preflux or an inhibitor coating/ preflux combination. Although this type of coating may not have the long term protection of 12.7 microns (0.0005") of tin/lead, it is far better than an inhibitor coating alone or the old type rosin coatings used on print and etch boards.

The Future of Organic Coatings

In Europe and Asia, the use of copper P.C. boards is much greater than in the United States where specifications are often influenced by government standards. One must realize that with soldering, military specifications assume that most printed circuit boards and components will not be assembled soon after manufacture. Therefore, long term solderability is most important - unlike conditions in commercial electronics. To remain profitable, inventories and manufacturing costs must be kept low. With emphasis on "just on time" (JIT), the need for long term solderability protection is lessened. The cost of applying this coating is much less than tin/lead. For those rare occasions where long term storage has affected solderability, the coating can easily be removed and then cleaned and reapplied.

HASL is a process which most fabricators would like to forget. It involves expensive equipment, heavy daily maintainance, long set up time, expensive quality control environmental concerns and is a leading cause of rejects.

Summary

HASL is ideal for multi-heat cycles if a minimum of 2.5 microns (0.0001") can be quaranteed. This will normally necessitate an average of 9 microns (0.00035") with a maximum of 20 microns (0.0008"). Alternatives to HASL will be needed for ultra fine pitch, requiring flat pads.

Each of the alternatives to HASL has strengths and weaknesses which must carefully evaluated before selecting the best process for a particular application.

Process	* Advantages # Limitations	
1) Inhibitor organic coatings	*	Low cost
	#	not suited for low solids "no clean" fluxes
2) Multi-heat cycle preflux	*	Low cost
	#	requires post solder cleaning
3) Inhibitor coating >5 microns	*	Moderate cost
	#	requires special equipment
4) Fused Solder Paste	*	Moderate cost/ideal for TAB
	#	miniscus of Sn/Pb > 25.4 microns (0.001") (0.001")
5) Chemical Deposited Sn/Pb	*	Precise thickness of Sn/Pb <12.5 microns (0.0005")
	#	high cost/unproven in production
6) Sipad/Optipad process	*	Flat pad with precise amount of Sn/Pb
	#	high equipment/process cost
7) Electroless nickel/gold	*	Ideal for die bonding
	#	high processing cost

PREVENTING REJECTS WHEN PLATING CIRCUIT BOARDS, MEMORY DISKS, ELECTRICAL CONTACTS AND OTHER ELECTRONIC COMPONENTS

by Jack H. Berg, President
SERFILCO, LTD.
Northbrook, Illinois

Reject levels of 1 to 5% increase the cost of plating and destroy confidence by the consumer if failures occur. Quality control, therefore, must take on a new approach to determining all sources of contamination and how best to eliminate each, so that plating can be done under a clean room atmosphere and conditions. Previous attention has centered only around the plating bath which, in spite of absolute type filter media, cannot always remove damaging particles before they are codeposited on the substrate. Therefore, attention must now be directed to filtration of the cleaners, rinses, air for agitation, water, chemical addition and all other possible sources of contamination and, if possible, step up filtration turnover rates to 10 or even 20 times per hour through the filter to approach 99.9% removal before a reject problem would occur. This paper discusses how all of the above can be accomplished easily and at reasonable cost with engineered plastic components for the best chemical resistance and purity.

The electronic industry uses many liquids in the various processes required to manufacture printed circuit boards or other electronic components. 'Good' quality water is most essential since it is used to make up most of the solutions, also for rinsing and cooling. Various water treatments may be required, including pre-filtration, deionizing, and purifying with carbon. Pre-filtration is required for solids removal to prevent surface loading of the resin or carbon, as well as post filtration to prevent migration of resin and carbon followed by several stages of trap filtration down to and including sub-micron sizes if absolute clarity is required.

All of the electroplating solutions such as copper, tin-lead solder, tin-nickel, nickel and the precious metal baths such as gold and rhodium, plus all of the electroless plating solutions such as nickel or copper, require filtration for the removal of solids, and some of the above require removal of organic impurities with activated carbon, which is a purification process sometimes handled with filtration equipment.

Perhaps the most critical plating is done on memory disks or drums which, like the plating of phonograph record masters, requires the ultimate in freedom from solids in the solution. This can only be accomplished by using filter media dense enough to remove the undesirable particles at flow rates high enough to have all of the liquid pass through the filter at sufficiently frequent intervals so that they will be picked up. The filter must also have sufficient solids holding capacity to maintain a high flow rate.

Another application requiring continuous filtration is the photosensitive resist. It is a 'must' to have this solution free of contaminants; otherwise, when using roller coating or dip coating methods, small particles of dirt or dust are co-deposited on the copper laminate, thus leaving a light impervious barrier. After exposure, this speck leaves a spot of unexposed photoresist on the circuit pattern. Since the ultraviolet rays are unable to penetrate the particle of dirt, the resist does not completely harden and would then dissolve around and under the foreign particle in the developing stage. The result is a small area of exposed copper which, after etching, produces a pinhole on the circuitry or a nodule in the land area of the printed circuit board. In either case, this would result in a substandard product or even a complete reject.

In semiconductor application, the use of engineered plastic such as PVDF and polypropylene are required to prevent leaching of organics into the pure water system. Submicron filtration with membrane cartridges requires special sealing devices with the 222 "O"-ring arrangement as the standard for the industry.

Flow rate with high velocity is the only means of carrying solids to a filter or bringing fresh solution into contact with the carbon. The rate of flow is referred to as turnover . . . total gallons pumped per hour in relation to the size of the tank . . . 200 GPH on a 100 gallon tank is two turnovers per hour. Dirt holding capacity is essential and can be attained with throw-away paper, or cartridges of differ-

ent porosities, or filter surfaces coated with filter aid; porosities of 100 micron down to less than 1 micron are typical.

If activated carbon powder is used to adsorb organic impurities, it may be added to a precoated surface or mixed with the solution in a treatment tank. Adsorption is quick, but the powdered carbon is messy to recover from the solution. Powdered carbon cartridges offer a more convenient method of using powdered carbon, but is more expensive per pound of carbon.

A granular carbon chamber offers large capacity, higher contact time and less cost per pound than powdered carbon. Therefore, granular carbon is generally preferred; it is held in a separate chamber for removal of organic impurities. Prefiltration to remove solids will increase the surface adsorption efficiency of the porous carbon granules.

All of these methods can be incorporated into a batch carbon treatment system or to continuous carbon treatment/filtration system.

It is generally accepted that total quality management requires both process control and product inspection. Progressive companies are employing both SPC and SQC techniques to assure that their processes are maintained within optimum parameters, since consistent quality cannot be produced by an out -of-control process.

Increased demands (re: line definitions, densities, etc. . . .) require higher purities in all process solutions which can only be attained by either higher turnover rates, finer media, or a combination of both.

In practice, the average plating solution is turned over once per hour. We are presently recommending at least twice per hour tank turnover; however, to achieve the ultimate in clarity, turnovers of up to twenty times per hour may be necessary in memory disk manufacture. Keep in mind that the initial flow rate is not average flow rate. In other words, if we started at 1000 GPH and cleaned the filter when the flow was reduced to 200 GPH, the actual average flow would probably be about 600 GPH, depending upon the type of filter media used; this is just over once per hour on a 500 gallon tank. The most common type of filter media used in the electronics industry is a depth type cartridge which is available in different porosities to achieve the desired particle retention, from 100 micron down to 1/2 micron on a nominal basis. These cartridges are wound from cotton fibers, or various synthetic fibers such as polypropylene, to achieve the desired compatibility with the chemicals in the solution.

The importance of flow rate cannot be overemphasized. For example, one study has shown that contamination levels over 15 ppm result in unacceptable reject levels. The same study indicated that contaminants were dragged in at a rate of 2 oz. /hr./1,000 gal. or 1 gram per minute/1,000 gal. In order to maintain a bath at under 15 ppm with that level of drag-in using filter media of 80-90% efficiency, an average turnover rate of four turns is required. (One gram per minute is only 16 ppm in a 1,000 gal. tank in one hour, or one 1/2 millimeter speck of copper in 100 cc.)

Figure 1 depicts the equilibrium contamination level achieved with turnover rates and various media efficiencies with 1 and 2 gram per minute contamination drag-in rates.

Higher flow rates are important in maintaining the stability of a bath. For instance, if the above mentioned 1,000 gal. tank should suffer an upset and contamination level increased from 10 ppm to 20 ppm, at three turnover rates it would take 30 minutes to bring the tank back to 10 ppm. At six turns, it would take less than 15 minutes. At one turn per hour, the same tank would take three hours to return to the 10 ppm level.

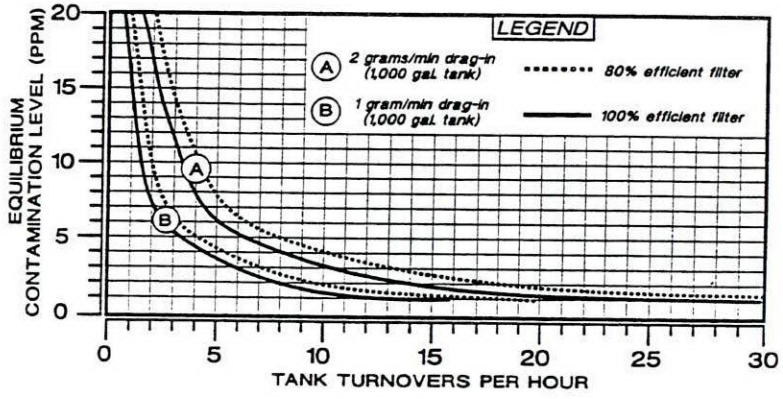


Figure 1

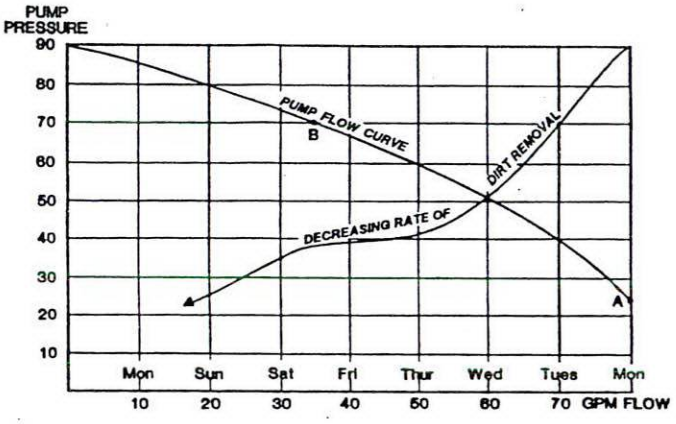


Figure 2

Figure 2 depicts the flow in a typical plating tank. A clean filter at point **A** will flow 4,800 GPH and dirt removal is maximum. Flow rate has dropped to 2,000 GPH at point **B**. Situation applied to a 1,000 gal. tank would represent a reduction in flow from almost five tank turnovers per hour to two tank turnovers per hour during a time interval of one work week. If the filter continued to operate without servicing, the rate of dirt removed would soon be less than the rate of dirt introduced to the system. The time interval during which the filter is performing effective filtration will be determined by job conditions.

The need for filtration and purification of plating baths cannot be emphasized enough in the manufacture of printed circuits, especially where copper is used for through-hole plating in order to achieve continuity through each hole, making it easy to solder and assemble the components. Any void in surface through-hole plating caused by small pieces of contaminate matter will reduce the area available to carry the electric current. A complete void would, of course, have no contact with the hole at all. Rejects would also be caused when tin-lead or tin-nickel are used as a resist in the etching process, since any non-plated surface would allow etching in unwanted areas. Nickel, gold and rhodium plating baths may be as critical, depending upon the requirement of a finished product. Contaminants in any of these solutions would result in a rough plate on circuits or connector tabs.

Important specifications which must be considered in selecting a filtration and purification system:

1. What is the degree of clarity necessary to achieve the quality of plating required?
   High - Average - Low
2. Amount of liquid (total amount of plating solution)?
   This affects clarity recovery time.
3. Impurities to be removed:
   Solids - size and type (slimy, gritty)
   + organics?
   Continuous filtration and carbon treatment required?
4. Flow rate - Tank turnovers/hour?

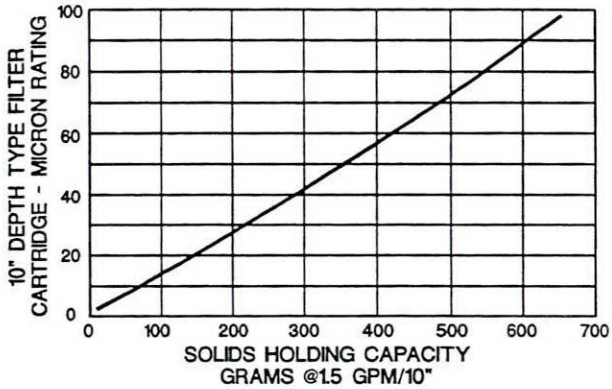
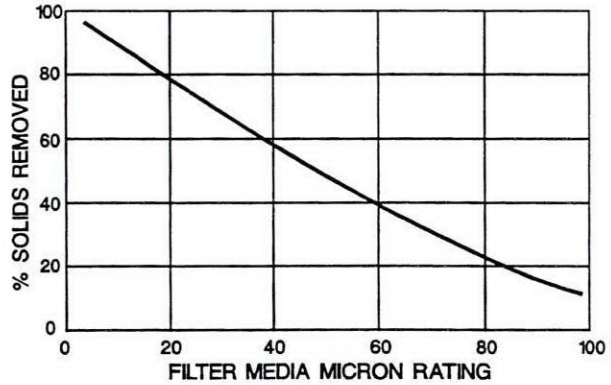


Figure 3



% solids removed from liquid with different micron filter media retention capabilities.

Figure 4

The coarser the filter media the greater the solids holding capacity, which can range from grams with dense media to over a pound depending upon the contaminant. (*Figure 3*)

Higher velocities across the media will result in reduced dirt holding capacity with a given pump system and, therefore, reduce average turnover rate.

Also note in *Figure 1* that turnover rate is the dominant factor in reducing contamination level, while filter efficiency has much less effect. Therefore, coarser media with higher flow rate will reduce contamination levels in spite of reduced initial efficiency (*Figure 4*). Average efficiency may well be the same since as the cartridge plugs, its efficiency increases.

5. Continuous or batch carbon treatment?
6. Pump specifications - intank or out-of-tank?
7. Filter media and porosity?

Other considerations are the materials of construction, which must be compatible with the solutions and the positioning of the filtration system. The amount of solids or organics present will determine the size of the filter chamber itself, which must provide a sufficient amount of dirt holding capacity, and whether or not carbon is to be used as part of the filtering process or as a separate function in another chamber. All of the above must, of course, be assembled into a compatible, functional piece of equipment, fitting into the usual limited amount of space available.

Finally, the best type of pump capable of delivering the flow and pressure, as previously mentioned, must be selected. Horizontal centrifugal pumps of all-plastic construction are quite popular for use on the tanks. Direct drive pumps use double water flushed mechanical seals, but pumps without any seal using magnetic-coupling have now become popular. Leakage is prevented because the pump does not have any opening for the shaft to pass through which would require a seal. Magnetic-coupled pumps are also available with encapsulated motors so that the entire unit may be submerged in the liquid. This is an extremely desirable feature for use on precious metal solutions to eliminate any liquid loss. There are also larger magnetic-coupled pumps with dry run capability on liquids with specific gravities up to 1.8 without reduction in flow rates.

Vertical sump type pumps are also available in metal or plastic construction. They generally are free of seals, per se, but use the liquid they are submerged in as a seal. They can be used on virtually any solution as long as there is room in the tank or reservoir. They are also used for the transfer of liquids used in the waste treatment system or any other recirculatory rinse or spray tanks. On certain solutions, they can also be used for tank agitation without filtration. However, some conditions may allow air to become entrained in the liquid, when wetting agents or other factors contribute to this affect . . . applying back pressure to the pump can minimize the problem; otherwise, a sealed pump should be selected.

Gear pumps of stainless construction are usually limited to use on the photo resist solvent solutions. Care must be taken to operate them at very low RPMs so as to prevent aeration and heating of the solution. Some resists are sensitive to even a few degrees rise in temperature. Gear pumps are self-priming and are equipped with packed stuffing boxes or mechanical seals.

Today it is not uncommon to find the cleaner / conditioner bath is both filtered and air agitated in spite of the low cost and long life of the bath. This is only one example of the improvements in quality the processor has taken to achieve the lowest rate of rejects. The same applies to the utilization of air agitation in the rinses throughout the process line to assure complete removal of residual chemicals from the baths preceding the rinse stations. Special care must be taken to avoid using water that is contaminated from its incoming source which might require deionization, softening or filtration, or air that is laden with oil if compressors are used.

Skimming pretreatment solutions and filtering, carbon treating or employing coalescers for oil removal are being used to meet the adhesion and coverage standards which often times were causes of rejects and failures.

When pumps and filters are assembled into a functional package, valves may be added to control or direct flow. A chamber for priming of the pump, or to be used for chemical addition, priming or precoating the filter and pump flow rate, may also be added. A pressure gauge to indicate the condition of the filter is also desirable. Finally, select a space to place the unit where it can be serviced conveniently.

Regardless of all the improvements in process technology and materials that have evolved in recent years, one basic fact still applies as much today as it did twenty-five years ago. If contaminants are not removed from the preplate, imaging, electroplating and bonding steps, the finished product will be defective despite the fact that the finest and most sophisticated chemistry was used.

FIXTURE DESIGN FOR PRINTED CIRCUIT WET PROCESSING
(Racks-The Keys to Proper Electroplating of Circuit Boards)
(Baskets-The Right Parts Carriers for Oxide and Electroless)

By Michael R. Faulman

Since 1975, when fixturing became common place in wet processing for the electronic and printed circuit industry, many design and process parameters have evolved. These changes have occured through the efforts of end users, fixture manufacturers, chemical suppliers and large equipment manufacturers. These changes have resulted from more stringent process requirements and new manufacturing techniques. The following overview concerns the items with which fixture manufacturers generally become involved, and the variety of methods for manufacturing these fixtures.

PLATING RACKS

As in any fixture, the critcal nature of its components lead to the success of the finished product. This is particularly true of the fixtures used in plating.

The plating fixture is the only item in this paper that must be designed to carry current. This statement is the stepping stone for plating fixture design. In most printed circuit fixture designs, the racks are designed for 30 amps per square foot, based on the required square feet of parts to be plated. For instance, if you have a tank that will hold 4 - 18" x 24" double sided boards, and the fixture will hold these 4 boards, then the fixture must be able to carry 180 amps (18" x 24" x 2 divided by 144 x 30 ASF = 180 amps) Often the structural considerations will dictate the size of material used to guarantee rigidity during processing, yet the above fixture must be capable of carrying a minimum of 180 amps. If the rack design does not insure the current requirement, the parts may not plate uniformly, may not plate to the required thickness, and (if the fixture is coated) will affect the adhesion of the coating to the base metal.

After the current requirement is determined, structural constraints come into focus. The fixture must:

1. Plate the board consistenly and uniformly.
2. Hold the board securely.
3. Have a minimum movement in the direction of travel when used on an automatic machine.
4. Securely fasten to the cathode flight bar.
5. Dimensionally fit into the tank with a minimum of 3 inch clearance between all sides and obstructions.
6. Be capable of accomodating a variety of board sizes.

In addition to these structural considerations, the fixtures must be user friendly to the loader/unloader of the fixture. Particularly on an automatic line, there is a prescribed time in which the operator must load and unload the unit. The most efficient and durable fixture which either takes too long to load or is too difficult to load quickly is discarded. In most companies, "If the operator ain't happy, ain't nobody happy".

After the structural requirements

are resolved and the current requirements have been determined, a decision must be made as to the materials required. Generally the rack splines are constructed of copper to allow the current to get to the individual contact areas. Copper is normally used because it will carry 1 amp per square inch, and stainless steel will carry .023 amps per square inch. In the above example, of the 180 amp requirement, one would need 3/8 x 1/2 copper and 1 x 8 if stainless steel. Economically, as well as the weight involved, makes it compulsory to use copper.

Most plating fixtures have stainless steel contact areas. There are a variety of designs that work adequately and are normally dictated by customer requirements. These designs are:

A. Thumbscrew type
B. Spring load type
C. Clamp type

The thumbscrew design is the one most commonly used in the United States and incorporates a "U" shaped piece of metal into which the board slides with a thumbscrew tightened against the baord. This design is flexible in that it will accomodate a variety of board thicknesses and sizes. It is also durable and requires a minimum amount of labor to load and unload the boards. However, there are some design requirements:

1. A 316 series case unit for the "U" shaped component should be used.
2. The thumbscrew should be molded with a teflon sleeve to prevent the plating of the screw.
3. A separate spline should be used for the left and the right hand side of the rack.

The only negative of this design is that, in a hand line environment, the racks may be heavy:

The spring load type incorporates a spring pressure to the sides of the boards. Normally spring flatstock stainless is used in this application and is very easy to load. However, there is not the flexibility in this design when compared to the thumbscrew and after a short period of time a plate-up of the contacts may occur. This results from an area of the tip being exposed to the copper plating and generally results in additional maintenance. This design of rack will be lighter when used on a hand line, and often the space required in the anode to anode direction is less then the other contact designs.

Finally the clamp type design is normally used in a vertical processing 1 board environment when the only contact area is on the top of the board. This clamp is more difficult to manually load, yet can easily incorporate a robotic load system. This style of contact is quite flexible, does not have a plate-up problem and forms a solid contact area to the board. However, because of the close tolerance machining required for the successful implementation of this design, the fixtures tend to be more costly.

Coating is a major component of the fixture after construction. Normally a poly vinyl chloride coating is applied after the fixture is sandblasted. This coating is extremely durable and pliable and insulates the base metal from the plating solutions. In more applications, this coating gives a long useful life, and if the fixture becomes damaged, the coating can be removed, the fixture rebuilt, and the coating reapplied. However, some copper baths are so active that the coating may plate. This can often be eliminated by applying a

high durometer coating (+90) and over-curing the coating at the time it is applied.

A number of hours have been devoted in research and development looking for an improved coating. Halar, kynar, nylon and teflon have been evaluated and eliminated for a variety of reasons. A polypropolene covering is an improvement over the other test coatings, yet the method of construction only allows for contact on one side of the board, and the polypropolene will plate up with more rapidity then PVC.

OXIDE BASKETS

The processing of thin inner layer material always has created problems for the multilayer manufacturer and the fixture supplier. It is most common that these inner layers are vertically processed through the use of a basket style of fixture. There have been a number of recent developments concerning the design and materials used in constructing these baskets. Recent chemistry changes have forced the basket manufacturer to design the fixture so that a thin or voided area on the inner layer will never result.

A stainless steel is the preferred material used in constructing oxide baskets, either 316 or 304 series, as the stainless will not be affected by the chemistries or heat of the oxide process. The most common method in the past was to use an uncoated basket, that had a series of horizontal and vertical wires across each inner layer to support the thin material. This method often caused serious problems when the inner layer touched the adjoining wires during processing, which resulted in a thin or voided area on the inner layer. In an attempt to eliminate this problem, fixture manufacturers coated these fixtures with plastisol, which prevented the inner layer from scratching against the stainless steel. The problems associated with the plastisol were that the useful life was reduced if the end user processed the inner layers in a dryer oven over 180 degrees F. Also it was difficult for plastisol appliers to achieve a uniform coating along each of the wires, resulting in some inner layers touching the wires, while others were free and open.

Efforts to reduce this coating problem have taken two turns. Oxide basket manufacturers now coat the inner wires with halar. This material is impervious to the heat, gives a uniform, thin (.010) coating along the wires, and will not create a surface tension environment between the inner layer and the wire. The halar does have one drawback in that it is applied in such a thin state, that it can be worn off through mishandling or through normal use. This problem can be countered by making the wires of the basket a removable item from the main support frame. This can be easily accomplished and allows the oxide processer to change the wires without sending the unit back to the fixture manufacturer for repair.

The other most recent design concept for inner layers has centered around the requirement to completely eliminate the center support wires. This can be accomplished by incorporating a side load unit through the use of a cam lock mechanism. This concept allows the inner layer to remain completely open to the solution without any possible problems with the stainless vertical and horizontal wires. The inner layer is held by applying a flat tension area to the inner layer along the sides of the layer. Although this concept works quite well, it presents a number of problems. The basket must weigh substantially more than the center

wire type of fixture, more square inches of surface area of metal is exposed to the bath, and it is more difficult to design the fixture so that the inner layer is easily loaded. Recent chemistry changes by a major chemical supplier have required that this design of fixture be in use. The chemistry is so sensitive, that the presence of wires causes the process to fail.

General concepts to always consider when designing oxide baskets are:

1. Allow for the inner layer to be held securely.
2. Construct the fixture so that it can be easily loaded.
3. Design the fixture to be as light asa possible yet structurally sound.
4. Always construct the basket out of 304 or 316 stainless steel.
5. Always construct the basket using TIG welding techniques and insure that the presence of rough edges and impurities are eliminated before the basket is used for processing.
6. If the basket or componet wires are coated, use halar.
7. Never build a fixture that will allow for the inner layer to be any closer than 3/8 of an inch from the adjoining layer.
8. The inner layer should be held relatively rigid during processing.
9. Educate the user of the basket to the value of the basket and the techniques for the proper care of the fixture.
10. Although it may not be a current requirement, oxide basket should be designed to accomodate a wide variety of inner layer sizes.

ELECTROLESS BASKETS

Fixturing for electroless processing has not undergone the significant changes experienced by the oxide and plating processes over the past years. However, there have been some ideas instituted for the industry, which have resulted in fixtures being more productive.

Without any doubt, electroless fixtures should be constructed of 316L stainless steel. If any lower series of stainless is used, the material will actually etch and the useful life will be greatly reduced. A number of different coatings have been applied to the stainless with negative results, due to the efficient, sensitive and active nature of the electroless copper bath. Also, a variety of plastics have gone through extensive experimentation in electroless baths with poor results. The other material option is titanium, which weighs 50% of stainless. Yet the high cost of titanium, coupled with the non-existent processing benefits, often eliminates its use.

End users and fixture suppliers often design baskets in much too complicated a manner. It has been proven, that if electroless baskets can be designed as simplistically as possible, the customer will benefit. Ideas that should be used in design are:

1. The fixture must contain as little exposed metal as possible, yet must be structurally sound.
2. Whenever possible basket components must be bent instead of welded to achieve a desired shape.
3. All sharp edges whether they be caused from welding, stamping or forming operations must be eliminated.
4. Circuit boards should be held along the edges of the board and, when designed properly, will easily load into the fixture.
5. The baskets should be designed

to be unloaded without the individual handling of each board. This can be accomplished through the use of a removable unit that can fit into a main frame or by incorporating a drop away bottom.

The most significant process problem when designing electroless fixtures concerns the position of the board during processing. When space allows, the board should be tilted in the left to right plane and the front to back plane during processing. This allows for the maximum solution flow through the holes, and the maximum drainage off the boards when they move from tank to tank.

Although it is important to use as much space in the tank, and to load as many boards into a fixture that the process will allow, end users often go overboard in their attempts to maximize production. Boards should never be closer than 1/2 inch from one another, and of course angling the boards will reduce the number of boards to be loaded into a fixture. A minimum of a 3 inch clearance from the sides of the tank or any additional items that are mounted in the tank (pipes, heaters, or agitation units) must be maintained.

Since most processors run more than one size of board, the electroless fixture should be adjustable in the left to right dimension of the basket. The methods to accomplish this can be a pin/slot type of unit or a trombone type slide with a locking device. Care must be taken to insure that the operator can easily move this slide mechanism into the proper location. This unit is susceptible to damage, and proper efforts must be taken when designing the slide unit.

General concepts to follow when designing electroless baskets are:

1. Securely holding boards in the proper position for processing.
2. Ease of loading.
3. Simplicity of design with structural soundness.
4. Use of 316L stainless steel.
5. Bulk unloading.
6. Flexibility of unit for different board sizes.
7. Correct spacing.
8. Overall size of unit.

Methods for Monitoring the Activity of Colloidal Tin-Palladium Catalysts; Part II - An Optical Method

S. Lal, C. G. Smith, W. Logan, Y. Okinaka, and H. S. Trop

AT&T Bell Laboratories
Murray Hill, New Jersey 07974

ABSTRACT

A novel optical method has been developed for monitoring the activity of colloidal Sn-Pd catalysts used in the process of manufacturing printed wiring boards. The method uses a strip of FR-4 glass-epoxy board as a substrate, and utilizes the fact that it is translucent. The substrate is activated in the catalyst solution to be monitored, rinsed, immersed in an accelerator solution, rinsed again, and finally placed in an optical cell containing an electroless copper plating solution. The decrease in optical transmittance due to the deposition of copper is followed as a function of time, and the time required for the transmittance to decrease to one half of the initial value is measured. It is shown that this time, $t_{1/2}$, can be used as a measure of the catalytic activity of the substrate activated by the catalyst to be monitored. Experimental data presented in this paper for two commercial catalysts demonstrate the practical usefulness of the proposed method.

1. INTRODUCTION

In Part I of this series of papers[1], a coulometric method was described, in which a glassy carbon electrode was used as a substrate for activation and electroless copper plating. Glassy carbon was used because the substrate must be electrically conductive for that method. On the other hand, the substrate used in actual applications of printed wiring board manufacturing is a non-conductive material such as epoxy resin reinforced with glass fibers. The board material called FR-4 is most commonly employed. Since surface properties of the substrate may affect its catalytic activity obtained after the activation treatment, it is preferred that the substrate material used for monitoring purposes be the same as that used in the actual manufacturing process.

We have subsequently developed an optical method using as the substrate a strip of FR-4 board, which is translucent. Others have used optical measurements to study the rate of electroless copper deposition[2], but our focus for the work reported here is to study the catalytic activity resulting from the application of a tin-palladium catalyst. In this method, the FR-4 substrate is first activated in the catalyst solution to be monitored, rinsed in water, immersed in an accelerator solution, rinsed again, and finally placed in an electroless copper plating solution of a known composition. The decrease in optical transmittance at the wave length of 600 nm is followed with time after immersion in the electroless solution, and the time required for the transmittance to decrease to one half of the initial value is determined and used as a measure of the catalytic activity of the treated FR-4 substrate.

2. EXPERIMENTAL

Experiments were performed on two commercial catalyst solutions. For this paper, these solutions will be denoted as Catalyst Solution A and Catalyst Solution B. Both solutions were prepared using the manufacturer's instructions.

For Catalyst Solution A, FR-4 strips were activated for 5 min in the catalyst solution, rinsed twice in air-agitated DI water, accelerated for 1 min in 1N HCl, rinsed in water, and finally immersed in a freshly mixed electroless copper plating solution contained in a 1-cm optical cell. The transmittance was measured with the setup illustrated schematically in Fig. 1. A 10-watt quartz- tungsten halogen lamp with a 600 nm narrow band interference filter supplies light to a fiber optic bundle. Light from the bundle is passed through a 1-cm cell containing an activated FR-4 strip and the electroless copper solution. The transmittance through the cell is measured as photocurrent with time.

For Catalyst Solution B, FR-4 strips were dipped in a Pre-Activator solution for 3 minutes at room temperature, transferred without rinsing into an Activator solution maintained at 32°C and kept immersed for 5 min, rinsed in water, immersed in a Post-Activator solution for 5 min at room temperature, rinsed in water, and finally placed in the electroless copper solution for transmittance measurement.

The electroless copper solution was prepared by mixing equal volumes of the following two solutions:

Solution I	
$CuSO_4.5H_2O$	0.04M (10 g/l)
HCHO, 37% solution	0.26M (20 ml/l)
Solution II	
NaOH	1.0M (40 g/l)
Na_2EDTA	0.1M (37 g/l)

3. *RESULTS AND DISCUSSION*

3.1 Catalyst Solution A

Typical experimental results obtained with the Catalyst Solution A are shown in Figs. 2, 3, and 4. Figure 2 shows the variation with time of photoresponse in mV, which is proportional to transmittance, with and without the acceleration treatment performed in 1N HCl for 1 min. The catalyst concentration was 1.5% by volume, and the activation time was 5 min. It is seen that the "take-time", which is the initial duration of time in which there is no change in transmittance or photoresponse, is decreased considerably by the acceleration treatment. It is also seen that the curve obtained with acceleration shows a faster decline in photoresponse than that without acceleration, indicating that the acceleration treatment is effective for increasing the catalytic activity of the surface. This difference in catalytic activity is also reflected in the difference in $t_{1/2}$, which is defined as the time it takes for the photoresponse to decrease to one half of the initial value.

Figure 3 summarizes the effect of catalyst concentration on the catalytic activity of FR-4 surfaces, as measured in terms of $t_{1/2}$, with and without acceleration. The inverse of $t^{1/2}$ has been used to amplify the magnitude of the relationship; the inverse changes more rapidly than does $t^{1/2}$. The result obtained with acceleration shows that the catalytic activity is constant at catalyst concentrations beyond 1.5%. Without acceleration, only about 50% of the full catalytic activity observed with acceleration can be obtained even at the catalyst concentration as high as 2.5%.

Figure 4 shows the effect of accelerator (HCl) concentration on the catalytic activity as measured in both "take time" and $t_{1/2}$. It is seen that the catalytic activity is constant when the HCl concentration is greater than about 1N. The catalytic activity decreases sharply at concentrations lower than 0.5N.

The effect of activation time on $t_{1/2}$ was studied using the catalyst concentration of 1.5%. The results are shown in Fig. 5.

The following generalizations can be made based on the experimental results described above:

1. The acceleration step is effective for increasing the catalytic activity. Presumably, the acceleration step exposes greater areas of Sn-Pd catalyst particles adsorbed on the FR-4 surface.

2. Either the "take-time" or $t_{1/2}$ can be used as a measure of the catalytic activity of the FR-4 surface. However, $t_{1/2}$ is a better defined quantity and can be measured more accurately.

3. The catalytic activity becomes constant at catalyst concentrations above 1%.

In addition, the effect of Sn^{+4} ions on the catalytic activity was investigated. When the molar ratio of Sn(II)/Sn(IV) was varied from 11 to 0.1, an increase in $t_{1/2}$ by 28% was observed, indicating that the presence of a large excess of Sn(IV) decreases the catalytic activity.

Experiments were also performed using strips of quartz/ITO (indium tin oxide-coated quartz) as substrates instead of FR-4. Both types of substrates exhibited similar behaviors in transmittance measurements.

3.2 Catalyst Solution B

Experiments with this solution were carried out in the same manner as described above. Effects of variables on the catalytic activity were investigated. The variables studied were catalyst concentration, activation time, and post-activation conditions. Effects of these conditions on the catalytic activity as determined by measuring $t_{1/2}$ were generally similar to those observed with the Catalyst Solution A system. The shape of the photoresponse - time curves obtained with the Catalyst Solution B was essentially the same as for Catalyst Solution A (Fig. 2). The effect of catalyst concentration on $t_{1/2}$ is shown in Fig. 6. At concentrations above 2%, the catalytic activity is constant.

FR-4 strips activated in the catalyst solution for 5 min were treated with the post activator for varying lengths of time. The results are shown in Figure 7. A minimum acceleration time of 60 sec is requred in order to achieve a constant catalytic activity. Also shown in Figure 7 is the effect of the activation time on $t_{1/2}$. It is seen that, for optimum results, an activation time of at least 3-4 min is required.

4. CONCLUSION

An optical method was developed for monitoring the catalytic activity of colloidal Sn-Pd catalysts used in the process of manufacturing printed wiring boards. The method is based on the measurement of the time required for the optical transmittance of an activated FR-4 substrate to decrease to one half of the initial transmittance after the substrate is placed in an electroless copper plating solution. Experimental results obtained with two commercial catalyst systems demonstrate that the method can be used for monitoring the effectiveness of the catalyzation processes. The simplicity of the method makes it particularly suitable for routine monitoring of the catalyst systems.

References

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2. J. Dumesic, J. A. Koutsky and T. W. Chapman, J. Electrochem Soc., **121** ,1405 (1974).

Figure Captions

Figure 1. Configuration of apparatus for the measurement of the transmittance of the translucent substrate characterizing catalytic activity.

Figure 2. Photoresponse of the FR-4 substrate for the Catalyst Solution A system. 1.5% by volume catalyst concentration with 5 minute activation time. With and without acceleration by 1N HCl for 1 minute.

Figure 3. Effect of catalyst concentration on the catalytic activity of the FR-4 substrate for Catalyst Solution A. With and without acceleration by 1N HCl for 1 minute.

Figure 4. Effect of accelerator (HCl) concentration on the catalytic activity for Catalyst Solution A. Catalyst concentration 1.5%, activation time 5 minutes.

Figure 5. Effect of activation time on $t_{1/2}$ for Catalyst Solution A. Catalyst concentration of 1.5% by volume has been used.

Figure 6. Effect of catalyst concentration on $t_{1/2}$ for the Catalyst Solution B system.

Figure 7. Effect of acceleration time and activation period for the Catalyst Solution B System. Activation period was 5 minutes for the effect of acceleration time, while the acceleration period was 5 minutes for the effect of the activation time.

Block Diagram for Transmittance Measurements

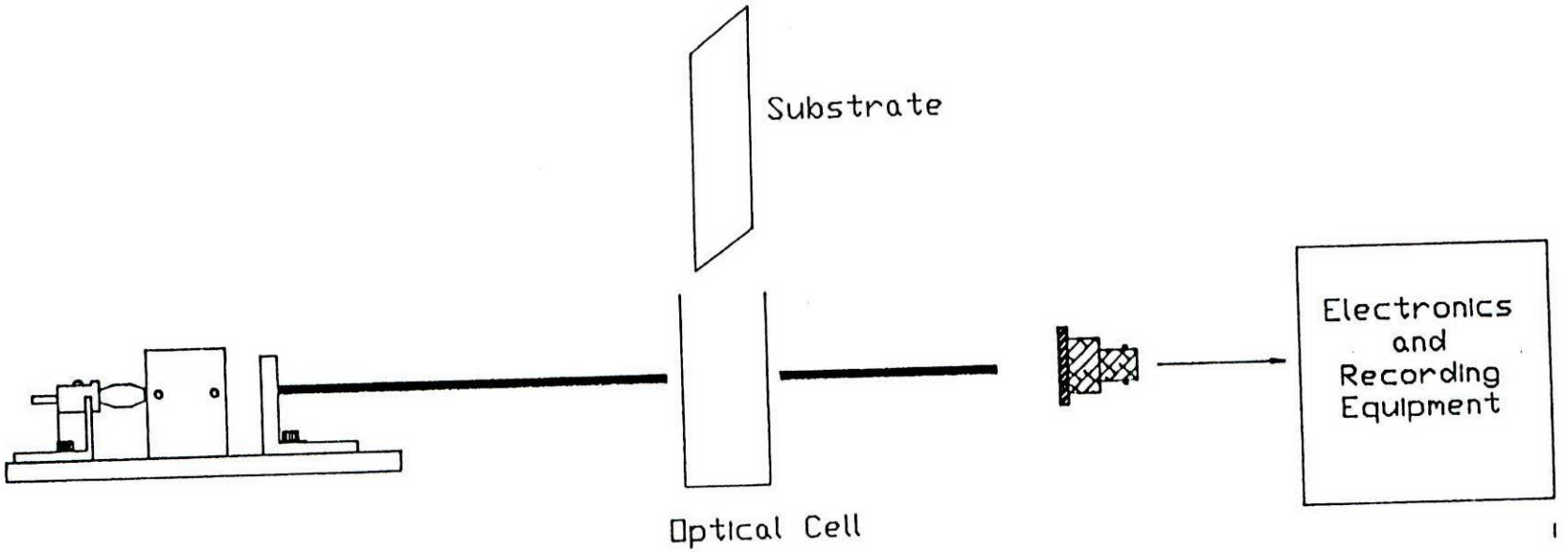


Figure 1

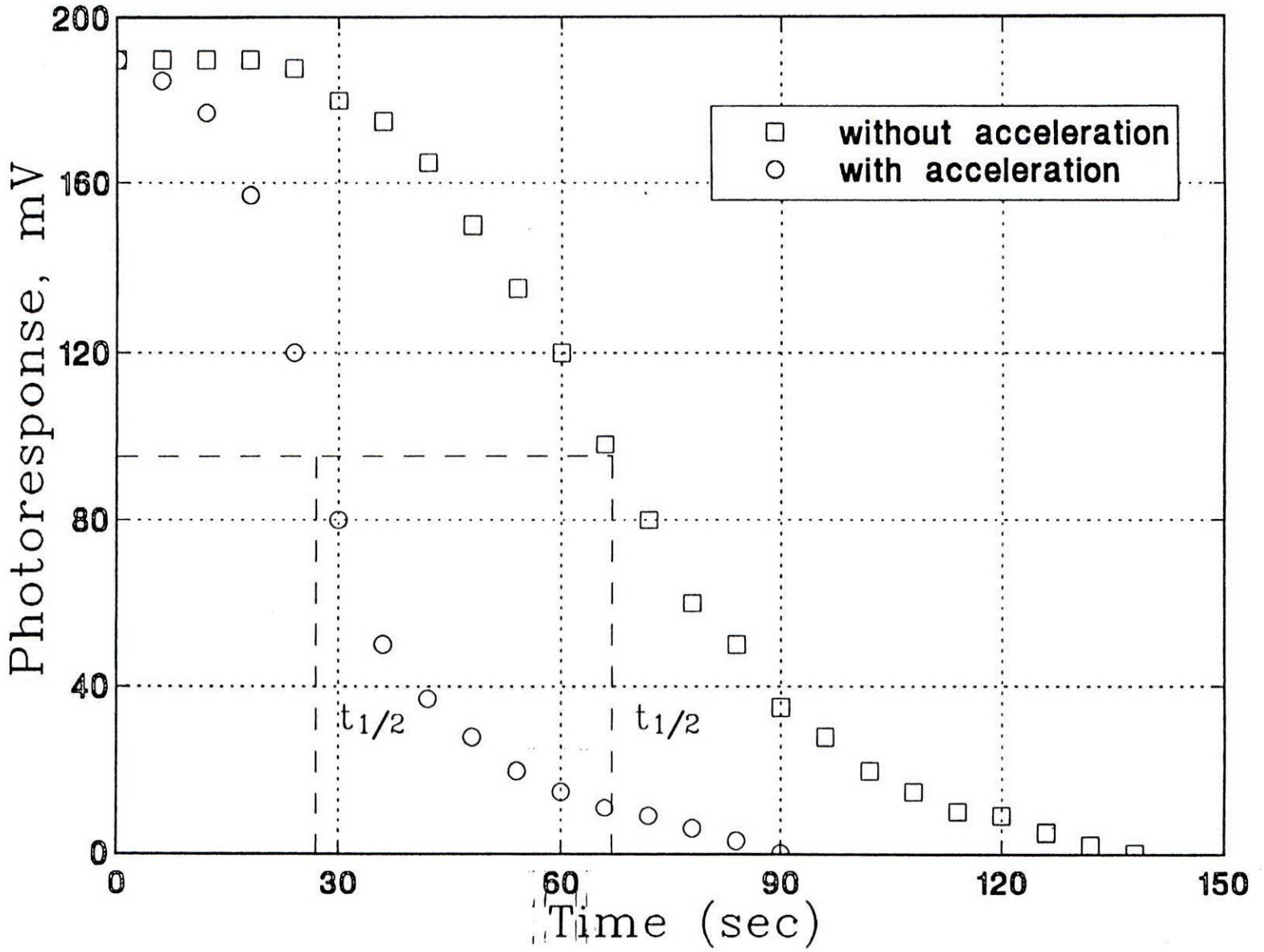

200
160
120
80
40
0
Photoresponse, mV
0
30
60
90
120
150
Time (sec)
without acceleration
with acceleration
t1/2
t1/2

Figure 2

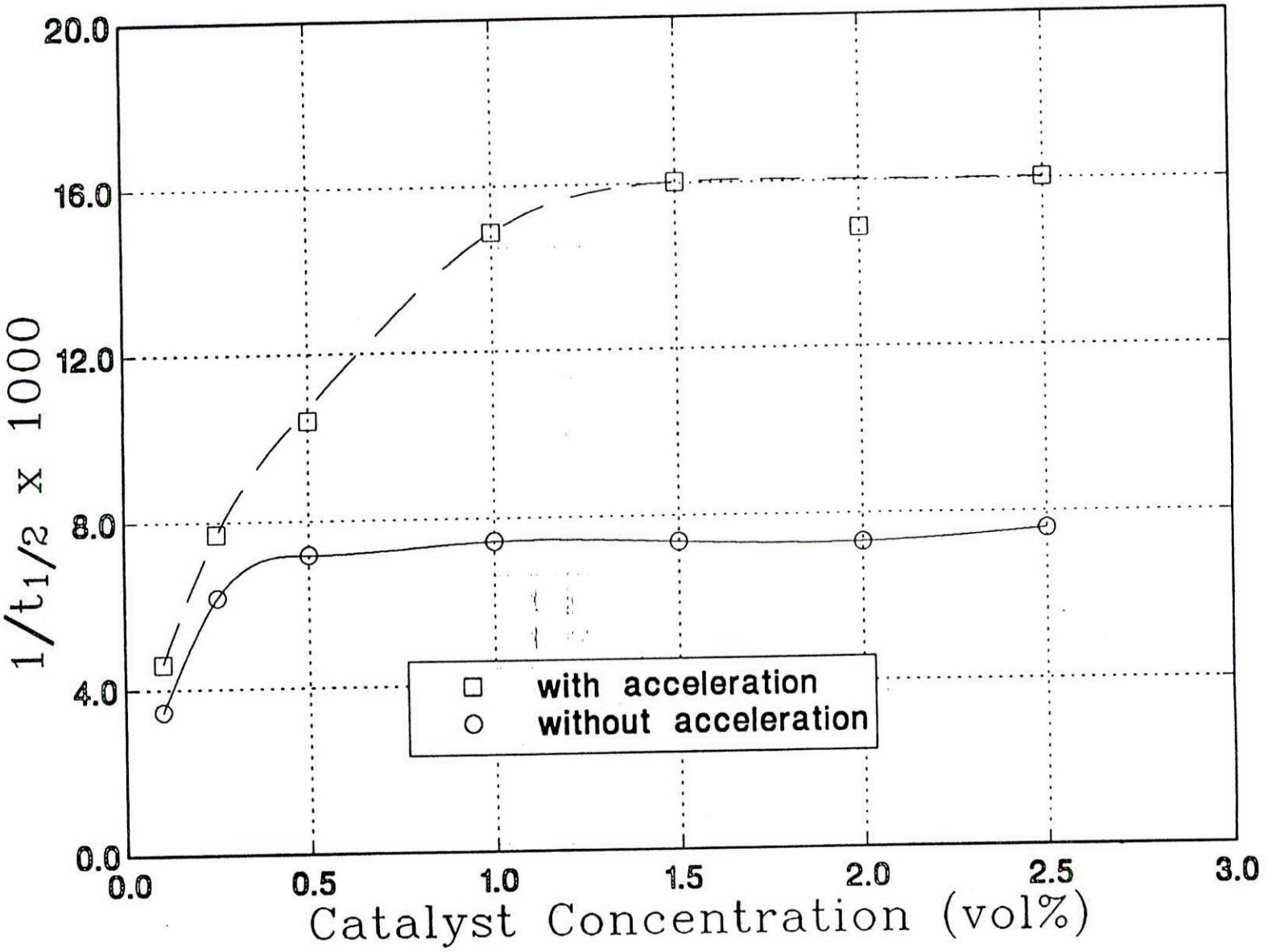

20.0
16.0
12.0
8.0
4.0
0.0
1/t1/2 x 1000
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Catalyst Concentration (vol%)
with acceleration
without acceleration

Figure 3

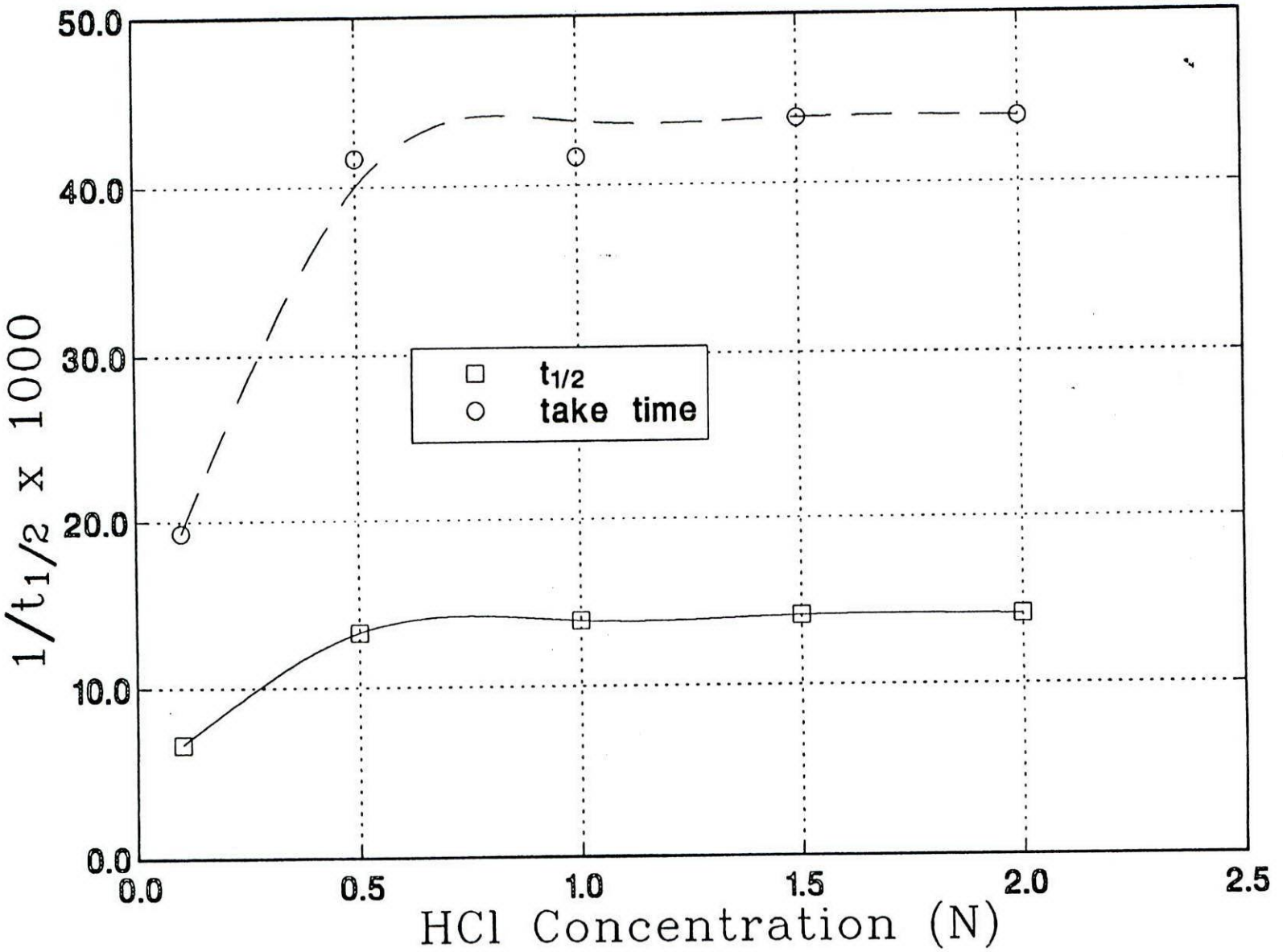

50.0
40.0
30.0
20.0
10.0
0.0
1/t1/2 x 1000
t1/2
take time
0.0
0.5
1.0
1.5
2.0
2.5
HCl Concentration (N)

Figure 4

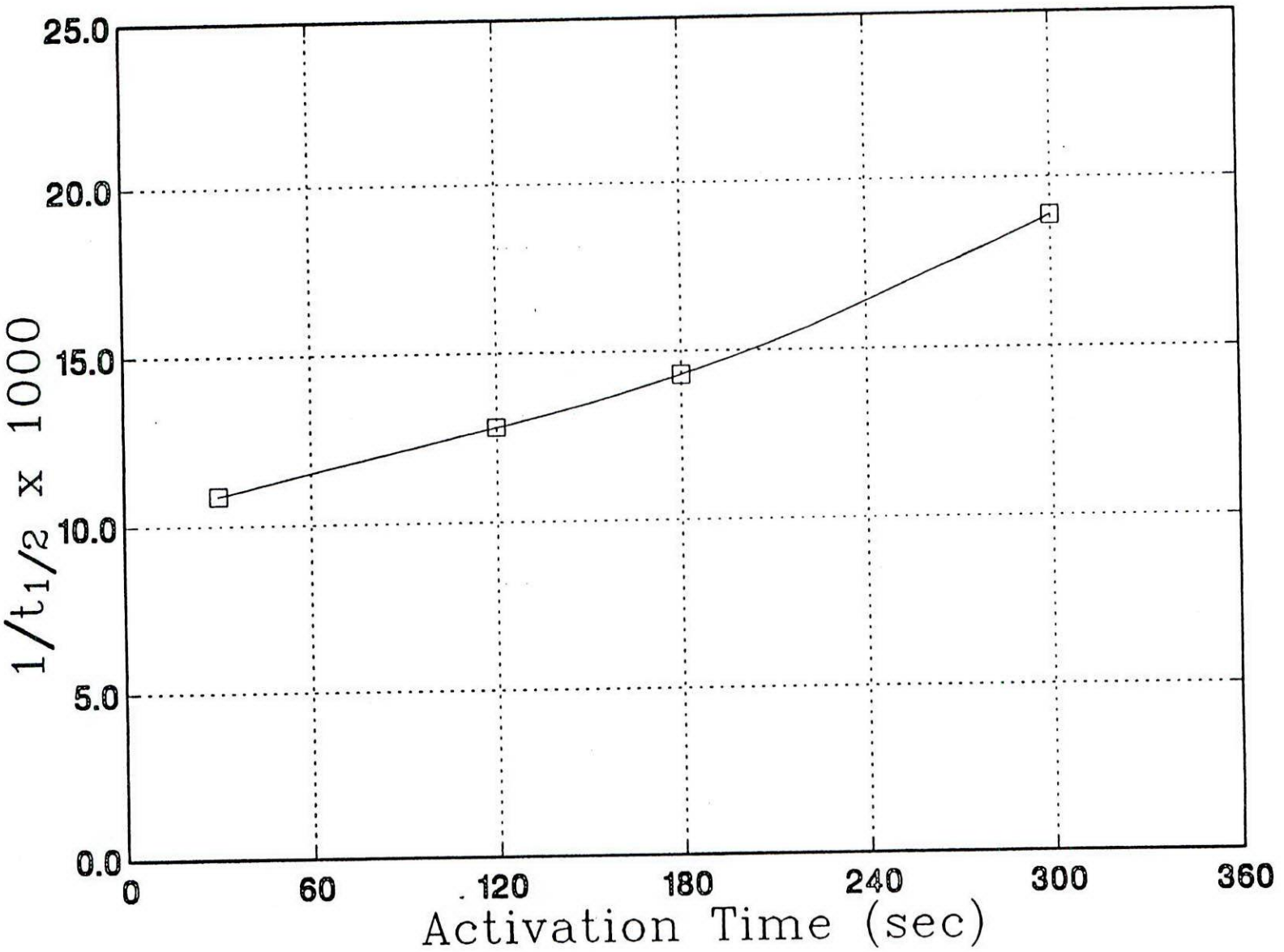

25.0
20.0
15.0
10.0
5.0
0.0
1/t1/2 x 1000
0
60
120
180
240
300
360
Activation Time (sec)

Figure 5

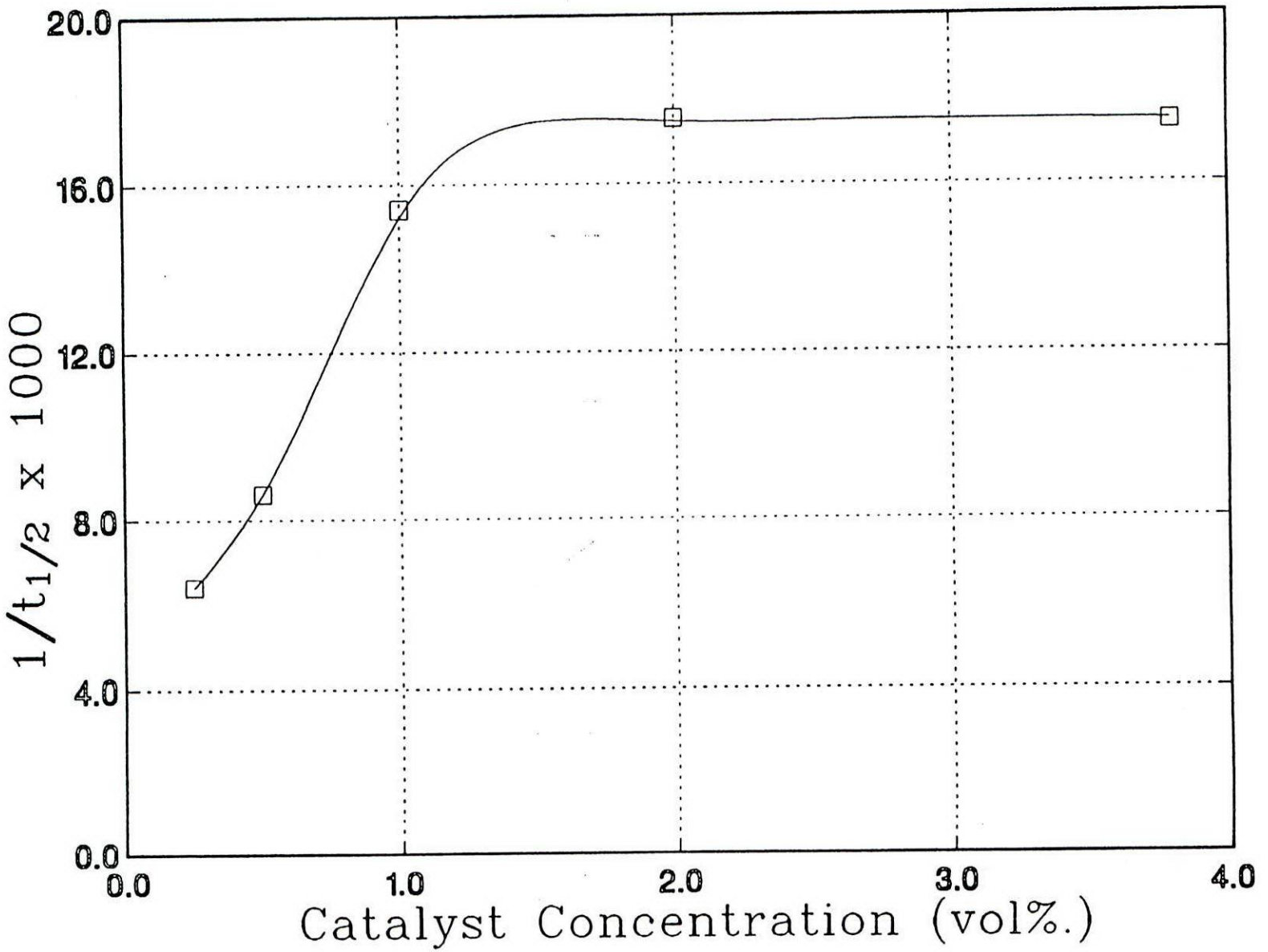

20.0
16.0
12.0
8.0
4.0
0.0
1/t1/2 x 1000
0.0
1.0
2.0
3.0
4.0
Catalyst Concentration (vol%.)

Figure 6

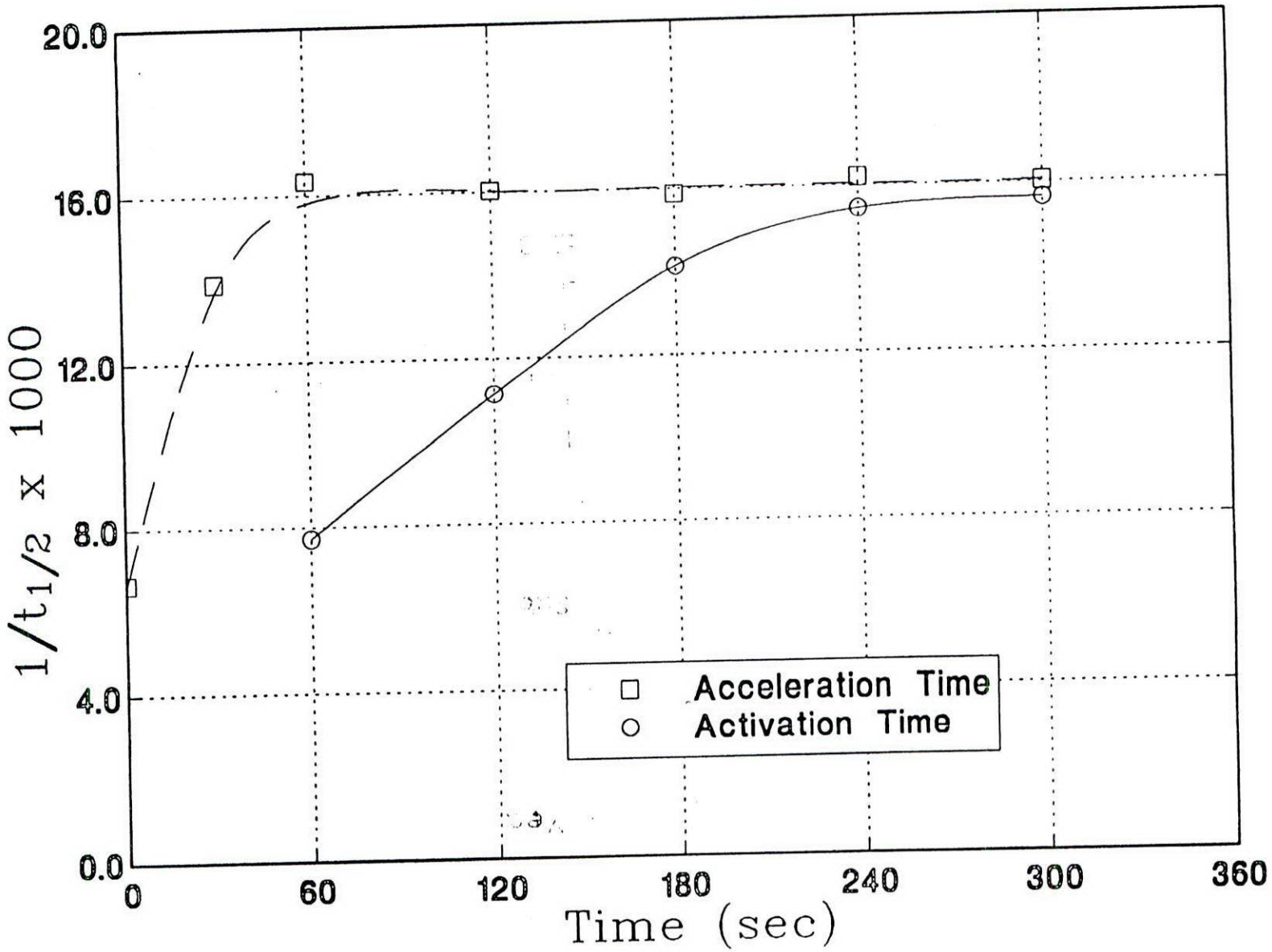

20.0
16.0
12.0
8.0
4.0
0.0
1/t1/2 x 1000
0
60
120
180
240
300
360
Time (sec)
Acceleration Time
Activation Time

Figure 6

SHE-1 Super High Speed Electroless Nickel Plating Process

Jing Li FANG, Yong WU, Min ZHANG, Jing FANG
(Applied Chemistry Institute,Nanjing University,P.R.CHINA)

Abstract

A new Super High Speed Electroless Nickel Plating Process (SHE-1) was developed,and the complexing agent,stabilizer and accelerator for SHE-1 were found,making it possible that the electroless nickel bath deposited nickel at the rate of 25-28μm/h in stable conditions. We also studied the effects of nickel sulfate,sodium hypophosphite,succinic acid,complexing agent CL-1,accelerator AL-1,pH value, bath temperature and time etc. on the rate of electroless nickel plating.

The corrosion resistance of nickel deposit was determined by the regular method. The morphology and crystalline state of nickel deposit were also determined by Scanning Electron Microscopy and x-ray diffractometry.

Key words:
Electroless nickel plating, Super high speed, Corrosion resistance, SEM, x-Ray diffractometry

INTRODUCTION

Because of its excellent corrosion resistance,wear resistance,solderability,low porosity and thickness uniformity and because it can deposit on complex parts and non-conductor,electroless nickel plating has been widely used in oil industry, chemical engineering,plastics,optical parts,printing,aerospace, automobile,electronics,textile,ship-making and food industry et.al.[1-3]

The deposition rate of regular acidic electroless nickel plating using sodium hypophosphite as reducing agent usually ranges from 13-17 μm/h. If the deposition rate is between

18-22 μm/h, it is called high speed electroless nickel plating. With the widely use of electroless nickel plating, a lot of businesses, such as mechanical, electronics, chemical engineering and printing demand thick deposit of electroless nickel plating. In order to improve production efficiency, super high speed electroless nickel plating with deposition rate 23-27 μm/h becomes a new topic that many people concern with.

There are many factors that have effect on the deposition rate, namely bath temperature and pH value, concentration of Ni^{2+} and sodium hypophosphite, types of complexing agent, accelerator and stabilizer and the load of the bath etc. When operating conditions(such as temperature, pH value, the load of bath, concentrations of Ni^{2+} , $H_2PO_2^-$) are kept constant, the factors influencing deposition rate are the types and concentrations of complexing agent and accelerator. There are mainly two ways to improve the deposition rate of electroless nickel plating. The first one is to change the complexing agent so that the activation energy needed for the reduction Ni^{2+} complexing ion will drop. The complexing agents used in electroless nickeling bath are mainly hydroxy-acid. For example, lactic acid, malic acid, citric acid, gluconic acid etc.. These organic hydroxy-acids can form one or more chelating cycles with nickel ion and the number of cycle are related with the concentration and structure of complexing agent and the bath pH value.[4] If one complexing agent is used, the deposition rate declines as the following:[5]

succinic acid > glycollic acid > lactic acid > phthatic acid > salicylic acid > glycine > tartric acid

R.Weiner suggested that lactic acid is a good complexing agent. It has good coordination ability, buffering ability and accelerating ability. If two complexing agents are used, then both of them can coordinate with nickel ion and mixed ligand coordination compound will be formed. This can decrease the activation energy needed by nickel complexing ions to reduce. Some characteristics that do not occur when using

monocomplexing agent will occur,and some unexpected results may be obtained.[6] When operating in an acetate-citrate electroless nickeling bath,the deposition rate is usually about 10-13 μm/h. K.Panker[7] studied the deposition rate when the second complexing agent is added. He found that if acetic acid,propanoic acid or glycine is added, the deposition rate will improve from 11 μm/h to 15-16 μm/h,that is to say the addition of the second complexing agent can properly improve the deposition rate and stability of bath and the tolerance of phosphite.

The second method to improve the deposition rate of electroless nickeling is to add suitable amount of accelerator. Gawrilov[8] proposed that fluoride can be used as accelerator. Small amount of fluoride can slightly improve deposition rate and promote the deposition on aluminium. But higher amount of fluoride will increase the internal stress. In recent years, organic accelerators attract more attention. Usually there are three kinds of organic accelerators:

1.Saturated monocarboxylic acids and their salts

2.Saturated amino-acids

3.Saturated non-substitute dicarboxylic acids

Among them dicarboxylic acid has wider application. It can improve the deposition rate from 11 μm/h to 16 μm/h. If better complexing agent is selected,deposition rate can reach 20 μm/h or so. In 1992 B.Bozzini[9] successfully developed a electroless nickeling process using gluconic acid as complexing agent and proper accelerator so that the deposition rate of electroless nickeling could reach 25 μm/h. It was reported that the new process of McGean-Rohco Inc. and Japan Mineral corp. had deposition rate 20 μm/h. In the recently years we have studied a series of electroless nickel plating processes (such as Ni-P of high and low phosphorus[10-14] and Ni-B using DMAB as reducer),and developed super high speed electrless nickeling process with deposition rate 25-28 μm/h using special complexing agent,accelerator and stabilizer. It not only has high deposition rate,but also has

excellent stability and deposit characteristics. It will find wide application in many industrial fields.

EXPERIMENTAL

1.Formulation

Selecting the bath with optimum seeking method. The formulation is as following:

Nickel sulfate	35 g/L,	pH	5-6
Sodium hypophosphite	25 g/L,	Temperature	90-95 °C
Succinic acid	20 g/L,	Loading of bath	1-1.5 dm^2/L
Complexing agent CL-1	45mL/L,	Deposition rate	25-28 μm/h
Accelerator AL-1	30mL/L,		

2.Making up of the bath

1)Respectively weigh calculated amount of nickel,sodium hypophosphite,succinic acid,complexing agent CL-1 and put them in 1000 mL beaker. Add distilled water to 800 mL and fully agitate until they desolve.

2)Add 30 mL of accelerator AL-1.

3)Adjust pH value to 5.8 using ammonia water and add water to regulated volume.

3.Methods of determination

1)Electroless nickel plating:

Put the bath into beaker and heat the beaker in thermostated jar. The deposition rate is measured by the increase of the sample weight with standard area in per unit time.

2) Determination of corrosion resistance

Put the sample respectively in the solutions of NaCl, H_2SO_4,HCl and NaOH.Observe the corrosion in different time periods.

3)Deposit morphology

By Hitachi Y650 Scanning Electron Microscope(SEM)

4)Crystalline state of the deposit

By Japan Rigaku D/Max-YB x-ray diffraction instrument

RESULTS

1.Effects of bath composition and operating conditions on deposition rate

To select the optimum bath composition and operating conditions, change one component or one condition and keep the others constant, measure the change of deposition rate. The following are the results.

1)Nickel sulface

Ni^{2+}ion concentration decided the composition of nickel complex ion and the stability of bath. The variation in deposition rate with the nickel sulfate concentration from 15 g/L to 75 g/L is shown in Fig.1. It can be seen from Fig.1 that with increasing concentration of nickel ions, the deposition rate first increases to a highest point and then drops. When the concentration of nickel sulphate is 60 g/L, the bath becomes muddy because of the hydrolysis of Ni^{2+}. Therefore, the concentration of Ni^{2+} should be controlled below 60 g/L, and 35 g/L is the optimum.

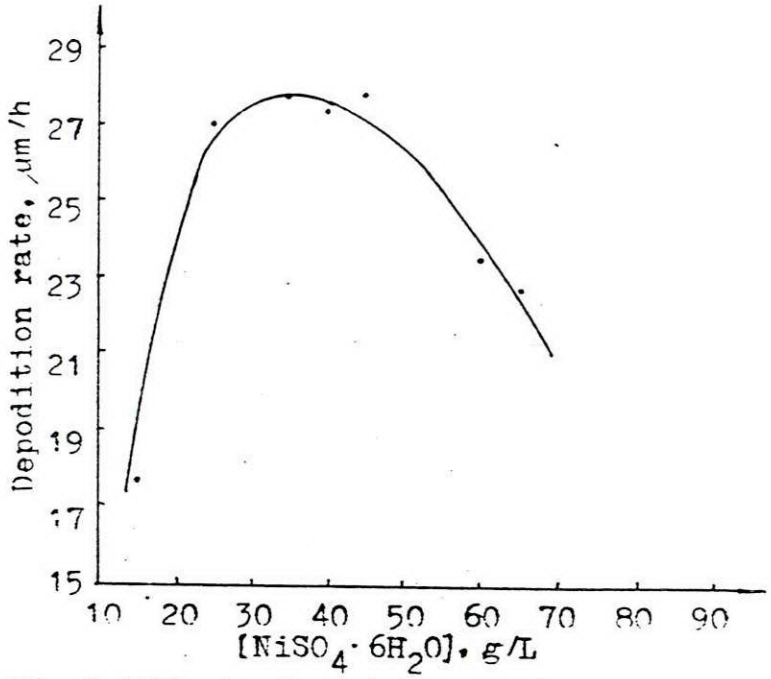
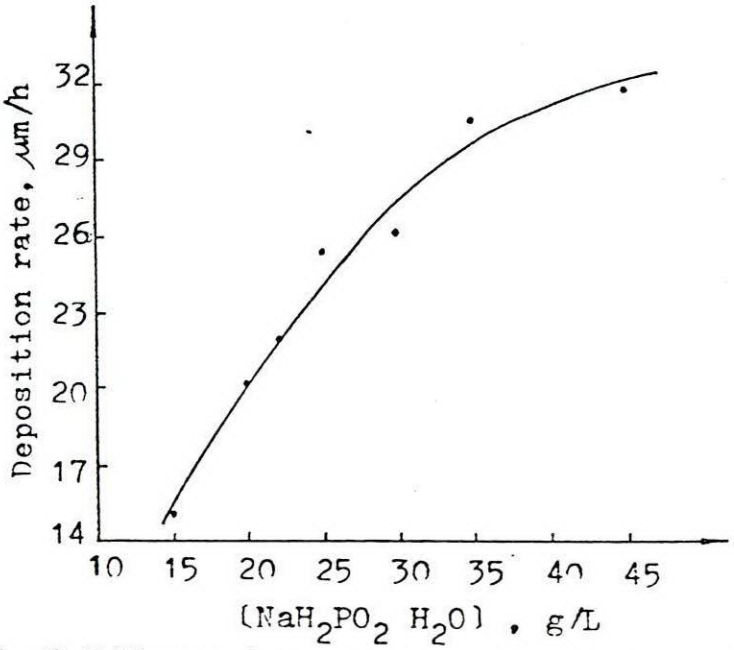


Fig.1.Effect of nickel sulphate concentration on deposition rate

2)The effect of sodium hypophosphite

Sodium hypophosphite is the reducing agent of Ni^{2+} and the source of phosphorus in the alloy. Fig.2 is the variation in deposition rate with sodium hypophosphite increasing from 15 g/L to 45 g/L.



ig.2.Effect of sodium hypophosphite concentration on deposition rate

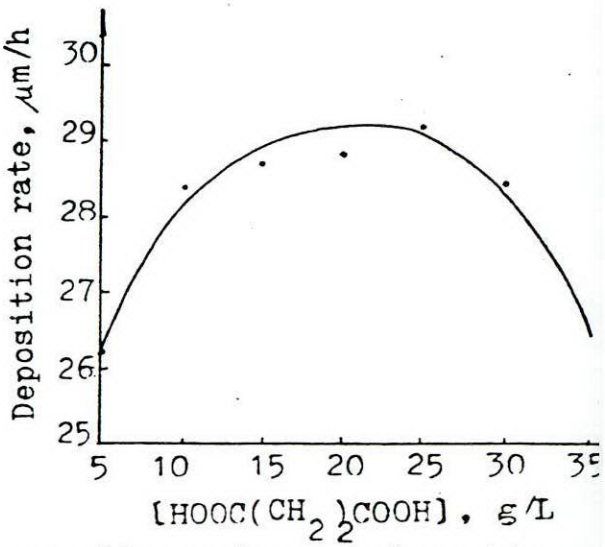


Fig.3.Effect of succinic acid concentration on deposition rate

It can be seen that the deposition rate increases with the increase in the concentration of sodium hypophosphite. When the concentration reaches 45 g/L, the bath becomes unstable and is easy to decompose. As a result, the concentration of sodium hypophosphite should not exceed 45 g/L. Considering cost price and bath stability, we regard 25 g/L as the optimum concentration.

3) Effect of succinic acid

Succinic acid is used for coordination acceleration and buffering. Fig.3 is the variation in deposition rate with the concentration of succinic acid 5-35 g/L. From Fig.3 we can see that with increasing concentration of succinic acid, the deposition rate of electroless nickeling increases

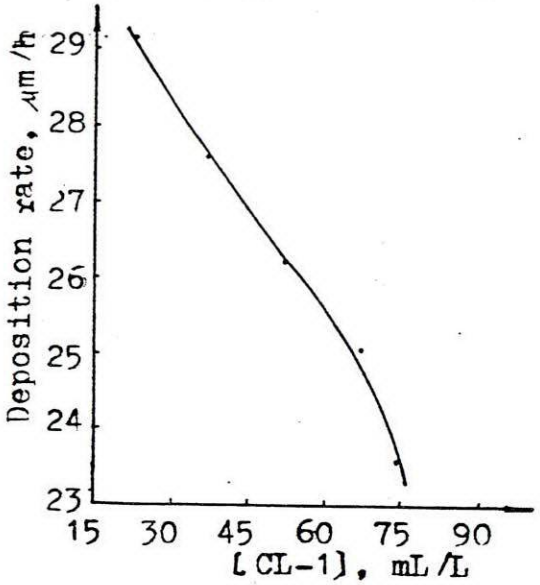


Fig.4.Effect of complexing agent CL-1 concentration on deposition rate

first and then decreases. The highest point is 20 g/L, which is the optimum value.

4) The effect of complexing agent CL-1

Complexing agent CL-1 can form stable coordination compound with Ni^{2+}, which makes Ni^{2+} stable in the bath. Fig.4 is the variation in deposition rate with the concentration of CL-1 increasing from 22.5 mL/L to 75 mL/L. The results show that the deposition rate increases while the stability of bath decreases with decreasing concentration of CL-1. Considering both rate and stability, 45 mL/L is the optimum concentration.

5) The effect of pH value

Fig.5 is the variation of deposition rate with pH value. The figure shows that the deposition rate increases with increasing pH value.

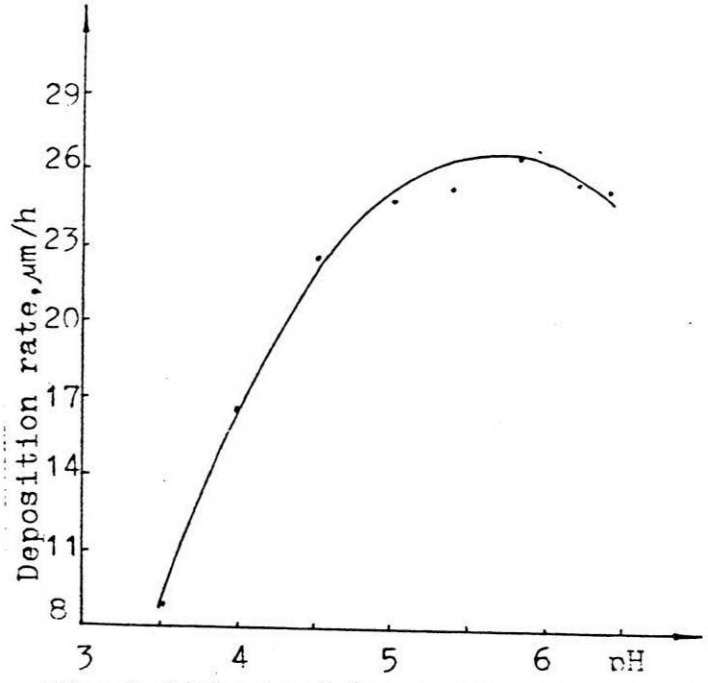


Fig.5. Effect of bath pH on deposition rate

Bath pH value has great effect on deposition rate. With increasing bath pH, deposition rate increases. The reason might be that some of the coordinated water dissociate into hydroxyl, which acts as electron bridge and accelerates the transmission of electron. The deposition rate is highest when pH=5.8. When pH value is above 5.8, some of the nickel coordination compounds begin to hydrolysis. When pH value is even higher, the bath tends to precipitace. This makes the concentration of Ni^{2+} drop and the deposition rate decreases too.

6) Effect of bath temperature

Fig.6. is the variation in deposition rate with temperature . The deposition rate is very slow at 70 °C. After 80 °C, the deposition rate increases markedly and the rate

increases linearly with increasing temperature. Observed from the experiments, the bath becomes unstable when temperature is above 98 °C. Usually the bath temperature is controlled between 90-95 °C.

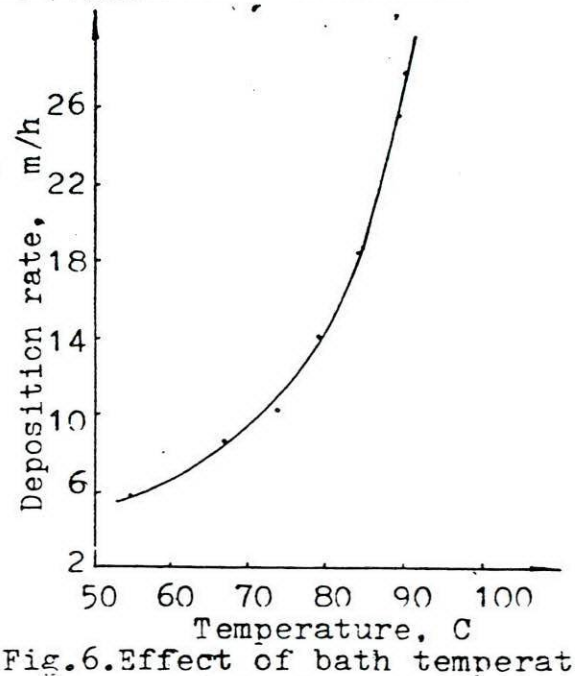


Fig.6. Effect of bath temperature on deposition rate

7) Effect of plating time

Fig.7 is the variation in deposition rate with plating time. It is seen from Fig.7 that in the first hour of plating, the variation of deposition rate is very small. After one hour, the deposition rate decreases slowly because of the consumption of various components. Therefore, replenishment should be make and adjustment of pH value should be done when the bath is used for sometime, so as to keep the deposition rate within suitable range.

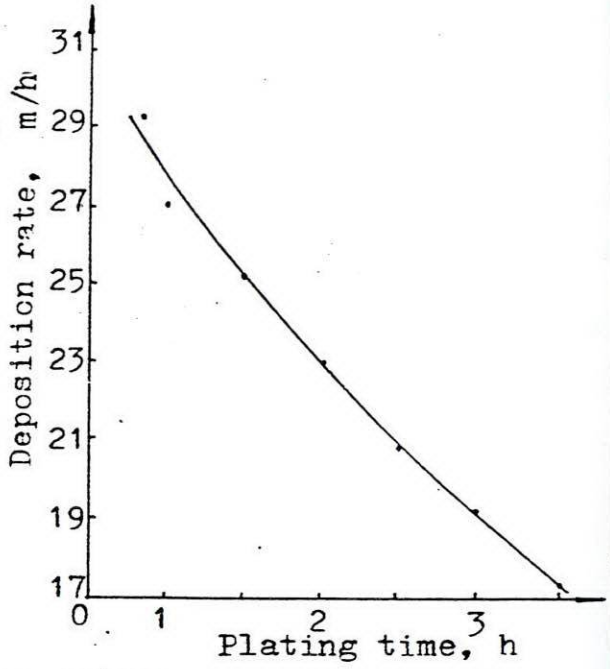


Fig.7. Effect of plating time on deposition rate

8) Effect of accelerator AL-1

Dip the samples in a series of baths in the same conditions except for the concentration of accelerator. Measure the deposition rate with gravimetric method. The results are shown in Fig.8.

When the concentration of accelerator AL-1 is 0-4.5 mL/L, the deposition rate increases sharply with increasing concentration, 4.5-110 mL/L is a constant area. When the concentration is above 110 mL/L, deposition rate decreases sharply, and when concentration reaches 120 mL/L, the electroless nickeling deposit can not be obtained.

2.The corrosion resistance of SHE-1 electroless nickeling

Table 1 is the corrosion resistance in different kinds of corrosion media.

It can be concluded from Table 1 that super high speed elctroless nickeling deposit has better corrosion resistance in sulphuric acid and hydrochloric acid than the other three systems,and in sodium chloride and sodium hydroxide solutions,its corrosion resistance can match the other three systems.While the concentration of sodium chloride,sulphuric acid, hydrochloric acid,sodium hydroxide is rather high,the samples made by our process kept unchange in 12 days. This demonstrates that our process has excellent corrosion resistance in these solutions.

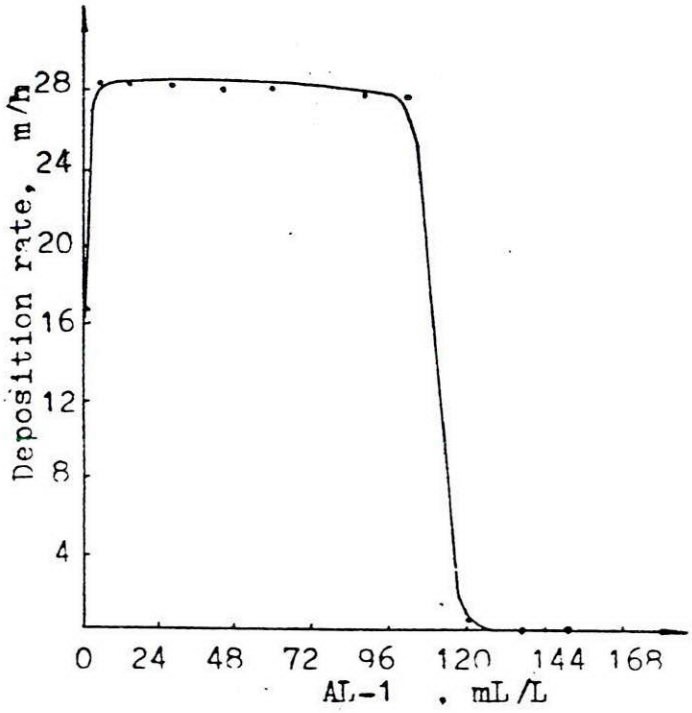


Fig.8.Effect of accelerator AL-1 concentration on deposition rate

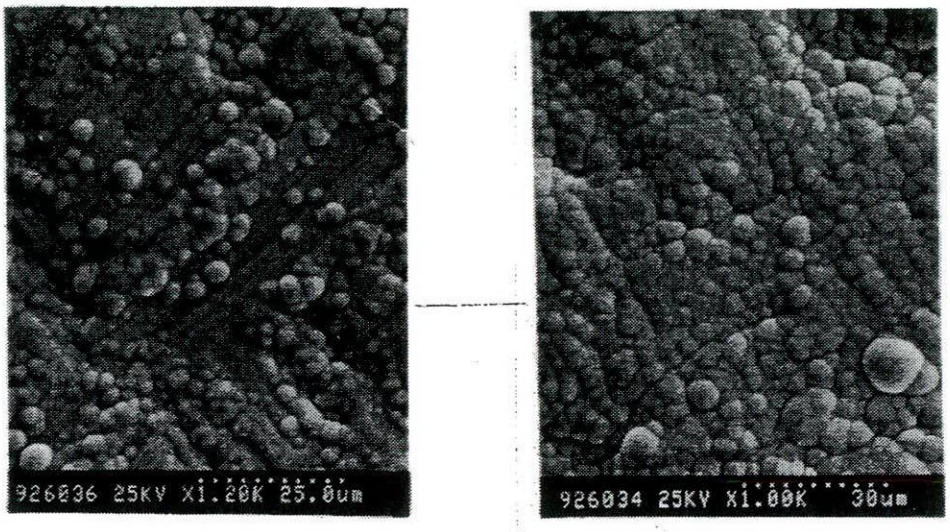
Table 1.Corrosion resistance in different kinds of corrosion media

Baths / Results / Cor. media	SHE-1 bath	Citrate-acetate bath (a)	Lactic acid-boric acid bath (b)	Succinic acid-malic acid bath (c)
10% NaCl solution	No change in 12 days	No change in 12 days	No change in 12 days	No change in 12 days
10% H_2SO_4 solution	No change in 12 days	Turns blue in 10 days	Turns blue in 10 days	Turns blue in 10 days
10% HCl	No change in 12 days	Turns blue in 9 days	No change in 12 days	Turns blue in 8 days
10% NaOH	No change in 12 days	No change in 12 days	No change in 12 days	No change in 12 days

* Formulation of (a): Nickel sulphate 30 g/L,Sodium acetate 15 g/L,Sodium citrate 15 g/L,Sodium hypophosphite 25 g/L, pH 4.5,T=90 °C.
Formulation of (b): Nickel sulphate 25 g/L,Lactic acid 25 g/L,Boric acid 10 g/L,Sodium fluoride 1 g/L,Sodium hypophosphite 20 g/L,pH 4.5,T=90 °C.
Formulation of (c): Nickel sulphate 25 g/L,Succinic acid 16 g/L,Malic acid 24 g/L,Sodium hypophosphite 24 g/L,Lead acetate 0.003 g/L,pH 5.8,T=90 °C

3.SEM analysis of super high speed electroless nickeling deposit

The topography of electroless nickel deposits from super high speed acidic bath and common citrate-acetate bath were examined in a Hitachi X650 Scanning Electron Microscope(SEM). The magnifying powers are 1200 and 1000 respectively.Fig.9 (a) and (b) are microscopic photos of electroless nickel deposit from super high speed bath and common citrate-acetate bath.



(a) (b)

Fig.9 The microscopic photos of electroless nickling deposit
(a) SHE-1 EN deposit; (b) Citrate-acetate EN deposit

It is seen(Fig.9) that the maximum diameter of the crystal of acidic super high speed electroless nickeling deposit is 7.0 μm,much less than that of citrate-acetate bath,which is 12 μm.This shows that the complexing agent we choose is excellent.It enables us to obtain denser deposit with smaller

crystal.

4. x-Ray diffraction of the deposit

A Japan Rigaku D/Max-rB x-ray diffraction instrument was used for measurement ,copper target working voltage 40 kV, working current 110 mA and scanning angle 30-90° . The results are shown in Fig.10. The peak is a wide diffuse one, which demonstrates that Ni-P deposit has non-crystalline structure.

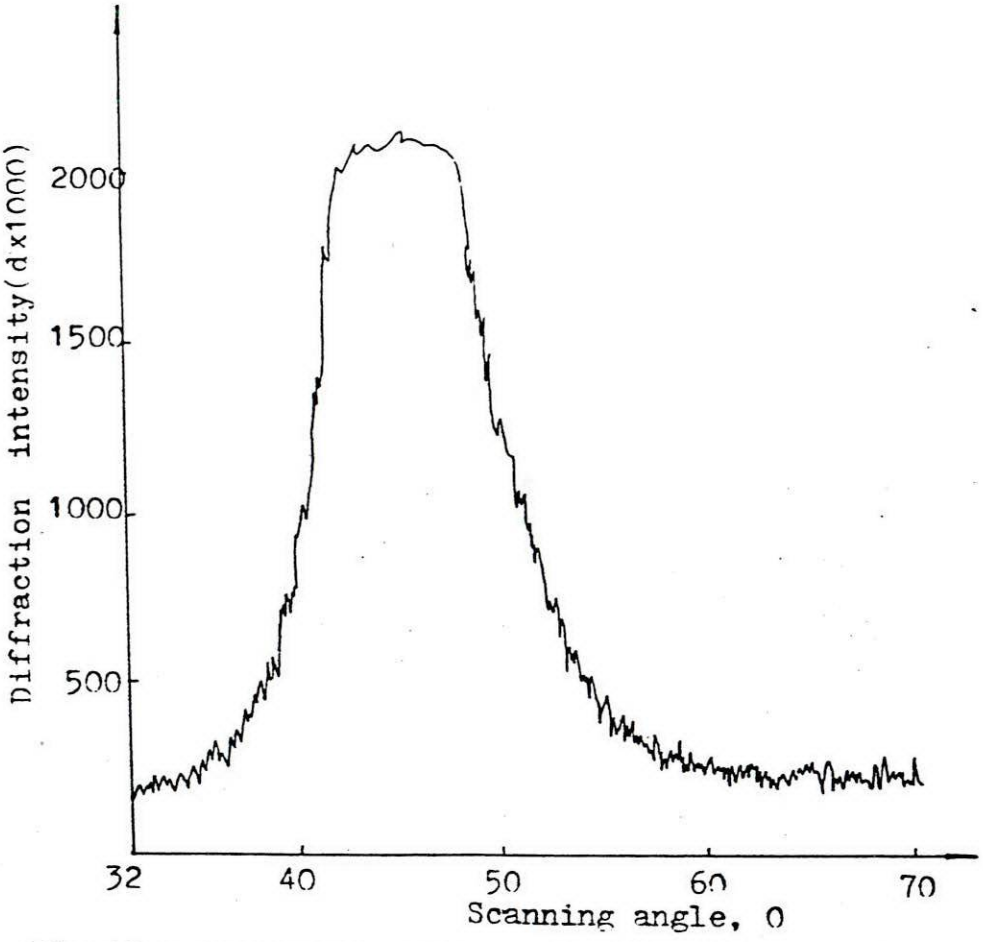


Fig.10. x-Ray diffraction peak of SHE-1 super high speed electroless nickeling deposit

CONCLUSION

(1) Based on optimum method, the formulation of the optimum SHE-1 is:

Nickel sulphate	35 g/L,	Succinc acid	20 g/L,
Sodium hypophosphite	25 g/L,	Accelerator AL-1	30 ml/L
Complexing agent CL-1	45 mL/L,	pH	5-6
Temperature	90-95 °C,	Bath load	1-1.5 dm^2/L

(2) SHE-1 electroless nickeling deposit has excellent corrosion resistance in solutions of NaCl, H_2SO_4, HCl and NaOH.

(3) According to Scanning Electron Microscope, the maximum diameter of the electroless nickeling crystal is 7 μm while that of common citrate-acetate bath is 12 μm. This shows that the deposit of SHE-1 electroless nickeling is denser.

(4) x-Ray diffraction of SHE-1 electroless nickeling deposit shows it has non-crystalline structure.

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TIN AND BISMUTH SUBSTITUTES FOR ELECTRODEPOSITED LEAD

P.L.Cavallotti°, L.Nobili°, G.Zangari°, V.Sirtori*

°Dip.Chimica Fisica Applicata, Politecnico Milano - Via Mancinelli 7, 20131 Milano, ITALY
*IBM SEMEA-ECAT, Vimercate(MI), ITALY

Abstract

Substitutes are proposed for electrodeposited lead, a toxic metal, for protection of steel from corrosion, for bearings and solderable coatings in the assembly of electronic equipments. Tin or bismuth plating, as metal or in alloys, are examined as main alternatives. Sn-Bi electrodeposited can substitute Pb-Sn for soldering and ternary Sn-Bi-Sb coatings are proposed for tribological applications.

Introduction

Lead is a very old metal, whose toxicity has been clearly stated and that will be substituted in the near future for many applications.

It is easily electrodeposited, either pure or as an alloy, giving adherent, smooth and ductile coatings. Its present uses are related to properties such as: solderability, lubricity for tribological applications and chemical resistance. The most important application is as a Sn-Pb alloy for soldering in Printed Circuit Boards PCB manufacture.

The use of Pb pipes and Pb for solders of drinking water connections is prohibited in USA; new regulations threaten to ban lead from solders and for other applications. The lead toxicity may be explained by the interference with different enzyme systems, inactivating them by binding with SH-groups or displacing essential metal ions. Data on health effect show that lead can be toxic even when present in very low concentration in the blood and a threshold limit of 10 µg/dl has been proposed.

A great effort is now devoted to research and develop lead substitutes for lead containing alloys and also for electrodeposited coatings. We will examine alternatives to lead alloys mainly for soldering and tribological coatings, focusing on tin and bismuth alloys as possible substitutes.

Experimentals

Baths preparation

Chemicals of reagent grade and double distilled water were used. Plating bath were made from stock solutions of tin, bismuth and a complexant: diethylenetriaminepentaacetic acid (DTPA).

DTPA solution was obtained dissolving the acid in a minimum amount of diluted ammonia under prolonged stirring [9,11].

Tin solutions were:

a) an experimental bath, from stannous sulphate to which the DTPA bath was added, to obtain Sn 0.1M and DTPA 0.1M, pH adjusted with ammonia;

b) a stannous methanesulfonate 0.6M bath with additives for high throwing power (Elga-Ronal);

c) a stannous methanesulfonate 0.34M bath with brightening additives (Elga-Ronal).

Two bismuth baths were used, with final DTPA complexation:

a) a chloride base obtained by dissolution of $BiCl_3$ in a diluted HCl solution with heating and stirring;

b) a methanesulphonate solution obtained by dissolution of Bi carbonate with methanesulphonic acid (MSA) with heating and stirring.

Deposit preparation and examination

The deposition was carried out in a pyrex cell, agitated with a magnetic stirrer, with insoluble anodes.

For potentiodynamic runs we used an AMEL 5000 potentiostat-galvanostat computer controlled, with an Ag/AgCl reference electrode connected to the cell through a lateral channel Piontelli probe. Scanning rate was usually 0.5 mV/s and potentiodynamic curves were obtained after deposition of a first layer, in optimum conditions for 10 min.

The surface deposit morphology and the cross section structure, after etching with diluted acetic acid, was examined by scanning electron microscopy (SEM) and the deposit analysis was carried out by energy dispersive spectroscopy (EDS) with ZAF corrections on a Cambridge Stereoscan 250MKII instrument. X-ray diffraction patterns were determined with a vertical goniometer in a Philips PW1830/1820/1710 equipment; deposit micro-hardness with a Shimadzu HMV2000 instrument.

Tin electrodeposition

Electrodeposition is the most important application of tin, either to assist joining through soldering or for protection against corrosion. General references[1-5] cover the most important aspects of this process, such as different plating solutions, coatings applications and tin alloys electrodeposition.

Tin is electrodeposited either from acid stannous or from alkaline stannate baths. Uniform and crystalline deposits are mainly obtained from the acid stannous baths, with additives and complexants. The potentiodynamic curve for a $SnSO_4$ 0.1M solution with addition of DTPA is shown in fig.1; the complexation by DTPA decreases the equilibrium potential, as well as the exchange current density. A similar behaviour is found for a commercial methanesulphonate bath with levelling additives (Elga-Ronal), as shown by the potentiodynamic curve of fig.2. When brightening additives are present the potentiodynamic cathodic run show a strong minimum, as shown in fig.3 and reported in the literature[6]. The deposit morphology is light grey and homogeneous and normally microcrystalline. It is difficult to obtain strong textures.

Tin alloy coatings are widely applied, the most important alloys being: Sn-Cd, Sn-Cu, Sn-Co, Sn-Ni and Sn-Zn.

For lead substitution all these alloys are interesting, with the exception of Sn-Cd and cyanide containing baths, that also presents toxicity problems.

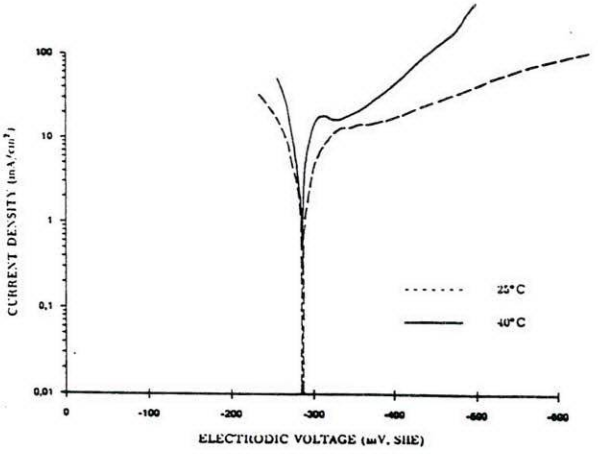

Fig.1 - Potentiodynamic curves for a tin plating bath of composition: $SnSO_4$ 0.1M, DTPA 0.1M, pH<1.

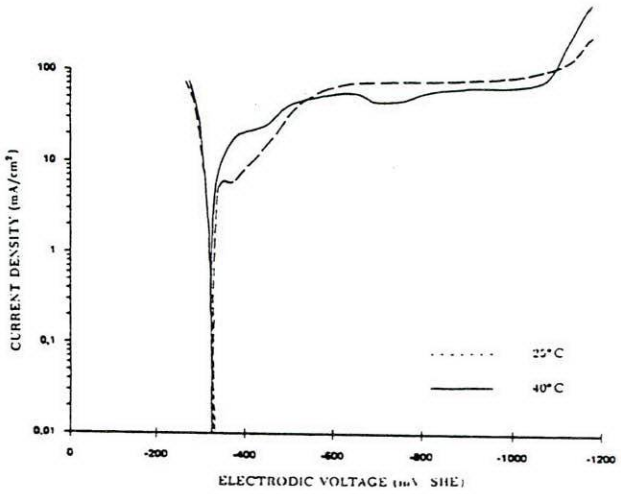

Fig.2 - Potentiodynamic curves for a tin plating bath of composition: $Sn(CH_3SO_3)_2$ 0.6M with levelling additives, pH<1.

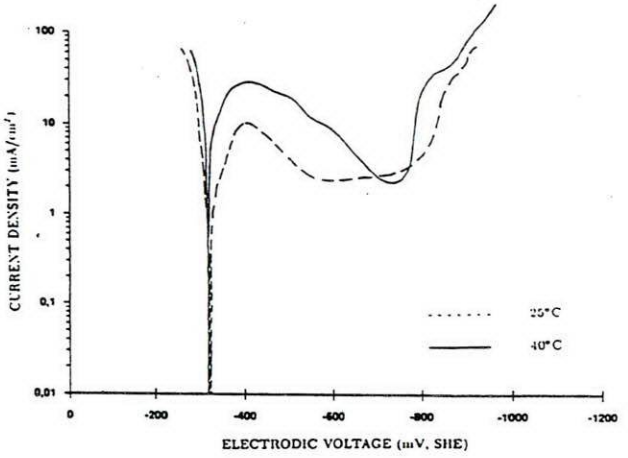

Fig.3 - Potentiodynamic curves for a tin plating bath of composition: $Sn(CH_3SO_3)_2$ 0.34M with brightening additives, pH<1.

Electrodeposition of Sn alloys with Co and Ni, from acid or neutral baths containing complexing agents such as fluorides, fluoborates or gluconates, gives interesting deposits. Among them the corrosion resistant Sn-Ni alloy coating of fixed composition, corresponding to the stoichiometric ratio SnNi, that can be interpreted as a stoichiometric compound.

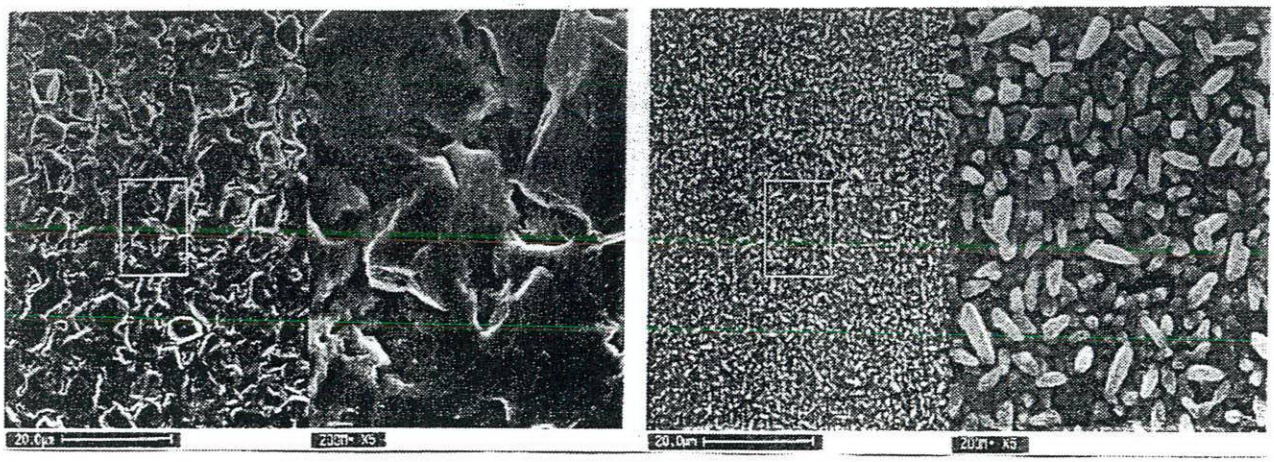

Fig.4 - Microstructure of the surface of deposits from a tin plating bath of composition: $SnSO_4$ 0.1M, DTPA 0.1M, pH<1, 40°C; left 5 mA/cm^2, right 40 mA/cm^2.

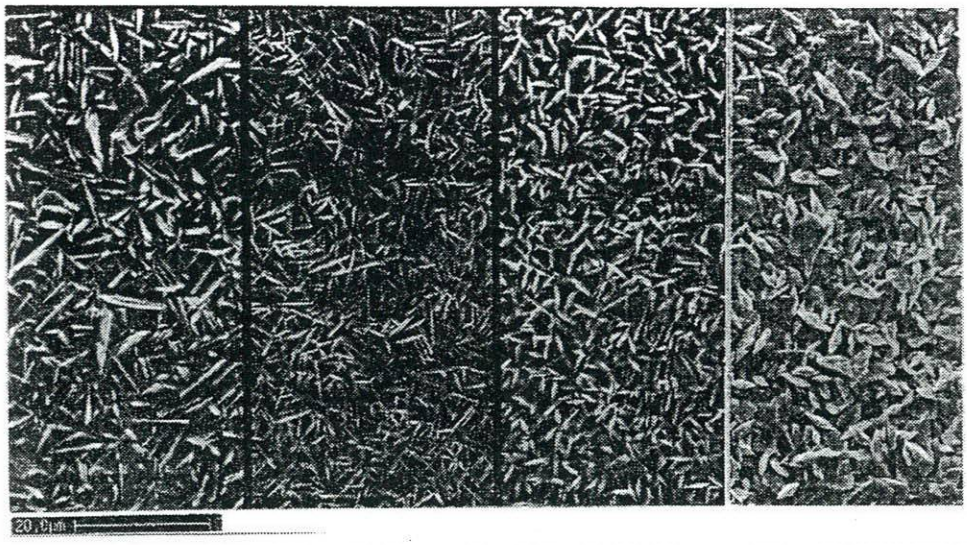

Fig.5 - Microstructure of the surface of deposits from a tin plating bath of composition: $Sn(CH_3SO_3)_2$ 0.3M, with levelling additives, pH<1, 20°C; 5, 10, 20, 50 mA/cm^2 from left to right.

Bronze and speculum (Sn 40% white coating) plating are usually deposited from cyanide baths, but interesting alternatives have been proposed, such as pyrophosphate, fluoborate or citrate-tartrate baths.

Sn-Zn alloys are now being extensively studied as possible alternatives, not only for lead alloys but also for cadmium. Also in this case researches regard cyanide free baths.

Among less studied Sn alloys of interest for Pb substitution we will examine Sn-Bi and Sn-Sb, with possible additions to improve the soldering or tribological properties.

Bismuth electrodeposition

Electrodeposited bismuth coatings do not find commercial application, at the moment, but these elements are of interest for the development of Pb substitutes.

Bismuth has been electrodeposited from acid baths; perchlorates and chlorides have been used for electrodeposition on single crystals surfaces[7,8].

Sadana and Venkatachalam[9] have proposed an interesting bath for Bi deposition based on the complexation with DTPA.

We have experimented a similar bath, starting from $BiCl_3$ or $Bi_2(CO_3)_3$. The potentiodynamic behaviour at low pH <1 and at a high pH of 7 or more is presented in figs.6 and 7.

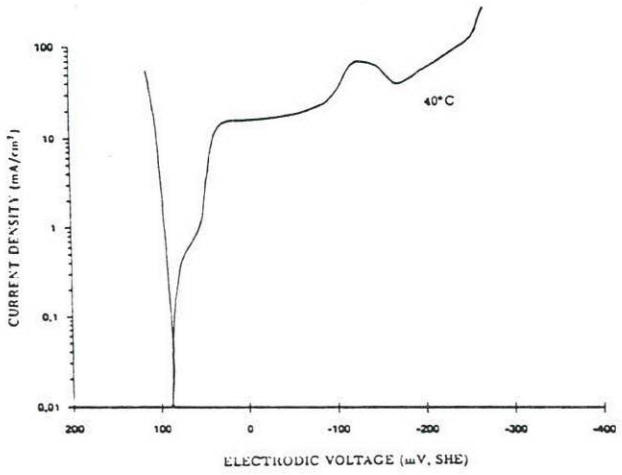

Fig.6 - Potentiodynamic curves for a bismuth plating bath of composition: $BiCl_3$ 0.05M, DTPA 0.05M, pH<1, T 40°C.

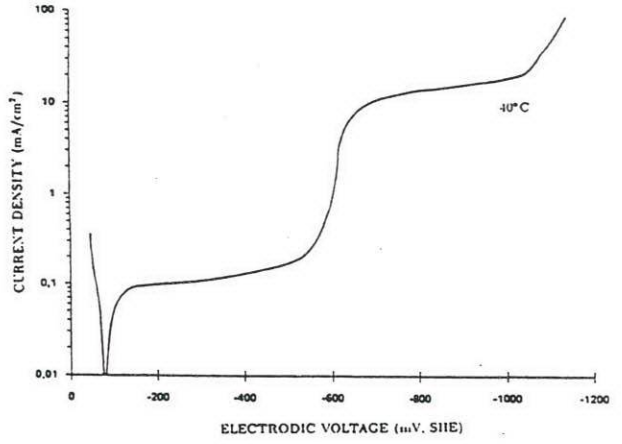

Fig.7 - Potentiodynamic curves for a bismuth plating bath of composition: $BiCl_3$ 0.05M, DTPA 0.05M, pH 7 with NH_3, T 40°C.

Increasing the pH the voltage at which Bi is deposited in the cd range 1-10 mA/cm^2 greatly increases. At low pH, grey uniform deposits are obtained, whose surface microstructure is shown in fig.9, with low preferred orientation PO. Increasing the pH, the brightness (see fig.8) and the texture also increase and we can obtain bright mono-oriented deposits of PO depending on the deposition cd, as shown in fig.10. PO (003) at 4 mA/cm^2, (102) at 10 mA/cm^2.

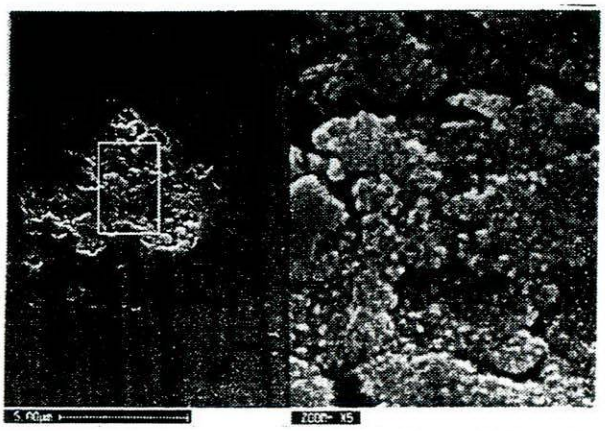

Fig.8 - Microstructure of the surface of deposits from a bismuth plating bath: $BiCl_3$ 0.05M, DTPA 0.05M, pH 7 with NH_3, T 40°C.

Bismuth-tin alloy electrodeposition

Few studies have been devoted to the electrodeposition of Bi-Sn alloys. Kudryatsev[10] has studied acid tin bath with addition of Bi to stabilize the white tin deposit; Sadana et al[11] have proposed the electrodeposition of Sn-Bi from a bath complexed with DTPA, obtaining encouraging results.

The Sn-Bi eutectic alloy has been proposed as one of the most interesting lead-free solders[12-16]. It is possible to obtain a 57Bi-43Sn alloy of well defined eutectic microstructure[13], very low melting temperature 139°C, good fluidity, with some problems related to strain rate sensitivity and possible oxidation.

We have examined the electrodeposition of Sn-Bi alloy from a bath with DTPA as a complexing agent for bismuth. The potentiodynamic behaviour of a Sn-Bi bath with DTPA as a complexing agent is shown in fig.11, from this bath we obtained almost pure Bi deposits, only at low T tin was deposited preferentially. Substituting Sn complexed with DTPA by means of the commercial Sn bath with levelling additives we obtained the potentyodynamic behaviour shown in fig.12. In this case Bi was preferentially deposited at low cd and Sn at high cd. T favours Bi deposition.

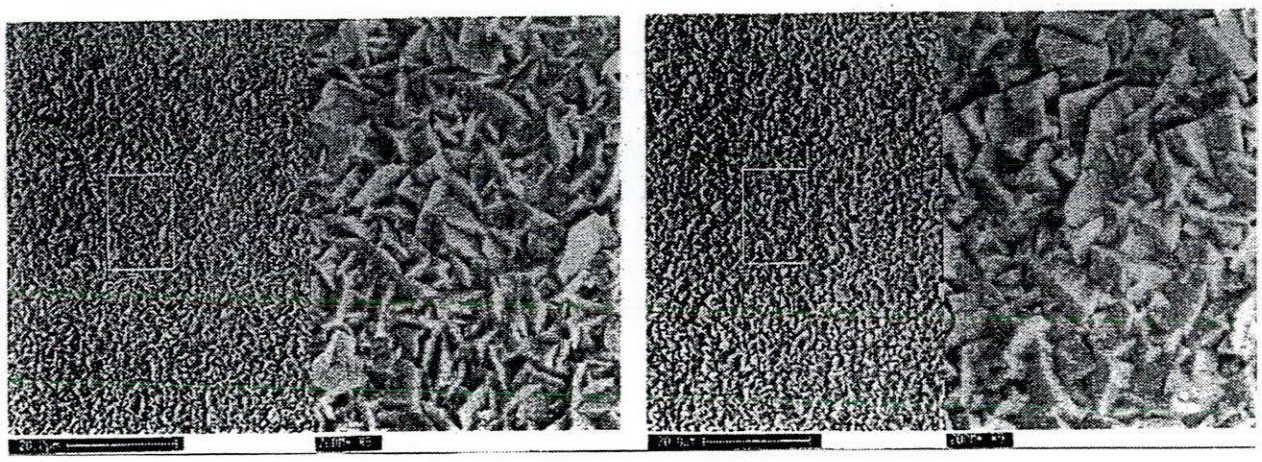

Fig.9 - Microstructure of the surface of deposits from a bismuth plating bath: $BiCl_3$ 0.05M, DTPA 0.05M, pH<1, T 40°C.

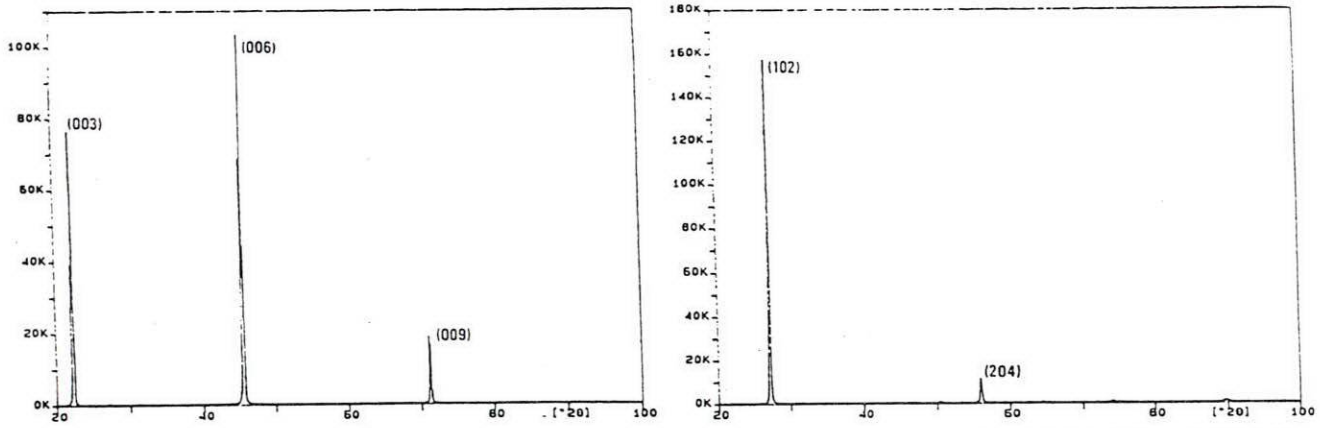

Fig.10 - X-ray diffraction patterns from Bi coatings deposited from a plating bath: $BiCl_3$ 0.05M, DTPA 0.05M, T 40°C; left 4 mA/cm^2, right 10 mA/cm^2.

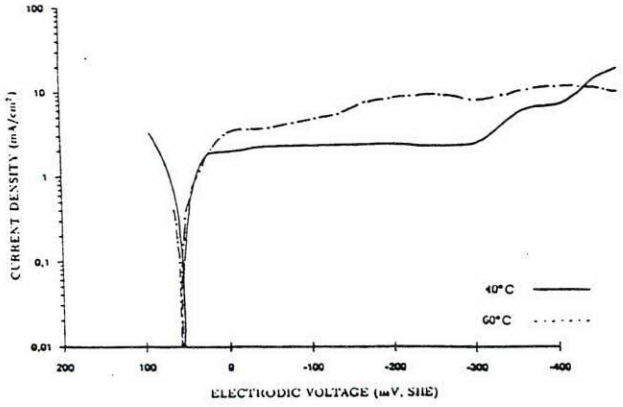

Fig.11 - Potentiodynamic curves for a Sn-Bi plating bath of composition: $SnSO_4$ 0.1M, $BiCl_3$ 0.05M, DTPA 0.15M, pH<1.

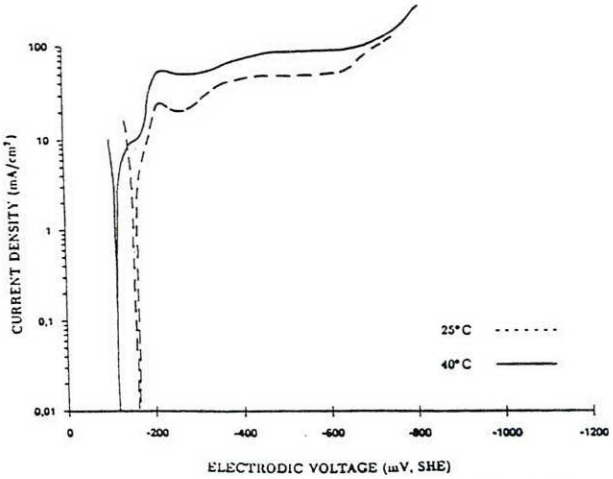

Fig.12 - Potentiodynamic curves for a Sn-Bi plating bath of composition: $Sn(CH_3SO_3)_2$ 0.3M with levelling additives, $BiCl_3$ 0.05M, DTPA 0.05M, pH<1.

It was possible to obtain deposits of eutectic composition. The deposit contained Bi and Sn of lattice constants very similar to those of the metallurgical alloys, as shown by the X-ray diffraction patterns of fig.13. Fig.14 shows the Bi (white) and Sn (dark) distribution in the cross-section of two deposits, of near eutectic and high Sn 86% composition. Fig.15 shows EDS Sn and Bi distribution after reflow under N_2 in an industrial oven at 280°C, and fig.16 the cross section at the border of the deposit on a copper substrate. The alloy wet very well the copper substrate, and Sn spreads preferentially on the surface.

Knoop hardness, masured on the cross section, of the Sn 86% sample was 22.6 HK and of the Sn 60% sample 26.7 HK.

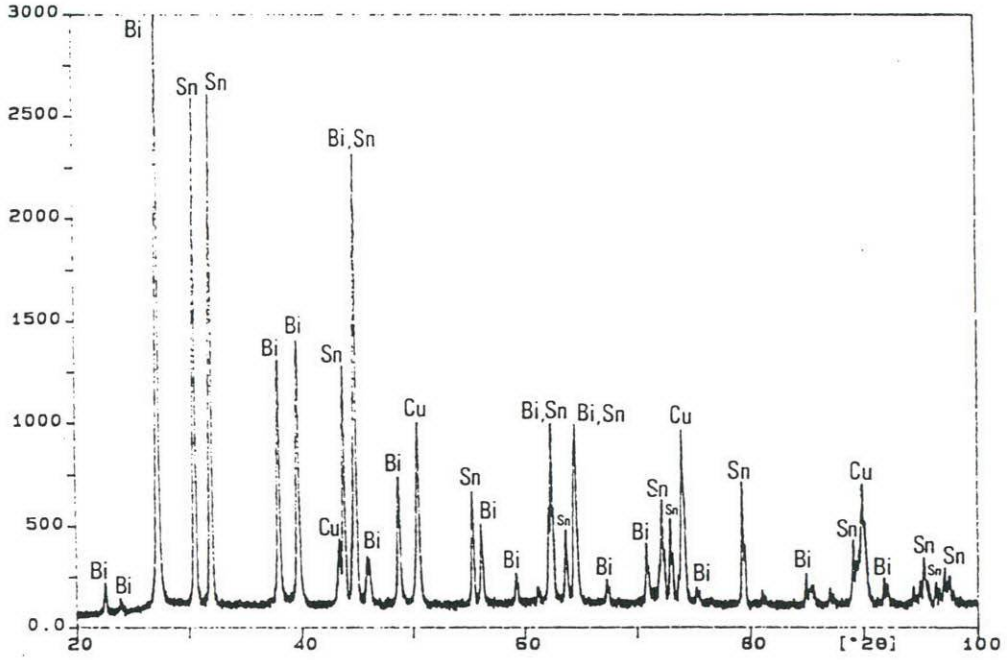

Fig.13 - X-ray diffraction patterns from Sn-Bi coatings deposited from a plating bath: $Sn(CH_3SO_3)_2$ 0.3M with levelling additives, $BiCl_3$ 0.05M, DTPA 0.05M, pH<1, T 40°C.

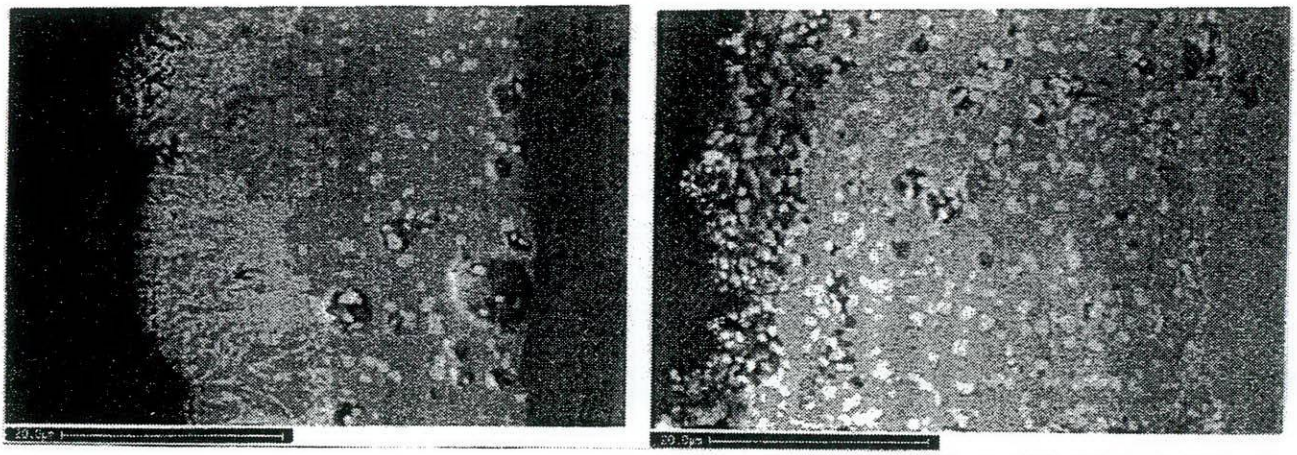

Fig.14 - Microstructure of cross-sections of deposits from a Sn- Bi plating bath: $Sn(CH_3SO_3)_2$ 0.3M with levelling additives, $BiCl_3$ 0.05M, DTPA 0.075M, pH<1; left, 25 mA/cm^2 40 °C Sn86%; right, 45 mA/cm^2 60 °C Sn 42%.

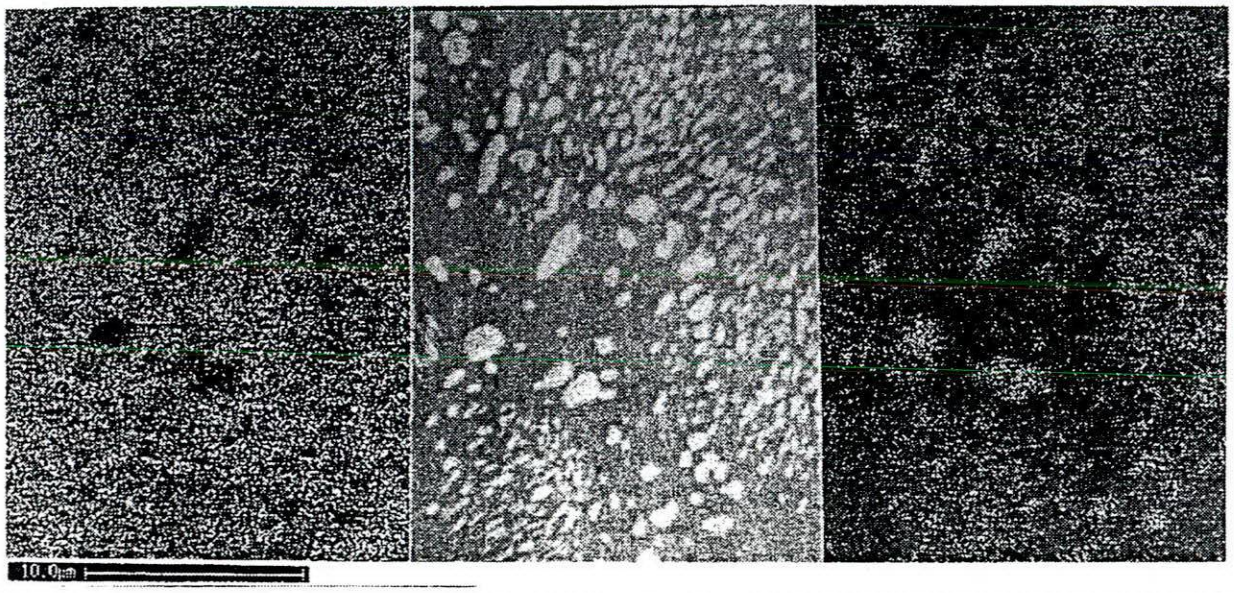

Fig.15 - Microstructure of the cross-section of a Sn-Bi coating from the bath: $Sn(CH_3SO_3)_2$ 0.3M with levelling additives, $BiCl_3$ 0.075M, DTPA 0.075M, pH<1, T 60°C, 45 mA/cm^2, after reflow in an industrial oven, N_2, 280°C.

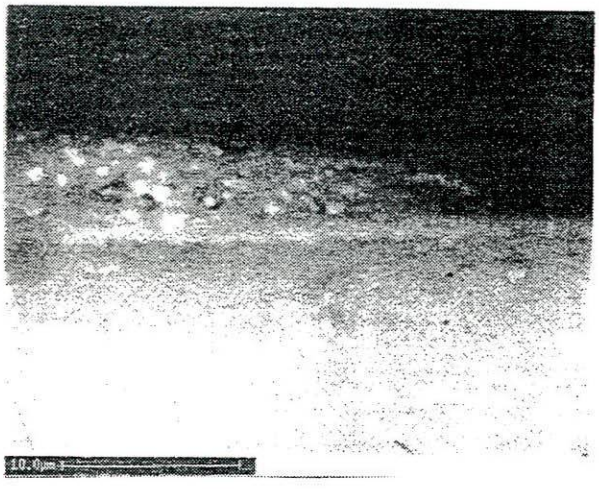

Fig.16 - Microstructure of the border cross-section of a Sn-Bi coating on a Cu sheet, obtained from the bath: $Sn(CH_3SO_3)_2$ 0.3M with levelling additives, $BiCl_3$ 0.075M, DTPA 0.075M, pH<1, T 40°C, 25 mA/cm^2, after reflow in an industrial oven, N_2, 280°C.

Discussion and conclusions

To understand the electrokinetic behaviour of Sn and Bi baths we can make reference to the normality-inertia parameter P_{ni}. We have already shown[17-19] that the electronegativity parameter must be modified, when the electrostatic potential plays an important role on the chemical reactions at the surface. For an ideal galvanic chain of the type:
- a semicell where the electrodic reaction occurs;
- an interliquid contact of negligible voltage;
- a reference semicell of constant voltage K_N (4.619 V for the standard hydrogen electrode);
- external contacts of same metallic conductor;

a Born-Haber cycle gives the standard emf E° from fundamental physical quantities, i.e. the enthalpy changes for atomization $\Delta h°_{at}$, ionization $\Delta h°_{ion}$, and ion solvation $\Delta h°_{sol}$:

$$E° = (\Delta h°_{at} + \Delta h°_{ion} + \Delta h°_{sol} + T\,\Delta s°_{cell})/zF + K_N \quad (1)$$

where z is the equivalence for the chain reaction, F the Faraday's constant, $\Delta s°_{cell}$ the standard entropy change for the cell reaction.

The electrokinetic behaviour in aqueous solution can be related to the relative importance of the different steps of the Born-Haber cycle, taking

into account the importance of the deionization step, from the solution to the atomic state, with respect to the crystallization step and the ionization step with respect to the same step for the reference H^+, obtaining:

$$P_{ni}=\frac{\Delta h^\circ_{at}+\Delta h^\circ_{ion}+\Delta h^\circ_{sol}}{\Delta h^\circ_{ion}+\Delta h^\circ_{sol}}\cdot\frac{\Delta h^\circ_{ion}}{\Delta h^\circ_{ionH}} \qquad (2)$$

P_{ni} values for elements of interest in the case of ECD alloy thin films are reported in table 1, together with the exchange cds for metal deposition and hydrogen reduction reactions.

Comparing P_{ni} with the Allred-Pauling electronegativity, cohesive energies at 0K, work function values, or Miedema's parameters Φ^* and $n_{WS}^{1/3}$, we observe that all these quantities roughly show a similar trend across the periodic table. However, the small changes in the periodic trend are of great importance in the relative electrokinetic behaviour of the elements.

Tin is a an electrochemically normal metal, as shown in table 1, with a low normality-inertia parameter: P_{NI}= 1.233. As a consequence the electrokinetic behaviour of tin is quite reversible with low overvoltages for metal exchange, whilst the hydrogen exchange at tin electrodes occurs with high overvoltages.

Additives with complexing function increase the cathodic voltage, increasing P_{Ni}; they modify the bath behaviour at current densities typical of electrodeposition, through adsorption and modification of the layer adjoining the surface. In the case of tin electrodeposition we have observed a strong influence of brightening additives, giving a minimum in the potentiodynamic curve, in agreement with published results[6].

Also the bismuth electrochemical behaviour is of the normal type with a normality-inertia parameter P_{NI}=1.421, as reported in table 1 and needs complexation. At high pH we have obtained bright mono-oriented deposits, of interest for tribological applications and as a sublayer.

The Sn-Bi alloy electrodeposition is normal from the stable bath that we have adopted, with bismuth more noble than tin and preferentially deposited at low cd. Sadana et al[6], on the other hand, reported that Sn was more noble, from a similar bath, but with higher DTPA content and with no additives. It seems possible to devise a bath with similar discharge voltage for the two metals.

Sadana et al[11] have observed an increase for the limiting solubility in the two phases present in the electrodeposit. In our case they seem very near to the metallurgical composition, that is the bismuth phase has a very low Sn content, while the tin phase contains a small quantity of Bi, as it is shown from the X-ray diffraction patterns. To establish the solubility limit these measurements are needed to ascertain the lattice parameters variation.

Bi-Sn coatings of near eutectic composition can be deposited even at high thickness from the bath we experimented with. Wettability of the copper substrate does not present problems, whilst the solder oxidation depends on a suitable choice of fluxes.

It is possible to increase the oxidation resistance and the mechanical properties of the coating, also in dependence on the working temperature. We have computed the free energy change as a function of the composition for addition of Sb and Ag to Sn and Bi. As shown in fig.17 Sb and Ag solutions with Sn show a strong negative free energy change, that promotes the formation of compounds in the solid state. As a consequence Ag, while decreasing the oxidation, can increase, with Sb, the fatigue and creep resistance of the solder alloy.

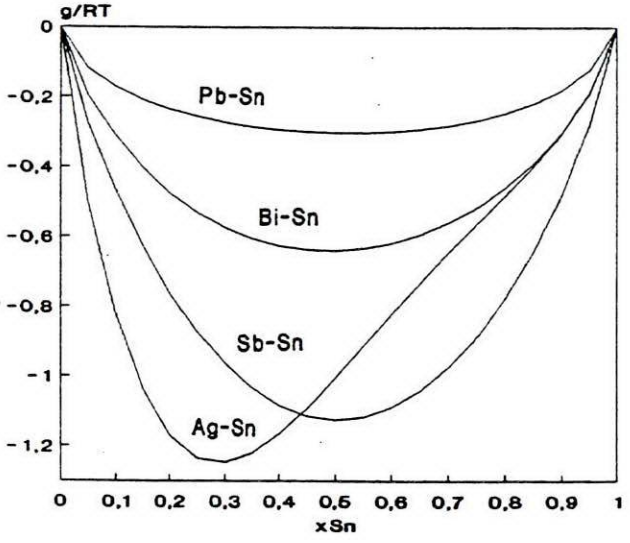

Fig.17 - Solution free energy change versus composition for liquid tin alloys of interest for solders, T=150 °C.

Table 1. Standard Electromotive Force E°, enthalpic contributions for Born-Haber cycle, Normality-Inertia parameter P_{ni}, exchange current densities for electrodic metal exchange and H^+ reduction of different elements.

COUPLE	E° V	$\Delta h°_{at}/zF$ V	$\Delta h°_{ion}/zF$ V	$\Delta h°_{sol}/zF$ V	P_{NI}	Log $i°_M$ A/cm^2	Log $i°_H$ A/cm^2
$H_2/2H^+$	0.000	2.259	+13.662	-11.307	1.960	--	--
NORMAL METALS							
Pb/Pb^{2+}	-0.126	1.016	+11.29	- 7.68	1.059	-1	-11.4
Cd/Cd^{2+}	-0.403	0.58	+13.01	- 9.36	1.104	-1.3	-11.6
Ag/Ag^{+}	0.800	2.951	+ 7.617	- 4.86	1.153	-1.7	-11.0
Zn/Zn^{2+}	-0.763	0.679	+13.74	-10.61	1.224	-1.85	-10.5
Sn/Sn^{2+}	-0.136	1.56	+11.046	- 8.05	1.233	-1.4	-10.0
INTERMEDIATE METALS							
Bi/Bi^{3+}	0.330	0.716	+16.578	-12.401	1.421	-1.85	-10.4
Sb/Sb^{3+}	0.152	0.906	+16.885	-13.054	1.529	-2.8	- 8.6
Cu/Cu^{2+}	0.337	1.752	+14.09	-10.89	1.587	-2.45	- 7.8
Pd/Pd^{2+}	0.987	1.96	+13.946	-10.52	1.605	-3.5	- 3.1
As/As^{3+}	0.248	1.045	+19.00	-14.579	1.720	--	- 7.3
INERT METALS							
Fe/Fe^{2+}	-0.440	2.157	+12.105	-10.127	1.854	-5.0	- 5.6
Co/Co^{2+}	-0.277	2.218	+12.551	-10.497	1.914	-5.3	- 5.3
Ni/Ni^{2+}	-0.250	2.203	+12.991	-10.911	1.958	-5.7	- 5.2
Pt/Pt^{2+}	1.20	2.929	+13.65	-10.875	2.053	--	- 3.0

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ALTERNATIVES TO NICKEL IN ELECTROPLATING PROCESSES

by

Dr. Franz Simon
Degussa Electroplating
Demetron GmbH
Klarenbergstrasse 53 - 79

D 73525 Schwaebisch Gmuend
Germany

1. Introduction

2. Function of nickel in electroplating processes
   - as intermediate layer,
   - as alloy partner in gold deposits

3. Possibilities to replace nickel as intermediate layer by bronzes or by palladium
   3.1. Application of bronzes as substitutes for nickel intermediate layers
   3.2. Application of palladium as a substitute for nickel intermediate layers

4. Nickel-free gold processes
   4.1. General remarks
   4.2. Gold/iron
   4.3. Gilding baths

5. Summary

1. Introduction

Nickel is widely used in electroplating processes for surface treatment. Typical applications are as intermediate layer or as partner for alloy depositions.

Some positive properties of nickel are the levelling power and the brightening capacity. By this very often polishing work can be reduced by applying nickel intermediate layers. Besides this, nickel plating is comparatively cheap.

Negative properties of nickel are the allergenic character and the carcinogenity of specific compounds. Nickel compounds can cause cancer in form of dusts or in form of aerosols in the electroplating industry.

The allergenic character of nickel has been discussed in the recent years with increasing intensity. Nickel allergy is certainly a serious problem nowadays and not only an insignificant skin irritation. People who suffer from nickel allergy can be considered to be ill. The part of people being allergic to nickel can be considered 10 % of all women and 1 % of all men of the western hemisphere. The main reason for this appearance is the ear-piercing especially of girls in early childhood to be able to wear earrings. By ear-piercing and avoiding of healing of the wound a pole is being brought into the wound to keep the channel open. In the past very often or mostly nickel-containing material was used for this purpose. By this a sensitization against nickel occurred. This is the main reason for later nickel allergy, especially for women who normally wear earrings. The allergies correlated to men are mostly caused by conditions of work (professional disease).

Nickel allergy is developed in two steps. First by a sensitization phase (ear-piercing), and secondly by the acute phase, the so-called allergy or disease. This later stage is caused by contact of nickel-containing material with human skin (costume jewellery).

We are surrounded by nickel-containing materials in form of metallurgically produced alloys, in form of many parts in our everyday life like cutlery, cooking pots, pans, protheses, watchbands, eyeglasses, coins, and containers of many kinds.

Nickel as an electroplated intermediate layer or as an alloying material in electroplated deposits we meet in various kinds of articles around us like watchbands, watchcases, costume jewellery, chains, eyeglass frames, buttons, writing utensils, scissors, and so forth. As nickel is defined as a serious allergen which causes the nickel allergy, nickel should only be used in applications where it is necessary and tolerable. This is mainly in the technical field. In other areas, especially in the decorative sector, nickel should be either avoided or replaced.

2. Function of nickel in electroplating processes and electroplated applications.

One of the main reasons for the usage of nickel is its capacity of levelling and brightening. By this, inferior substrate quality can be improved without costly polishing work. So nickel has been used to improve the quality of silver surfaces or white gold surfaces as well as the surface quality of all substrates which are further to be plated with subsequent processes. Furthermore nickel is a diffusion barrier against components from the substrate, especially copper-based alloys. If nickel would not be used, the substrate material might diffuse into the final top layer, for example gold, which can cause tarnishing and deterioration of quality. In the opposite direction a nickel underlayer under gold avoids diffusion of gold into the substrate, avoids vanishing of the gold by diffusion into the substrate. By this even thin gold deposits on a cheap substrate can perform in a reasonable way. Additionally an intermediate layer of nickel is a corrosion protection for a base material during plating generally, especially in aggressive baths, and, last but not least, nickel intermediate layers improve the corrosion properties of a substrate in practical use.

Nickel is used as an alloy partner in electroplating processes. This paper concentrates on gold alloys where nickel as an alloy partner is used to increase hardness, to reduce abrasive wear, and to improve brightness. Besides this nickel is a very important colour-determining component for gold alloys. So many greyish or reddish-grey gold alloy deposits could until now only be achieved at a reasonable price with nickel as co-deposited partner.

Any potential alternative to nickel has to comply with theses demands either for intermediate layers or gold alloy processes.

3. Possibilities to replace nickel as intermediate layer by bronzes or by palladium.

3.1. Application of bronzes as substitutes for nickel intermediate layers.

There are different potential alternatives to nickel as intermediate layers like bronzes, palladium, or cobalt. This paper deals with bronzes and palladium as possible alternatives, not with cobalt. The reason for excluding cobalt is the fact that cobalt to some extent has been under discussion to be classified as an allergen or carcinogenic likewise as nickel. In the recent past, cobalt has been rehabilitated to some extent. For intermediate layers bronzes are very apt systems to replace nickel. There are processes available to deposit white or yellow bronzes. White bronzes are hard and tarnish-resistant whereas yellow bronzes are also hard but of inferior corrosion resistance compared to white bronzes.

The systems under investigation are based on hydroxide and cyanide using copper cyanides and stannates. Complexing agents, buffers, brighteners, and levellers were used to develop proprietary processes to achieve reproducible, reliable results. Nowadays processes to deposit white or yellow layers are available for decorative as well as technical applications. Modifications were created for rack and barrel plating correspondingly. White bronzes are very corrosion resistant, for example in the salt spray test according to DIN SS 50021, in the Kesternich test (DIN 50017), in the artificial sweat or in the thioacetamide test. Yellow bronzes based on copper/tin or copper/tin/zinc are - because of their high copper content - not so resistant against corrosive attack, but on the other hand yellow bronzes have levelling power and a brightening effect so that they can improve the substrate quality significantly. A combination of yellow bronze with a top layer of white bronze can be considered a full replacement of bright nickel of the same layer thickness.

The hardness of bronzes is high, with 400 to 550 HV it is significantly higher than electroplated bright nickel with only 300 HV.

The diffusion properties of white bronzes were tested depending on temperature and time. If the temperatures do not exceed 80 °C, a diffusion of the constituents of the bronze does not diffuse into the lop layer of gold causing tarnishing or deterioration of the gold top layer quality. Only at temperatures above 165 °C a significant diffusion takes place. This leads to the conclusion that for decorative applications where such temperatures are not applied or do not occur bronzes are a sufficient diffusion protection layer for a final top layer of precious metal like gold. For technical applications where higher temperatures might occur or severe tests are being applied bronzes certainly are not a replacement. Here nickel or palladium certainly will have their justification to be used.

As to the levelling capability and brightness-forming properties of bronzes, one can consider ten microns of a combination of yellow and white bronze to be equivalent to the same thickness of bright nickel.

Also thickness distributions of bronzes are better than for bright nickel. Bronzes exhibit a better throwing power than nickel resulting in a better, more even thickness distribution.

The advantageous properties of bronzes allow their application in various fields and not only there where skin compatibility is required to avoid allergies. Such applications are for example where solderability, hardness, corrosion resistance, brightening properties, thickness distribution, wear resistance, or the diamagnetic properties of the bronzes contrary to nickel are needed.

So a big field of application for bronzes are costume jewellery like chains, buttons, haberdashery, buckles, trouser clips, zip strippers, and also parts for the high-frequency technology (diamagnetic not paramagnetic properties).

An additional field of application is using the bactericide property of bronze alloys. Bronzes kill bacteria very quickly as copper itself, and better compared to silver. Investigations were made with staphylococcus aureus, staphylococcus epidermidis, and enterococcus. After a short period of time the bacteria were so strongly diminished that one can speak of a bactericide character of this alloy. So there is use for bronzes to plate door handles and bathroom fittings, especially in places like hospitals. The use of bronzes for such an application is superior to the application of copper or silver because bronzes do not tarnish.

3.2. Application of palladium as a substitute for nickel intermediate layers.

Palladium can be considered a substitute for nickel as an intermediate layer to avoid nickel allergy. Besides this palladium is being discussed to be a replacement for gold because of cost reasons.

In the recent past there have been some discussions about the so-called palladium allergy. According to the information available, a palladium allergy does not seem to exist. There might be a skin irritation especially being reported from the dental area. It is not proven that it is a real allergy. The reported skin irritations are not comparable to a real allergy like the nickel allergy. The way of sensitization via the skin is not known, it is only correlated to the oral area. These facts allow the usage of palladium for applications which are determined for costume jewellery and utensils for everyday use.

It is the target of this presentation to inform about a new palladium plating bath which allows very ductile deposits, crack-free bendable around a diameter of 20 mm. A subsequent corrosion test (Cass test) yields a good result even after 70 hours exposure time. This new system is based on palladium chloride as a palladium salt and specifically developed proprietary additives. The deposits are of 99.9 % purity, they are bright and brilliant. The maximum available thickness is 10 microns with a hardness of 250 HV. Those layers are already being used as an underlayer under gold for decorative applications like eyeglass frames, watches, and jewellery. As a diffusion barrier under a final gold top layer 0.3 to 0.7 microns of palladium seem to be sufficient.

The electrolyte works with a palladium content of 8 to 12 g per litre at room temperature with a pH of 8.9.

At 1 A/dm² a deposition speed of 0.3 microns per minute is achieved.

Rack and barrel applications are possible likewise. To avoid contamination of the electrolyte, a preceding gold flash or palladium flash are recommended before the main palladium layer is deposited. The well-known sensitivity of all palladium baths versus silver, copper, zinc, and cyanide should be observed to guarantee a long lifetime. To show the superiority of the new system with regard to bendability and corrosion properties, a comparison has been made with deposits plated from three different systems:

Deposits were plated from an acid palladium sulphate based bath, second from a slightly alkaline palladium salt based electrolyte, and third from the new palladium chloride based bath were compared. The result is that the bath based on palladium chloride with the newly developed additives shows superior test results with no crack formation and no corrosion in the Cass test even after 70 hours exposure time.

Palladium functions as a diffusion barrier as good as nickel. This is well known and does not need further explanation in this paper.

Finally in this chapter there should be made an attempt to compare the replacability of nickel by bronzes or palladium. This attempt can only be incomplete and certainly leaves a lot of questions open, but to make basic tendencies clear such an abstraction should be allowed:

With regard to hardness, colour, corrosion protection, solderability, further platability, and wear resistance, nickel, bronzes, and also palladium are definitely comparable. With regard to levelling and brightening properties, nickel and bronzes, especially the combination of yellow and white bronzes, are comparable and both superior to palladium because palladium usually has not a significant levelling and brightening power but reproduces the quality of the substrate. As to diffusion properties, nickel and palladium are equal; the usage of bronzes for diffusion barriers is limited to decorative applications and to some technical applications, but not in the broad range as nickel can be applied. As to ductility, bright nickel is certainly the most brittle compared to the other two. Yellow bronze can be pretty ductile whereas white bronze is pretty brittle, too. Palladium in this context from the new system with the newly developed additives shows a very high ductility. With regard to cost, palladium is by far the most expensive, so that for many applications the bronzes are the real replacement and the costwise acceptable alternative to nickel. Palladium by itself has its importance especially in the eyeglass frame industry, but here it is not so much a replacement for a nickel underlayer but more a corrosion-resistant noble metal intermediate layer before the final gold plating.

4. Nickel-free gold processes.

4.1. General remarks.

Nickel-containing gold alloy deposits being used till today contain between 0.05 to 4 weight percent of nickel in the deposit. They are being used for technical and preferably decorative applications. Alloys to be mentioned are gold/nickel or gold/nickel/indium, or systems for gilding based on gold/copper/silver/nickel, gold/copper/cadmium/nickel, or gold/copper/nickel.

Because the decorative application of such deposits is the area of major use, nickel as an alloy partner must be avoided, but limiting conditions like identical colour and deposit properties like wear, tarnish, and corrosion resistance should be observed.

For many years nickel-free gold-depositing processes have been available, for example gold/indium, gold/tin, gold/silver, gold/copper/silver, gold/palladium, and gold/copper/palladium, as well as gold/cobalt. But these deposits sometimes have a different colour or different deposit properties so that one cannot generally speak of an identical replacement for nickel-containing deposits.

This paper deals with systems based on gold/iron, where iron is the replacing component for nickel. And these gold/iron systems are compared with the very well-known and widely applied gold/nickel/indium deposits which are applied for decorative use in costume jewellery and for bathroom fittings, etc.

Gold/nickel/indium baths and deposits are systems widely used and highly appreciated because a wide range of colour shades is possible (including 1N and 2N colours according to standard DIN EN 28654). The wear resistance and corrosion resistance as well as the tarnish resistance are excellent. The wear resistance for gold/nickel /indium is superior to that of conventional gold/nickel and gold/cobalt baths. So a substitute has to be compared with the standard set by gold/nickel/indium plating systems.

4.2. Gold/iron

The target to be reached has been accomplished by the development of new gold/iron systems depositing 1.7 respectively 1.4 % of iron in the gold lattice. The caratage is therefore in the range of 23.5 carats. The hardness of 220 HV is high. The tarnish resistance is good. The colours achieved are 1N respectively 2N.

It should be mentioned that the operating range with regard to applicable current density, pH, and temperature is extraordinarily large, resulting in the same colour over the whole range of parameters.

The question arose how iron is co-deposited in the gold lattice. The question is if iron is co-deposited homogeneously or heterogeneously because 1.4 respectively 1.7 % are comparatively high to that what we know from conventional systems with a co-deposited amount of iron of maximally 0.3 %.

Magnetic susceptibility measurements on conventional gold/iron layers with maximally 0.3 weight percent of iron showed that the ferromagnetic part of the susceptibility is nearly negligible and the paramagnetic amount is low corresponding to the low amount of iron. So one can say that the low co-deposited amount of iron is diluted in the gold lattice homogeneously. As to the newly developed systems with high iron amounts of 1.4 to 1.7 weight percent co-deposited, the values for the ferromagnetic part of the susceptibility is significant as well as the paramagnetic amount. Concluding from the ferromagnetic part of the susceptibility, one can calculate a proportion of mass of magnetizable iron, which are absolutely 13 respectively 14 ppm of iron. This means that only one thousandth part of the total co-deposited iron is present in a heterogeneous stage. This is absolutely very little.

X-ray emission spectroscopy resulted in a homogeneous distribution of iron and gold in the layer. There are no indications that there are heterogeneous agglomerations of iron.

Also the roentgen contrast pictures show a uniform greyish appearance. If iron would have been deposited heterogeneously there would be spots visible of lighter colour indicating an element of lower ordinal number compared to gold. This is not the case.

Also the determination of the lattice constant of the gold/iron lattice did not lead to conclusive results: there was only found one lattice constant for deposits with 1.7, 1.4, respectively 0.3 weight percent of iron, by diffractometry diagrams. So elementary iron could not be determined. But one should take into consideration that reflexes for gold and iron to some extent appear at the same angles so that this method does not lead to totally conclusive results.

Because of this fact more importance had to be given to definite corrosion and wear test results, because these properties are finally important for practical use.

Deposits with 1.7, 1.4, respectively 0.3 weight percent of iron were compared with gold/nickel/indium deposits with 2.3 respectively 0.8 weight percent of nickel. All test results were compared with each other. The tests applied were salt spray test, ammonia vapour test, nitric acid vapour test, thioacetamide test, and artificial sweat test. The results were the following: Gold/iron deposits with different amounts of iron co-deposited in every case were at least equal to gold/nickel/indium layers. In the case of the ammonia vapour test gold/iron deposits were even superior to gold/nickel/indium layers. In all cases there was no attack and no tarnishing in the thioacetamide and artificial sweat test.

As to wear test results, gold/nickel/indium - the target to reach - exhibit a wear rate of about 2.5 - 4 mg/(cm^2 x 1000 strokes) according to the Erichsen test. The wear rate of gold/iron deposits is in the same range of order which means between 4 and 4.5 mg / (cm^2 x 1000 strokes). If we compare conventional gold/nickel and gold/cobalt baths, these baths exhibit a slightly higher wear rate. Concluding from this one can say that gold/iron are in the same range of order of wear properties.

4.3. Gilding baths

Conventional colour gilding baths contain nickel as hardening agent and /or as alloying partner. With nickel as additive a quite interesting range of colour shades can be achieved. Conventional gilding baths contain about one gram per litre of gold and 1 to 2 g per litre of potassium cyanide. Alloying metals are silver, copper, cadmium, nickel, and iron, or combinations of those. As to layer properties by the co-deposition of this variety of alloying elements about fifty different colour shades can be achieved with a caratage of equal or higher than 20 carats. The thickness which is reachable is limited to 0.2 µm. The tarnish resistance and the equality of colour is very good. And this fact is the reason why colour gilding baths are plated as a top layer on decorative pieces to guarantee the uniform colour over the whole piece, independently of areas with high or low current densities. Newly developed systems avoid nickel using instead iron for the same function as nickel was used before.

So in the colour range of 0N, 1N, 2N, 3 and 4N, and in the range of the pure gold colour new systems which are totally nickel-free are available. The compromises with regard to colour are negligible. The caratages which are achieved with the new systems are very high, i.e. 20.8 to 23.8 carats. The alloys deposited are based on gold/silver/copper or gold/silver/copper/cadmium.

5. Summary and conclusions.

Nickel in electroplating processes can be replaced for the deposition of intermediate layers and for final gold alloy layers.

As to intermediate layers, bronzes or palladium can be applied with good results. Bronzes are costwise competitive to nickel whereas palladium can be used at the upper end of the cost range. Newly developed systems to plate white and yellow bronze and a very ductile palladium have been presented.

As to gold alloy deposits, the nickel can be replaced by iron. Iron is physiologically unproblematic and does not cause any allergies. New plating baths using iron as an alloying partner have been developed with properties which are at least as good as those from gold/nickel or gold/nickel/indium systems.

Nickel allows a lot of colour shades desired by the industry. Therefore a lot of development work will be necessary to replace nickel more and more.

If nickel has to be avoided totally, the range of colour shades will certainly shrink, and this will demand more flexibility from the applier of colour golds with regard to colour wishes.

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ALTERNATIVES TO CADMIUM

DAVID R. GABE

IPTME, Loughborough University of Technology
LE11 3TU, UK

SYNOPSIS

Is an alternative needed for Cadmium or is it an alternative to cadmium processing that is required? Objections usually cited include

- Toxicity
- Product hazard
- Poor processing
- Poor process effluent control

If the response is positive, is there a single alternative or are there a number of alternatives required?

These and other related questions are addressed in the quest for viable alternatives.

INTRODUCTION

The toxicity of cadmium is well-known, as is the toxicity of hexavalent chromium, although such toxicity is no worse than that of a number of other metals which are relatively widely used, e.g. lead, mercury. The consequence is that the uses of cadmium have been under review recently, applications have been analysed and challenged and alternatives examined for viability and credibility. It is often believed that this need is attributable to political and ecological pressures but in fact its shortcomings have been a matter of concern for thirty years although the appraisal of alternatives for cadmium was formerly more novel than it is today. Thus a widely read review of that time rehearsed relatively new arrangements[1]; such arguments have been deployed at regularly decreasing intervals[2-11] until the periodicity has now reached a few months in length! Within the last two years the present author has considered the issues twice[12,13] albeit from differing viewpoints, but the arguments remain essentially the same.

The facts about cadmium can be summed up in two tables: Table I gives the main properties and Table II the main applications related to specific characteristics. In volume of usage terms five main categories can be identified.

Batteries	~ 3000 tons p.a.	rising
Pigments	~ 1800	rising
Electroplating	~ 1800	falling
Stabilisers	~ 1000	falling
Alloys	~ 400	falling

In objective terms the battery and pigment categories should be of much greater concern than the metal finishing sector and the reasons may be worth considering, e.g. the public demand for rechargeable batteries when the obvious alternative could involve mercury!, while cadmium electroplate is not considered vital by the general public. Another view is that battery pollution is in principle adequately contained by the recycling trade while the electroplating trade considers its conscience at 0.07 - 0.7 ppm in effluent or whatever the prevailing limit is deemed to be.

In this paper we shall consider only electroplating trade aspects and shall consider the technical problems arising. The toxicity is not disputed although as has been pointed out [12] maximum intakes of 200-2000 µg/day have been set while normal dietary intakes of 12-50µg/day are usual; no well-defined examples of this gap being breached, or instances of food being contaminated, have been recorded. Similarly the product itself has not been cited as a hazard largely because electroplated cadmium has long been eliminated from the domestic scene and has never been used in the food or canning industry where tin reigns supreme as an electroplated metal. (If the analysis concerned pigments the story is quite different because the yellow cadmium pigment is a fairly recent dominating outlet). Thus the fact that cadmium may corrode and thereby pollute the environment is a relatively trivial issue compared with process effluent leakage or misdirection. This paper therefore concentrates on the fact that cadmium may be used in a few essential applications which cannot be easily

substituted and that some process effluent necessarily arises. The corollary is worth noting: if cadmium effluent treatment had been perfected twenty years ago the move to eliminate cadmium might have been challenged earlier to the industry's and nation's satisfaction.

PRODUCT OPTIONS

A perusal of Table II clearly reveals the dilemma of cadmium. Its attractive properties encompass a number of widely differing characteristics - protectiveness and low melting point, lubricity and electrochemistry. Thus it is highly unlikely that a single or even two or three alternatives will be readily available to the engineer, and any additional consideration of the thicknesses of coating proposed by say ASTM A165

3.9 μm minimum	Indoor, mild corrosion
7.5 μm	Outdoor, moderate corrosion
13 μm	Outdoor, marine corrosion

is likely to lead to confusion as it may be substantially influenced by other considerations such as cost, or screw thread tolerance factors.

The corrosion resistance of bulk cadmium is not particularly good so many of the applications are related to the protection of steel under conditions where its potential is protective or sacrificial. [Note that the thermodynamic reduction potentials are not favourable to sacrificial behaviour

$$E^{\theta}\ (Cd^{2+}/Cd) = -0.403V; \quad E^{\theta}\ (Fe^{2+}/Fe) = -0.44V$$

but that in the presence of chlorides cadmium is sacrificial but in the presence of sulphate and bicarbonate is not. If it is well-passivated it is even less sacrificial but has intrinsically improved corrosion resistance and is effective as a pore-free thicker coating].

The main property requirements can be summarised as follows

Good corrosion protection
Good lubricity
Low volume corrosion product
Compatibility with aluminium
Good solderability

The list of alternatives as electrodeposited coatings can be given as follows

Zinc	plain or passivated
Zinc-tin (80%Sn)	"
Zinc-nickel (10-15%Ni)	"
Zinc-cobalt (0.3-1.0%Co)	"
Zinc-iron (20-80%Fe)	"
Zinc-manganese (40-60%Mn)	"
Tin	"

A number of general rules can be offered and these are given in Table III. This could be a dangerous approach, however, because it is rare that a substitution situation can be reduced to "rules of thumb"; nevertheless, they can be considered as useful guidelines. For more detailed information the reader should refer to the listed references which give tables and graphs of data.

The inevitable conclusion is that 95% of cadmium usages are replaceable by equivalents and the residual 5% may well be retained for prejudicial reasons especially historical necessities originating in Defence and Military specifications.

PROCESS CONTROL

The electroplating process for cadmium suffers from two separate toxicity hazards: the cyanide amion is a well-known toxic complexant while the cation itself cadmium is the subject of this discussion. However, there ought to be a lesson to be learned from this juxtaposition because cyanide is now subject to very efficient treatment so that its use can be accepted for a number of metals - copper, gold, silver, zinc etc. No real alternatives to cyanide are known and it remains as an extremely versatile complexant stable in alkaline solutions giving good 'strike' deposition characteristics with an electroplating process that is good and flexible. But the toxicity is well-known and has long been respected but more particularly has caused efficient effluent processing to have been established. (Once understood, the oxidation of cyanide to harmless species can easily be achieved

e.g.	CN^-	$\rightarrow$	CO_3^{2-}	$+N_2$
	cyanide		carbonate	nitrogen

by a number of oxidising agents - chlorine, hypochorite, anodic oxidation etc. - and the use of cyanide therefore is readily accepted).

This is probably the crux of the problem with cadmium. A number of treatments are feasible but until recently have not been carried out efficiently.

Precipitation
Ion exchange
Electrolytic recovery

Consequently, the acceptable limits have been lowered to create greater incentive and have now verged on the unrealistic. More than one electroplater can therefore make a legitimate claim that his effluent is purer than his main water feed!

The optimisation of any process is vital to its efficient operation and this may involve

Selecting the correct plant
Investigating the process parameters
Designing the plant size to encompass the range of optimal performance
Establish the optimal parameter values and create and maintain 'standard practice'.

In the case of electrolytic recovery such an approach has been demonstrated for cadmium using a rotating cylinder cell[14] and although it was aimed primarily at the primary metal extractive industry the principles hold good for effluent recovery. Other analogous studies have been reported for cadmium using other cell designs[15-17]. As the industry holds relatively little interest in exploiting this technology and steadfastly insists on retaining precipitation techniques followed by mixer-settling and filtration or sedimentation, a few comments on the chemistry of precipitation are appropriate. Cadmium is one of those metals which have insoluble hydroxides and this provides the traditional key which is turned by the use of a cheap alkali precipitant - lime. However, lime is neither very soluble nor very alkali having a pH at saturation of about 9.5. Fortuitously this is an effective and near optimal pH to precipitate several metals (copper, nickel, chromium) as shown in Fig. 1. However, cadmium is still quite soluble at pH 9.5 typically to 100 ppm and is only optimally precipitated to 0.01ppm at pH = 11.5. Such a pH usually requires a combination of soda ash and caustic soda with good control otherwise an excess pH may be achieved at which re-solubilization of the precipitate can occur. Thus the critical requirements are the use of a strong alkali plus close pH control. Enhanced precipitation can be promoted using flocculating agents but these primarily act as coagulating agents for fine colloidal precipitates and thereby produce physically coarse easily separated solid particles and do not create the required chemical conditions as pH modifiers.

It can thus be seen that a well-controlled precipitation plant should achieve a residual cadmium content of 0.01ppm and which if followed by an ion exchange 'polishing' unit would meet all requirements. Alternative more effective precipitation agents do exist, one well-known one being sulphide. As shown in Fig. 2 precipitation of cadmium sulphide at pH = 9.5 gives a residual metal level of 10^{-5}ppm (or 0.01ppb). However, the toxicity problem now becomes one of residual sulphur not cadmium! An alternative might be dimethyl dithiocarbamate although it is probably little used at present.

CONCLUSIONS

Thus the technology exists to obtain effluent containing very low residual cadmium. The disinclination to use it effectively in the past, however, has created an aura of technological inability although in reality it is disinclination.

In the USA drive has been provided by the EPA and litigation opportunities. In Europe the legal framework exists, both nationally and in the EC, and a philosophy of environmental consciousness is incorporated in the Treaty of Maastricht. The USA having set a clear lead the target and direction is not in doubt. The rate at which eco-technology is demanded and installed varies from country to country tempered by local political considerations. The metal finishing industry is now, as a result of having buried its head in the sand for many years, in a defensive position. To maintain its product and process technology it needs to do two things rapidly.

1. Install eco-technology and operate it effectively to demonstrate the industry's ability to meet legal frameworks thereby creating a reputation of effective environmental protection. An obvious example is to exploit known practised technology in its most effective way. Fig. 3 illustrates how precipitation or electrorecovery are most effectively used at high residual metal levels, typically >20ppm; although both can be used down to <1ppm the time and effort required can be counter-productive. Similarly ion exchange used at high residual metal levels is effective at removal but because it has to be eluted so frequently is inefficient in overall processing terms; it is much more effective on this basis as a polishing unit, to remove <10% of the overall metal loading but down to <1ppm residual metal in solution.

2. To make clear to the public how reliant they are on surface finishing that the domestic hazard is trivial and that the industrial hazard can be efficiently contained. Such public relations exercises so far have been relatively ineffective.

Such action obviously relates to cadmium but equally applies to a number of other metals.

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APPENDIX(18)

E.C. Regulations for Cadmium Coating Usage

The European Community has adopted a Directive on the use of cadmium coatings which will harmonise restrictions on their use within EC Member States. The Directive does not ban their use but simply restricts their use where they are not seen to be essential.

The considerable advantages of cadmium coatings in a variety of applications have been recognised by the regulators.

The provisions are summarised below.

From 31 December 1992 Cadmium coatings may not be used in:

Equipment and machinery for food production, agriculture, cooling and freezing, printing and book binding. Equipment and machinery for production of household goods furniture, sanitary ware and central heating and air conditioning plant.

Household goods, furniture, sanitary ware, central heating and air conditioning plant.

From 30 June 1995 Cadmium coatings may not be used in:

Equipment and machinery for the production of paper and board, textiles and clothing, industrial handling equipment and machinery, road and agricultural vehicles, rolling stock, vessels.

Industrial handling equipment and machinery, road and agricultural vehicles, rolling stock, vessels.

Products and components in the following industrial sectors are NOT the subject of any restriction

Aeronautics and Aerospace
Mining
Offshore and Nuclear engineering
Safety devices
Electrical contacts

TABLE I: PROPERTIES OF CADMIUM

Atomic Number	48
Atomic Weight	112.4
Valency	2
Density	8.65 g/cc
Melting point	320.9°C
Boiling point	765°C
Crystal structure	c.p. hex
Lattice parameter	2.979°A
Reduction potential	-0.403V
Brinell Hardness	21-23 Kg/mm^2
Ductility/elongation	50%
Toxicity	dissolved Cd^{2+} ions
	vapour Cd metal

TABLE II: APPLICATIONS FOR CADMIUM

Decorative:	lustrous white metal
Protective:	sacrificial in marine and humid environments
Coating:	electrodeposition well-established
Soft lubricity:	bearing alloy (Cd-Pb; Cd-Ag or Cd-Cu-Ag)
	threaded component surface
Low m.p.	Solderable coating
	Solder alloy joining ferrous to
	non-ferrous metal
Batteries	Ni-Cd rechargeable cells
Amalgams	amalgamates with Hg
Pigments	Yellow CdS
	Red Cd-Se-S
Polymer Additive	Stabiliser

TABLE III: GUIDELINES FOR CADMIUM SUBSTITUTION

1. In rural environments cadmium and zinc can offer similar protection although zinc is usually superior.
2. In industrial atmospheres zinc is superior.
3. In marine atmospheres zinc and cadmium but in contact with sea water and salt spray cadmium is superior.
4. In sea water or salt spray cadmium should be replaced by zinc of 50% greater thickness.
5. Zinc is substantially cheaper than cadmium and the electrodeposition costs are similar.
6. For screw thread lubricity cadmium is superior. For screw thread tolerance and protection diffusion-coated zinc or 'sherardizing' should be considered.
7. For screw threaded matings, zinc electro plated bolts may be used with cadmium plated nuts. If both nuts and bolts are to be zinc electroplated the nuts should be tapped after plating on order to minimize risk of seizure.
8. Zinc alloy coatings can give better corrosion resistance than plain zinc, consequently thinner coatings can be employed to give equivalent protection.
9. Passivation treatments can improve service life by several orders of magnitude and should always be employed, unless there are compelling reasons against.
10. If solderability is required, tin rich alloys must be used.
11. Use of zinc in place of cadmium may enable other coating techniques to be employed (e.g. spraying, hot dipping, peen plating) and in electroplating the risk of hydrogen embrittlement is substantially reduced.
12. If it is essential to employ cadmium electrodeposition the effluent treatment process must be optimised to maximize recovery of cadmium metal and minimise residual dissolved cadmium in discharge liquor.

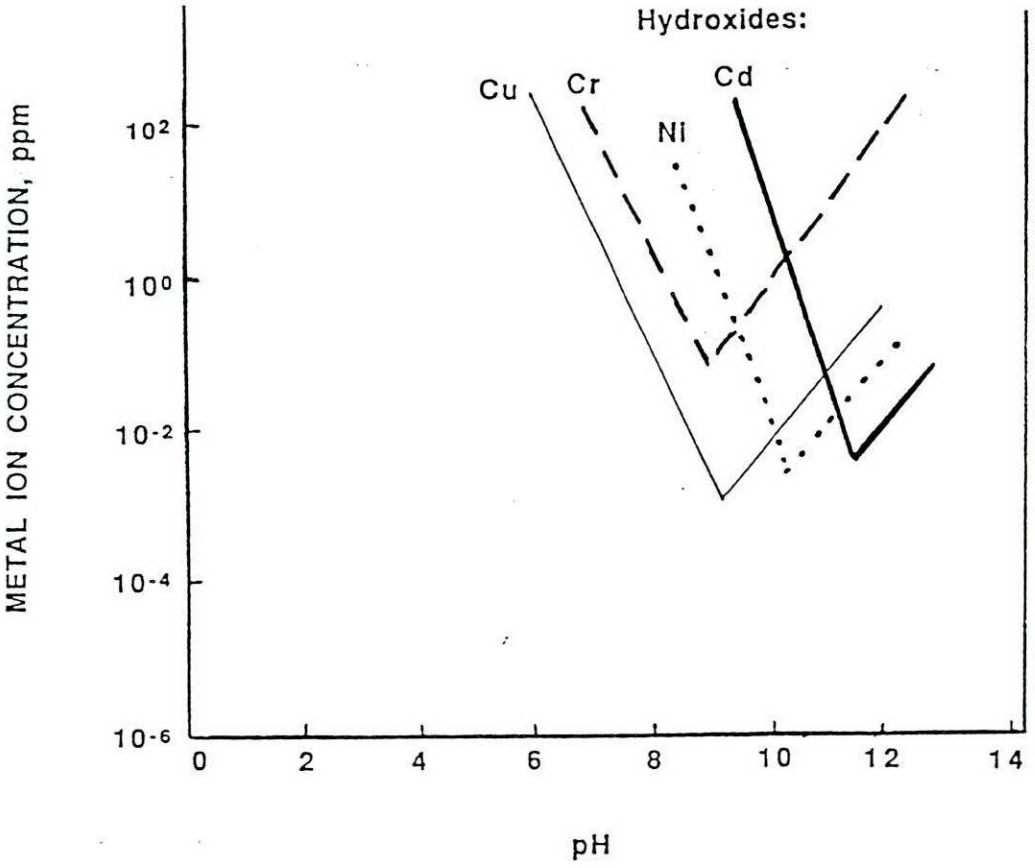


FIGURE 1. Hydroxide precipitation for four metals (copper, nickel, chromium, cadmium).

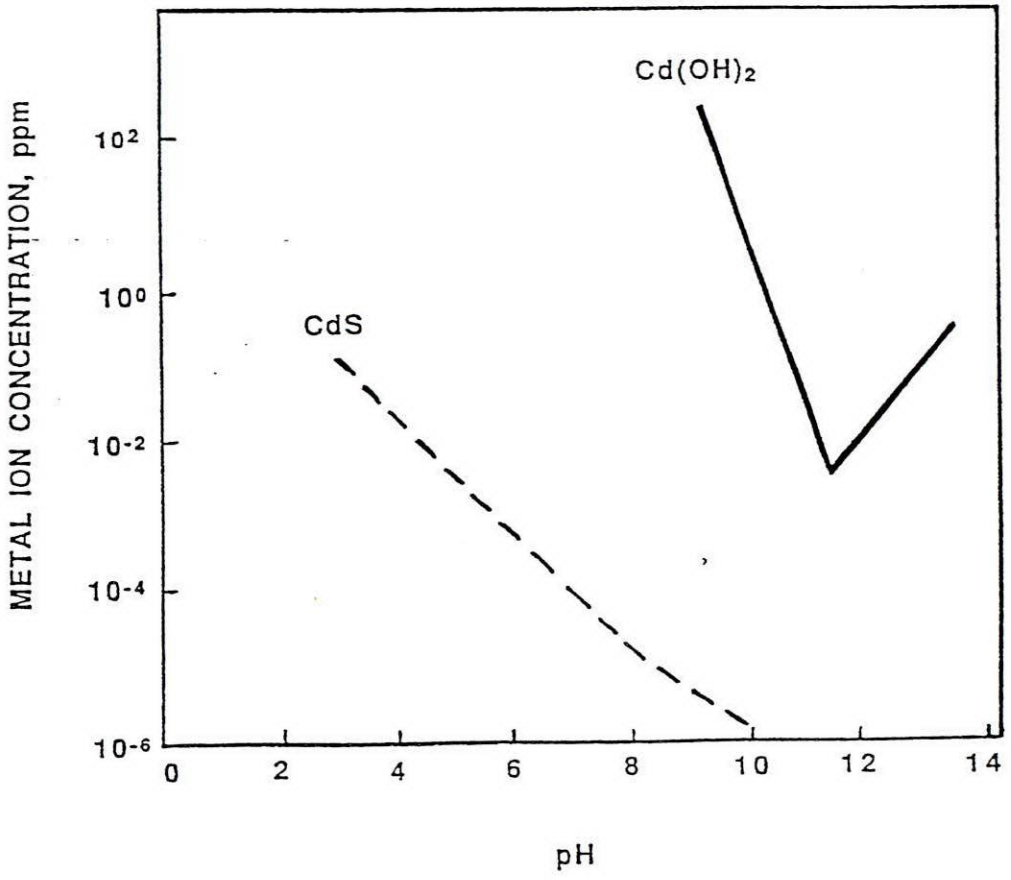


FIGURE 2. Precipitation of cadmium as hydroxide and sulphide.

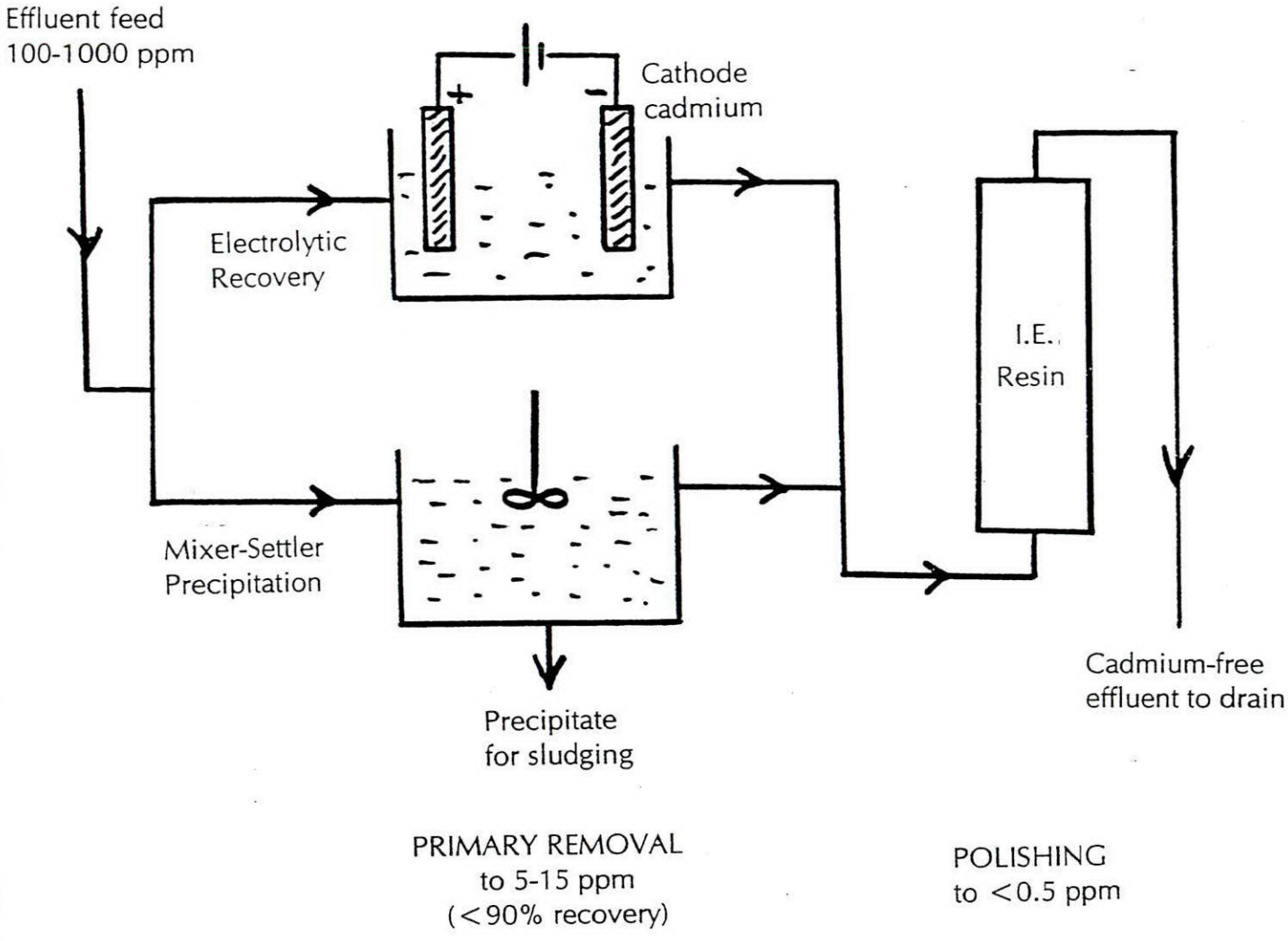


FIGURE 3. Process sequences for treatment of cadmium-containing effluent

Molybdate Based Alternatives to Chromating as a Passivation Treatment for Zinc

PETER T. TANG, GREGERS BECH-NIELSEN AND PER MØLLER
Centre of Advanced Electroplating (CAG)
The Technical University of Denmark, building 425
2800 Lyngby, Denmark

Abstract

In order to slow down corrosion, zinc plated parts are usually passivated with chromate based solutions. Recently chromates have caused increasingly environmental concern, for both allergic effects among persons touching chromated parts and toxic effects on fish, plants, bacteria etc.

A molybdate based alternative has been developed to replace chromates in several or all passivation treatments. Depending on the environment in which the passivated parts are to be exposed, the alternative treatment is sometimes more efficient, and in some cases less efficient, than chromate based conversion coatings.

These aspects as well as issues such as: cost, stability, chemistry, layer composition and numerous test results from several corrosion tests will be discussed.

Introduction

Chromated zinc parts are widely used in various industries such as the automotive and aerospace industry (fasteners, coil coating etc.), the electronics industry (frames, cabinets, fasteners etc.) and many others.

The treatment used to protect these parts, often referred to as a passivation process (or a surface conversion coating), creates a thin protective film on the zinc plated steel part. This film, especially when formed by yellow chromating, contains significant amounts of Cr^{6+}-compounds that have become increasingly unpopular because of environmental hazards such as chromium allergy and cancer for workers and severe toxic effects on water environments and nature in general.

This paper is an up-to-date report on the current status of an investigation project set up by the Danish Government in 1989 at the Centre of Advanced Electroplating (CAG). The aim of this project is to find an alternative method for protecting zinc coated steel against white rust.

Experimental

The following procedures have been used for pre-treatment of the samples and for the passivation process itself. Occasionally some post-treatments have also been applied.

At an early stage of the development of the molybdate/phosphate treatment, called MolyPhos*, an extensive optimisation of the treatment parameters (temperature, duration, concentrations, etc.) resulted in the formulation of two baths, one with a molar ratio of Mo/P equal to 0.33 and a pH-value of 2.1, the other with Mo/P equal to 0.66 and a pH-value of 4.6. These two baths, which gave similarly good results, have been used for the tests to be discussed, and will be referred to as MolyPhos 33 and MolyPhos 66.

Pre-treatments

It should be noted that during a MolyPhos treatment there is hardly any gas evolution. The amount of zinc dissolved during treatment of a zinc surface is modest, and therefore it is very important that the zinc surface is clean and without oxides, organic surfactants or

* Patent WO 93/10278 pending.

other films that may hinder the formation of the passivation layer.

It is strongly recommended that the passivation takes place immediately after the zinc coating has been applied (the samples should not be allowed to dry). If the zinc plating bath is a cyanide based one (cyanide zinc) and if the zinc bath contains additives, it is furthermore necessary to rinse the samples in a very dilute nitric acid (approximately 0.15 mole/litre HNO_3). This pretreatment (called a bright dip) will clean the zinc surface and remove traces of organic additives (especially important for cyanide zinc).

Passivation Conditions

The passivation process itself is simply a dip for approximately 2 minutes in the MolyPhos bath at 60°C. To ensure constant concentration of the active components everywhere in the bath, and to avoid local changes in temperature, a good stirring using air bubbling, sample movement or similar, is recommended.

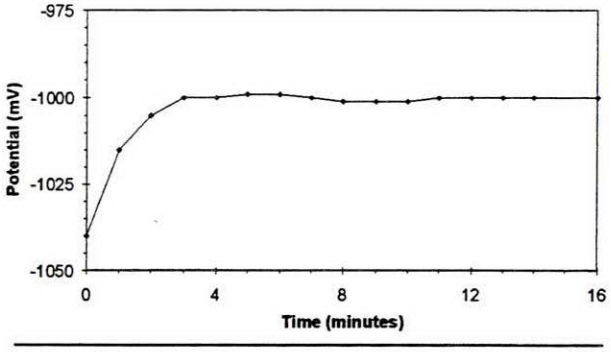


Figure 1: Typical potential versus time chart, measured during the passivation of a cyanide zinc sample. Potentials are measured versus SCE.

The process time is not critical, although baths with high pH values usually require longer dipping time for a good layer to develop. Process times between 80 and 130 seconds for MolyPhos 33 and 100 and 180 seconds for MolyPhos 66 are fully acceptable. A temperature range of 60°C ± 5°C is adequate and small differences in temperature should give rise to no changes in coating properties. When the passivation is completed, the samples are washed in clean (preferably de-ionised) water and dried at room temperature or in hot air (up to 60°C).

The potential versus a saturated calomel electrode (SCE) was measured for several of the samples during the treatment. Although there were some differences in the results, the basic pattern was the same.

From figure 1 it is clear that a process time of more than 2 minutes is unnecessary. There has even been some indication that too long dipping times could become disadvantageous.

Post-treatments

Experiments have shown that MolyPhos passivated surfaces accepts post-treatments such as paints, sealers and lacquers.

Recent tests, which are not yet concluded, have shown that some organic sealers (also involving a short dip in a warm solution) will improve corrosion resistance of the combined system.

Corrosion Tests

In order to identify the best passivation parameters using optimisation, it is necessary to have at your disposal a reliable and reasonably fast method for measuring the corrosion rate. A vast number of methods exist; salt spray tests, outdoor exposure tests and various simulation programs in which temperature, salt concentrations etc. are controlled and changed systematically. All of these tests are very slow and depending on a rating system based on experience and personal (subjective) judgement.

Corrosion Measurement by Titration

A new chemical method[9,10] meets the demands for a fast and reliable method perfectly. The method is called Corrosion Measurement by Titration (CMT)* and is based on a very precise pH control provided by a pH meter, a titration unit and an auto-burette (figure 2).

When a zinc plated sample is submerged into the corrosion cell containing a 3% sodium chloride solution,

* Corrosion Measurement by Titration is developed by the Centre of Advanced Electroplating (CAG)

the chemical reactions involved in the corrosion of the zinc coating are:

Anodic metal dissolution:

$$Zn \rightarrow Zn^{2+} + 2\,e^-$$

Usually combined with one of the following cathodic reactions:

$$2\,H^+ + 2\,e^- \rightarrow H_2$$

or

$$\tfrac{1}{2}O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O$$

In both of the cathodic reactions H^+ is consumed and pH is increased in the electrolyte in which the experiment takes place. To maintain a constant pH value in the corrosion cell, fresh acid is added continuously from the burette controlled by a high accuracy pH meter and a titration unit (figure 2). The equipment is capable of maintaining the pH value at the same level within ±0.001 pH units.

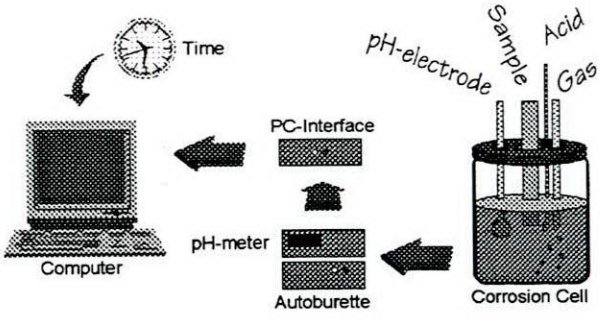


Figure 2: Corrosion Measurement by Titration (CMT). Simplified drawing of the corrosion cell and the basic flow of information.

The zinc plated sample is a cylinder inserted in a Teflon tube, exposing an end-face of 2 cm^2 to the solution. This forms a rotating disc electrode, rotating at 1000 rpm. In this way uniform corrosion of the sample can be expected, and efficient stirring of the solution is ensured. CO_2-free air is bubbled through the cell in order to avoid interference from carbonic acid.

The time passed since then last addition of a volume of acid (e.g. 10 µl) is registered by an interface unit - from which the information is transmitted to a computer (figure 2). The computer has already all information concerning the area of the exposed surface and the strength of the acid used for the additions. From this set of input the corrosion rate is calculated and displayed continuously.

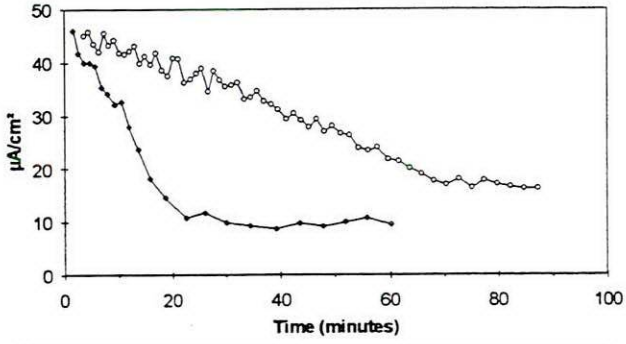


Figure 3: Typical CMT-charts for cyanide zinc passivated with MolyPhos 33 (◆) and 66 (O).

Compared to other corrosion tests the CMT method provides almost continuous measurements that, presented as a chart, tell a lot more about the samples than a single value obtained from e.g. a salt spray test. Depending on the material, the corrosion rate may change considerably during an experiment. For the samples tested in this project a typical pattern includes a rather high corrosion rate in the beginning, followed by a curve descending towards a fairly stable and constant region. The rather high corrosion rate measured in the beginning (first 20-30 minutes) of the experiments, is caused by oxides dissolving from the surface. Since these components participate in reactions that also consume acid, the system will respond and a "false" corrosion rate is recorded. In all experiments an average value, calculated from the last 10 measurements before the 60 minutes mark, is used as the reported result.

If we want to use the CMT measurements consistently, it is necessary to have a well-known frame of reference. We need to know how other materials behave in the test, and we have to make sure that the test conditions allow us to compare the results. In figure 4 a number of well known and a few new zinc coatings have been tested and the results compared. Corrosion rate, measured in µA/cm^2, is listed for unpassivated zinc made

from a cyanide zinc bath, for an unpassivated nickel/zinc coating (15% nickel) and for an unpassivated composite coating (containing zinc and small amounts of chromium and aluminium oxide)[7].

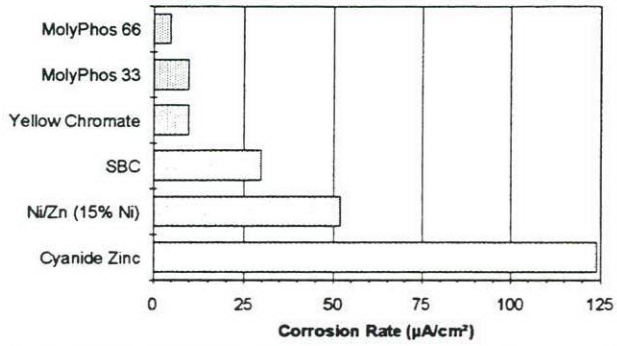


Figure 4: Frame of reference. CMT results at pH=5.000 for selected passivated and unpassivated zinc coatings.

Furthermore figure 4 contains CMT results of cyanide zinc coatings passivated with standard yellow chromate and with MolyPhos 33 and MolyPhos 66 (the numbers 33 and 66 refer to two different bath compositions having different pH-values when used).

Neutral Salt Spray Tests

The CMT method provides us with a true measurement of the "flux" of zinc through the conversion coating, but we do not know how the test conditions (rotated sample in 3% NaCl) simulate natural exposure. This problem however, exist for all accelerated tests!

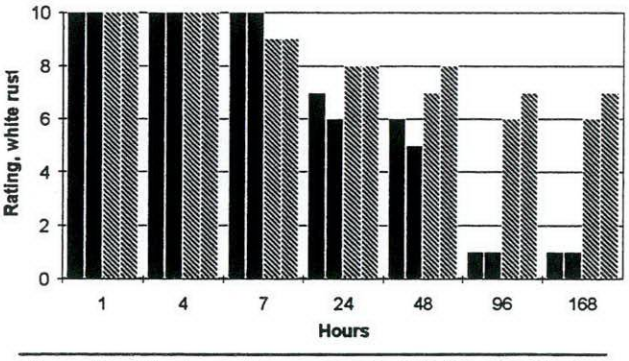


Figure 5: Neutral salt spray test of Zn/Co (0.8% Co) plated steel panels, protected by MolyPhos 66 (solid bars) and yellow chromate (patterned bars). Evaluated according to ISO 4540 at Danfoss A/S, test confines with AESF B117.

Without a post-treatment (see above) samples protected with the MolyPhos treatment does not perform very well in a neutral salt spray test. In fact there seem to be a correlation between the pH-value used in the test and the corrosion protection provided by the MolyPhos conversion coating (see also summary).

A typical salt spray result is shown in figure 5. The substrate is a zinc/cobalt alloy with 0.8% cobalt (see also figure 7).

Prohesion Tests

The Prohesion test[2], used by several British, Danish and other European Companies, is a cyclic slightly acidic salt spray test.

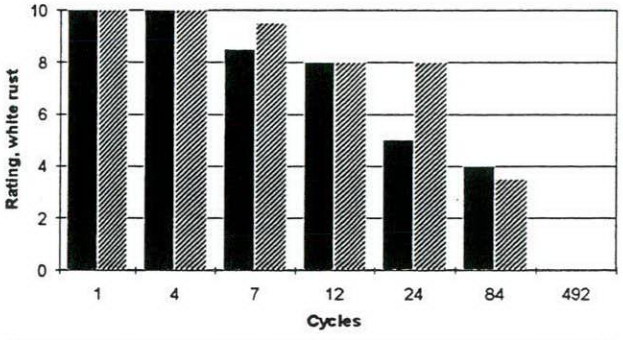


Figure 6: Prohesion test results. Solid bars represent MolyPhos 66 on acidic zinc, patterned bars are yellow chromate on the same substrate. Each cycle equals 2 hours.

Each cycle consists of 1 hour with salt spray and 1 hour drying period. The salt spray solution is a mixture of 0.5 g/l sodium chloride and 3.5 g/l ammonium sulphate.

Out-Door Exposure Tests

An out-door exposure test, situated near a Danish power plant called "Kyndbyværket", was finished in October 1992. The test included steel sheets plated with cyanide zinc, acidic zinc, zinc/nickel (15% nickel) and zinc/cobalt (0.8% cobalt) passivated with yellow chromate (four different types, one for each substrate), MolyPhos 33 and MolyPhos 66.

The samples (two of each) were exposed during 8 month to normal weather, SO_2 coming from the nearby

power plant as well as sea water sprayed onto the samples 5 minutes every hour.



Figure 7: Out-door exposure test showing the difference between four popular zinc coatings and the passivation processes MolyPhos (solid bars) and yellow chromate (patterned bars).

Measuring the degree of red rust (evaluated according to ISO 4540) on these samples, it turned out that chromated cobalt/zinc was much better than all the others (not even visible white rust!) and that zinc/nickel failed completely - independent of the conversion coating applied. For cyanide zinc yellow chromate was a little better than MolyPhos 33 and for acidic zinc MolyPhos 66 was a little better than yellow chromate.

Coating Properties

After the first promising results with the MolyPhos treatment, numerous tests became very urgent. Throughout the development and optimisation of the method's[12] corrosion resistance was the only parameter investigated. New tests, involving properties such as adhesion, paintability, electric conductivity, heat resistance and many others had to be planned and carried out.

Chemical Composition

The passivation coatings or layers formed by MolyPhos on different surfaces and alloys have been studied in detail. For the studies of the surface and the chemical composition of the coatings, Auger analysis[13] and several other methods such as EDAX[12], XPS[13] and SEM[12] have been used. This investigation indicates a significant difference between MolyPhos 33 and MolyPhos 66. Whereas MolyPhos 66 exhibits a homogeneous surface with a constant composition within the entire passivation layer, coatings made using MolyPhos 33 are usually much more rough and thinner.

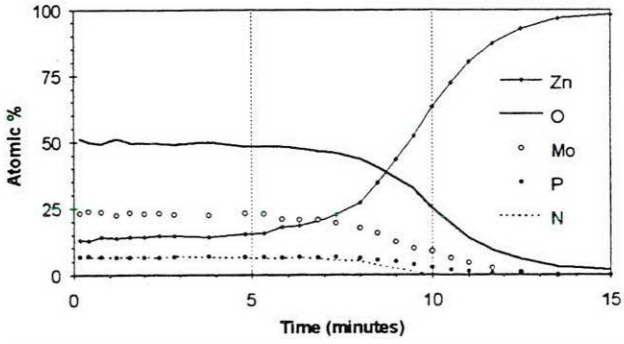


Figure 8: Auger profile of MolyPhos 66 on acidic zinc. The sputtering rate is about 180 monolayers per minute.

It is also clear, thanks to the Auger profiles, that the thickness of the MolyPhos passivation layer is within a range from 0.2 to 0.4 μm, and that the layer formed on acidic zinc using MolyPhos 66 is significantly thicker than the others. This is hardly a coincidence since this combination also had the lowest corrosion rates using CMT - between 4.0 and 7.0 $\mu A/cm^2$ (twice as good as yellow chromate!).

As for the chemical composition of the MolyPhos layers, they all contain the following components:

Zn: Large amounts of zinc (18-22 atomic %) were found in all coatings. This indicates that some zinc dissolved during the passivation process, but was precipitated as part of the layer on the surface. The Auger signal for sodium (Na) is at the same position as zinc, but using XPS it was possible to separate the combined signal into some 13-15% Zn and 5-7% Na.

O: Oxygen is found in large amounts (45-50%), but this is hardly surprising since both molybdate and phosphate hold 4 oxygen atoms. The amount of oxygen, being the lightest element in the film, is possibly higher than the 50% indicated in the diagram (figure 8).

Mo: The amount of molybdenum (20%) is quite constant in all tests. The oxidation state of molybdenum is presently believed to be Mo^{2+}, except for the first few atomic layers where Mo^{5+} and Mo^{6+} have been identified.

P: Phosphorus (approximately 7%) was expected, but the relatively low amounts are somewhat surprising. The low amounts of active components in the passivation film, explain why the bath is used up relatively slowly.

N: Nitrogen (less than 6%) origins from the additives used in the zinc baths. The presence of nitrogen was not intended.

C: Carbon is only found in the first few monolayers of the surface. This pollution is impossible to avoid (the carbon signal has been removed in figure 5).

Adhesion and Paintability

Concerning the use of surfaces in general, it is important that the passivated surface will accept paint and different printing techniques. Furthermore it is, of course, very important that the coating itself is firmly attached to the surface and that the coating is reasonably resistant against scratches and damage during handling.

MolyPhos 33 does not work with acidic zinc baths and there has been some problems with cyanide zinc as well. MolyPhos 33 can therefore not be recommended for items exposed to rough handling or rubbing. The adhesion problems do not exist with alloys such as zinc/nickel or zinc/cobalt. No problems have ever been observed using MolyPhos 66 - in fact the adhesion for this treatment is better than for chromate treatments in general.

As far as paintability is concerned, the coating accepts ethanol based paint, powder coatings and different "silk" or "screen" printings. The resistance towards organic thinners is good.

Other Properties

The electrical contact resistance of passivation layers formed using molybdate/phosphate based treatments, is less than 0.5% of that of chromate layers[5]. MolyPhos, which is based on molybdate/phosphate, is within the same region as some pilot tests have indicated. This major difference in contact resistance could make it possible to use MolyPhos passivation for applications where chromate causes to high contact resistance.

Friction and adhesion properties have also been tested, and the general result was that MolyPhos has about the same frictional properties as yellow chromate. Friction properties are important for assembly and construction tasks using passivated fasteners.

The heat resistance of the MolyPhos passivation film has been tested at 90 and at 120 °C without any measurable change in corrosion resistance after the test.

Bath Maintenance

After having discussed the properties of the coatings obtained by a short dip in the treatment baths, a number of questions may come into mind as to how stable and reliable the baths are. It is of importance to know exactly how long the baths will last, and what can be done to recover them.

A bath stability experiment has been performed and a total zinc surface of approximately 20 dm^2 has been passivated in each of the two test baths (1 litre total volume each).

Using atomic absorption analysis the concentration of zinc in the baths was measured continuously. There seems to be a constant relationship between zinc concentration and passivated area. The big difference in zinc concentration between the two baths can easily be explained by the difference in pH value. MolyPhos 33, being more acidic than MolyPhos 66, will dissolve more zinc, since process time and temperature were the same in both experiments (2 minutes at 60°C).

The most simple bath analysis is a pH measurement, but even if this value is within an acceptable range, we can not be sure whether other concentrations are out of control or not. Especially the accumulation of zinc

could be dangerous, since it will not show directly in a pH measurement.

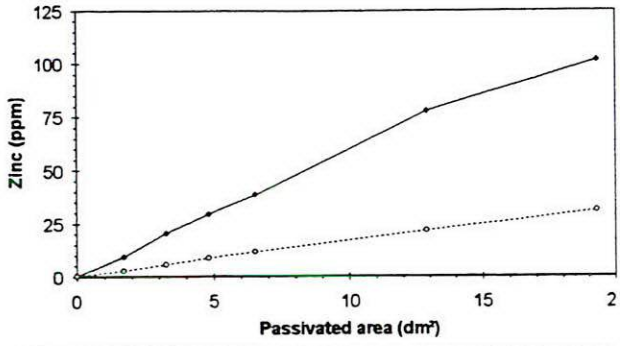


Figure 9: Accumulation of zinc in MolyPhos 66 (O) and MolyPhos 33 (◆) baths, as a function of the total zinc area treated.

The pH value of the bath is controlled by the buffer system formed by ortho phosphate (see figure 10) and molybdate. The points in which the concentration of more or less protolized phosphate ions meet (figure 10), are extra pH stabile. It therefore hardly a coincidence that the MolyPhos 33 and MolyPhos 66 turned out to be the best baths since they have pH values of 2.1 and 4.6. Experiments with baths containing up to 400 ppm of zinc did not indicate any reduction in the quality of the passivation. MolyPhos baths (especially 66) are believed to last as long as yellow chromate baths.

Figure 9 showed that the relationship between zinc accumulation and passivated zinc area is quite predictable. Using this chart it will be possible to keep track of the zinc concentration in the bath and make sure that it does not get completely out of hand. With this in mind, frequent analysis of the zinc contents using atomic absorption spectrophotometry (which is the most reliable method), normal spectrophotometry or voltametry should still be conducted frequently.

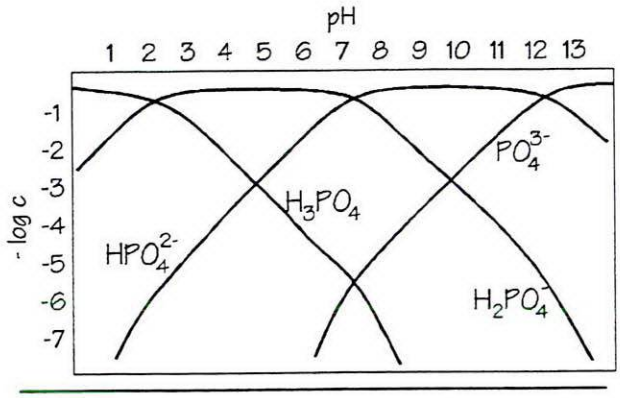


Figure 10: Hägg diagram for the ortho phosphate system. The initial concentration c is 0.3 mole/litre.

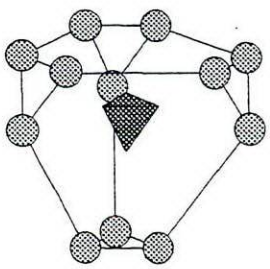
Since the main components in the MolyPhos baths are used relatively slowly, continuous analysis of molybdate and phosphate is not necessary. When there is a need for these analyses, the well-known strong blue colour (maximum absorbance at 620 nm) formed by hetero polyacids* in which one or more of the molybdenum ligands has been reduced from Mo(VI) to Mo(V), can be used for a spectrophotometric determination.

Cost Analysis

To be a realistic alternative, a new method must be technically equal to the method it is replacing (and preferably a little better!) and it must not be very much more expensive. The following cost analysis is based on the current knowledge of the new method, and on available information about prices and discounts for the necessary chemicals.

Approximately 65% of all costs in a passivation process can be related to pay-rolls and investments[6]. These costs will remain the same if chromate treatments are replaced.

* A very important part of the chemistry in the MolyPhos baths, is played by hetero polyacids formed by molybdenum and phosphorus[14] at low pH-values. These rather large molecules are made up by four ligands, containing molybdenum, surrounding each phosphorus atom. The hetero polyacids are usually written as $H_3[P(Mo_3O_{10})_4] \cdot x\ H_2O$ but a number of different conformations with molar ratios (Mo/P) of 11, 10, 9, 8, 8.5 and 6 are known to exist as well.



The remaining 35% of the costs are related to chemicals, water, heating and waste processing. The price for 1 litre MolyPhos bath is approximately 7 times more than the price for 1 litre (yellow) chromate bath. Furthermore MolyPhos requires a bath temperature of 60°C, while chromate works at room temperature.

Since a bath temperature of 60°C will make water evaporate quickly, addition of fresh water is necessary. This water should be taken from the first rinse bath after the passivation process, and in this way extensive recycling of the chemicals can be obtained. These considerations concerning recycling of the active components will make it possible to eliminate almost all costs concerning waste destruction and water cleaning. Since waste water disposal is about 10-15% of the total costs it might be possible to regain what has been lost on chemical prices and bath heating.

Depending on how realistic the estimates are, how an increased interest in molybdenum will affect the price levels of the chemicals involved and how critical the environmental authorities will be in the future concerning dumping and use of chromates, we believe that the cost level for the passivation process alone will be increased 0 to 10 per cent by replacing yellow chromate passivation with MolyPhos.

Summary

A realistic alternative to chromate based conversion coatings have been found in the molybdate/phosphate system called MolyPhos. The procedures used for the alternative process are very similar to the chromating procedures.

The protection provided by MolyPhos against corrosion of zinc plated parts, is comparable to that of the best chromates. Depending on test conditions, and especially the pH-value, MolyPhos is better than chromate at low pH-values (f. ex. the Kesternick test) equal to chromates in out-door exposure tests and Prohesion tests but not quite as good in neutral tests such as the salt spray test.

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Paper Not Available In Time For Publication

Recent Improvements in Physical Vapor Deposition

Dr. Brent Lee, Vacuum Plating Technology, San Jose, CA

Two major problems associated with the PVD process that prevent wide application in the surface finishing industry are restricted size and shape of the coating product and slow production rate. Improvements in PVD technology, including magnetic controlled cathodic arc-plasma technology, have been developed and are commercially available. This technology provides a high deposition rate, a high ionization rate and operates in low temperatures. In addition, other advantageous features of PVD, such as hardness, chemical resistance and a wide range of color selection, enable broad market applications.

For copies of this paper please contact:

Brent Lee
Vacuum Plating Technology
1706 Leigh Avenue
Suite 176
San Jose, CA 95125-5653
408/947-7692
FAX: 408/998-4795

DIRECT CONNECTED PLASTIC ANODE BASKETS

This paper will review the problems associated with the existing hanging type of anode basket and their effect on plating efficiency and uniformity, etc. The paper will then detail how the new design overcome these problems to improve the plating performance.

I believe almost everyone is familiar with the electrical contact problem associated with corrosion and salt build-up between a typical copper anode bar and a hanging type of anode basket, this corrosion reduces current flow there by reducing plating thickness or extending plating time and reducing efficiency.

Actually, there are two separate mechanisms which reduced plating efficiency. The first is very obvious - simply an increase in electrical resistance between the copper anode bar and basket hanger. This resistance reduces electrical current flow and typical worsens as time goes on and corrosion increases, in extreme cases this resistance causes smoking or burning contacts between the anode bar and basket hanger.

The second mechanism is more subtle. I think most people have seen the "gouging" or "pitting" or "wearing" of the copper anode bar at the point of contact with anode basket hangers. Normally, the pitting is not caused by resistance, it's caused by electrical arcing which is caused by intermitting electrical contact. In

other words, the basket moves slightly during normal operation to break through the corrosion and make contact for a brief period of time with the copper anode bar. Then it rocks some more and contact is lost. The basket is switching off and on during the plating cycle. The important thing to note here is that during the off cycle no plating is taking place from that basket even though the basket next to it is working. This effect causes damage in several ways.

First of all electrical power is wasted (as with the simple resistance) electricity is generating heat and smoke and vaporizing copper instead of plating.

Second of all the non-conducting basket is absorbing zinc or is anodic for the off cycle time. In extreme cases where the basket becomes permanently insulated, an anodic basket becomes incased in metal - metal which should have been plated on to parts.

Finally, it means that the effective anode area is much lower than what it appears because of the baskets that are not connected.

These conduction problems can be overcome by simple frequent cleaning with wire brushes, etc. However, electrical conductivity continues to decrease between cleaning, and frequent cleaning requires increased labor and downtime costs.

These problems can be permanently and completely overcome and the labor and downtime costs eliminated by changing the design. This will be explained later in this paper but first lets look at another set of problems associated with the hanging style baskets.

For the sake of illustration, let's look at a ball type of

basket in a zinc system. Assume none the anode bar contact problems exist and let's further assume you just filled a basket with brand new shiny zinc balls. Now let's look at what you have every zinc ball is touching the basket at one point (perhaps 18 - 24 points total) and touching each other. Let's turn on the plater and see what happens. Electric current flows down into the basket and contacts each zinc ball individually. Zinc starts disloving and moving toward the part to be plated - very basic.

Now notice something, electrical current takes the easiest path to the part we are plating so only the half of the zinc ball in the basket that faces the work will disolve and plate out. The other half of the ball basket just gets dirty and/or oxidizes over time and eventually becomes electrical insulated from the basket. Also, don't forget that titanium forms an oxide film on it's surface that protects it from corrosion, and that this film is an electrical insulator that means that in order to have a good electrical contact you have to have to provide enough force to "scratch through" the titanium oxide film as well as the zinc metal oxide film. As time goes on all the ball which were touching the basket on the side opposite the work are electrical insulated form the basket side so that current has to flow from the zinc ball above or below it; assuming the contact points on these balls aren't too oxidized to conduct electricity. This up and down conduction and possible insulation of some individual ball causes "anode balls" and replating of zinc on zinc ball which effectively starts gluing balls together into a solid structure. Now let's

look at the side of the balls facing the work. They are bright a shiny and are pushed into the titanium on the work side by t weight of the ball above it. This happens until the balls becom so glued together that they can't push out to the active fac Don't forget that this has to continually happen to overcome th effect of zinc dissolving and shrinking away from the titaniu there by losing electrical contact.

Assume the above process goes on over a week or so, and no let's look at the basket. The zinc balls have more or less glue themselves together in a long blob and are probably touching th basket at only two places. The top ball at the top of the baske and the bottom ball at the bottom of the basket. Let's look a those contacts; the top contact has very little pressure associate with it, probably not enough to break the oxide films. The botto contact has a lot of pressure associated with it, the entire weigh of all the zinc balls, but look at what else is in the bottom o the basket: mud, dirt, oxidized metal, etc. The bottom ball has t push its way through all this insulation material to make contact

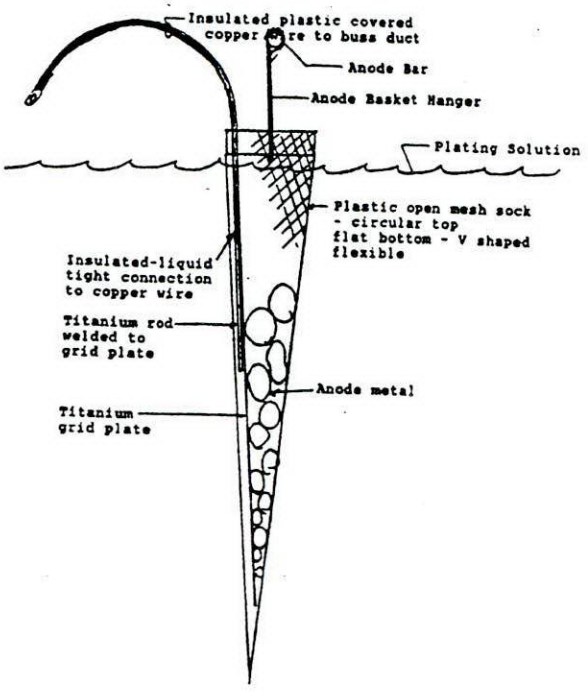
The conductivity problems described above are usually attacke by beating on the basket with a hammer to obtain some temporar electrical conductivity. In short, the very design of the baske itself, provides a very poor electrical contact system.

You have a system where the electrical current that gets past the poor anode bar to anode basket hook contact, has to flow down the entire length of a titanium basket which is a relatively poor conductor through the dirty bottom of the basket and back up

through partially oxidized zinc balls and out into the work. This is not a good system from an electrical stand point and all of these electrical problems exist to some degree in every plating application.

So how do you eliminate these problems? You build a new type of anode, one that is radically different. As an example let's construct a simple ball type of anode basket. We start with a non-flattened expanded titanium grid plate about 3" X 24" and we weld a stub piece of titanium rod to the center. We the connect a length of insulated copper wire to the stub titanium rod by means of a special submersible insulated connection.

We then fabricate a special open mesh plastic sock with an open top and a flat V shaped closed bottom. The titanium grid plate is inserted into the sock and the sock is suspended above the plating tank with the grid plate under the solution level and the wire running outside the plating tank to the electrical bus. The wire is connected to the bus through a fusible link which operates as a safety device. You then simply add anode metal to the sock in such a way to orient the titanium guide plate between the anode metal and the work to be plated. This construction is illustrated as follows.



Now let's look at what we have built and see how it improves things.

First of all, the direct wire from the copper buss outside the plating tank to the center of the titanium grid plate eliminates any electrical connection above the plating tank. This eliminates cleaning the connection, hot spots, electrical connection resistance, intermittent contacts, electrical burning, pitting and the potential for anodic baskets. This also allows a much higher basket current carrying capacity; 100 amp/basket is smallest size available and much higher capacities can easily be constructed. The normal hanging type bail type basket is rated at only 25 to 50 amps. If you are looking at new installation; it eliminates the expensive solid copper buss bars and the flat buss to round buss adapter casting and this amounts to a respectable amount of money.

The smaller titanium grid plate also allows a substantial savings for those platers that use platinum or other types of

coated anode baskets.

Now let's look at the improvements in electrical contact between the anode metal and titanium grid plate. As anode metal (zinc 'balls) are added to the basket the additional weight stretches the plastic sock wedging the balls into the titanium grid. The sharp edges of the non-flattened titanium easily cut through any oxide or dirt accumulation assuring good contact. As the anode metal dissolves and is size decreases it continuously drops lower into the plastic "V" notch where it is still pushed into the grid plate to assure good contact.

To summarize you now have a system where ALL of the anode metal is 100% in electrical contact 100% of the time. This improves the total plating system in the following ways. The electrical efficiency is improved which provides more current per station. This higher current provides faster plating time and or high plating thickness. The electrical efficiency is essential constant (it doesn't deteriorate between anode bar cleanings) so that plating thickness is more uniform.

The anode to cathode ratio is reduced. The old anode baskets systems operated at a ratio of around 2 to 1. The theoretical is 1 to 1, and the new baskets operate at about .8 to 1. This lower ratio allows the plater to reduce the number of anode baskets per station without increasing the dissolved metal contact of the bath. Conversely in applications which require higher metal concentration conversion will increase the metal content. A side effect of the conversion to plastic baskets is the elimination of metal falling

into the tank because of titanium deterioration. These plastic baskets obviously last longer than titanium.

Examples of actual installations include one plater with a six station acid zinc barrel line. This shop had 26 ball type Anode Baskets per station. And pulled an average of 485 amps per barrel. After conversion only 6 direct contact plastic baskets per station provided an average of 550 amps per station.

Another zinc plater with 8 baskets/barrel required expensive dissolved zinc additions to maintain the plating solution concentration. After conversion only 6 direct contact plastic baskets/barrel provided higher current flow and completely eliminated dissolved zinc additions.

This patented technology should significantly improve most platers efficiency, quality and profitability.

DISTRIBUTING YOUR PRODUCTS AND THE ANTITRUST LAWS

By Larry J. Saylor

Your product distribution practices may subject you to an expensive lawsuit by your customers or competitors, and may even expose you to criminal prosecution. The antitrust laws, popularly thought to be dead during the Reagan and Bush years, are being vigorously enforced by the Clinton Administration. This paper outlines the antitrust laws related to product distribution, and how to comply with them.

The Sherman Act

Sections 1 and 2 of the Sherman Act, and similar provisions of state law, are the basic antitrust laws. These prohibit:

- **Contracts and other agreements which result in an unreasonable impact on competition; and**
- **Monopolization and attempts to monopolize.**

The federal antitrust laws are enforced by the Department of Justice, and state laws are enforced by state attorneys general. Violations are felonies, punishable by fines and imprisonment. Under the Federal Trade Commission Act, the FTC can obtain civil penalties for anti-competitive conduct. Private individuals or corporations injured by antitrust violations may file lawsuits and recover treble damages, injunctions and attorney fees.

The courts have concluded that certain types of agreements are unreasonable "*per se*." This Latin phrase means simply that where one of these agreements exists, an unreasonable impact on competition is **presumed**, and need not be proven. These agreements are unlawful regardless of the size of the participants, and regardless of whether they produce beneficial effects. The "*per se*" violations are:

- **Agreements to fix prices.**
- **Agreements between competitors to divide markets.**
- **Certain group boycotts.**
- **Certain tie-in sales (refusal to sell a product unless the customer also purchases another product it does not want).**

While an oversimplification, it is essentially accurate to say that group boycotts and tie-in sales are actually analyzed under the rule of reason, discussed below.

Horizontal Price Fixing

Agreements to fix prices come in two varieties: "horizontal" and "vertical." Horizontal agreements, that is, agreements *between competitors* to "raise, lower or stabilize prices," are the classic *per se* violation of Section 1 of the Sherman Act. "Price" includes credit and other terms of sale. Agreement may be proven by circumstantial evidence, for example exchange of price information followed by similarity in prices.

The Department of Justice has always strictly enforced the antitrust laws against this type of agreement. It has investigations ongoing in a number of industries, and regularly obtains convictions and guilty pleas. Under the current Sentencing Guidelines, convictions for these offenses almost always involve prison sentences and substantial fines. The Justice Department has also announced a corporate amnesty program, which allows companies who voluntarily report violations to obtain immunity from prosecution in return for an agreement to cooperate with prosecutors.

Vertical Price Fixing

"Vertical" price fixing agreements (agreements between buyers and a sellers on resale prices) are, despite arguments by conservative economists and legal scholars, still

considered unlawful *per se*. The Department of Justice last summer rescinded its Vertical Restraints Guidelines, signalling an intent to increase antitrust enforcement against manufacturers who terminate discounting dealers and distributors as part of an agreement on resale prices. A bill has been introduced in Congress which, if enacted, would make it much easier for terminated dealers and distributors to bring antitrust suits against manufacturers.

The Rule of Reason

Under Sections 1 and 2 of the Sherman Act, restraints of trade which are not subject to *per se* treatment are analyzed under the "rule of reason". These include:

- **Exclusive dealing arrangements.**
- **Territorial restrictions on distributors.**
- **Many tie-in sales.**
- **Most group boycotts.**

The "rule of reason" requires the court to weigh the anti-competitive impact of the challenged practice and determine whether there are legitimate justifications which outweigh that impact. In general, only justifications which increase efficiency or promote competition can be considered; abstract ethical principles cannot justify a restraint of trade.

In applying the rule of reason, the first step is to determine the boundaries of the "relevant market" in which the competitive impact is felt. The goal of market definition is to determine whether the defendants have "market power" -- the power to raise prices, reduce quality, or impose burdensome terms customers would not freely choose. The relevant market comprises (1) all products services which are reasonably interchangeable with the product in question, (2) within the geographic area to which customers would reasonably turn to obtain lower price or higher quality. Potential competitors who could readily provide the product or service are included in the relevant market. The legality of any specific restraint thus depends on a detailed analysis of competitive conditions.

Price Discrimination

Private suits for price discrimination are one of the current "growth areas" in antitrust law. Price discrimination is governed by Section 2 of the Clayton Act, as amended by the Robinson-Patman Act. A few states have similar statutes.

Section 2(a)

Section 2(a) of the Robinson-Patman Act prohibits discrimination in the price of goods. The prohibition is not absolute, however. Section 2(a) applies only if a number of elements are satisfied:

- One of the challenged sales must be made across a state line.
- The sales must be at different prices. The prices to be compared are the actual net prices paid by the buyers. Where invoice price and delivery terms are the same for each buyer, there is no price discrimination, even though seller or buyer may incur different costs. However, where delivery terms differ, there may be price discrimination even though invoice price is the same.
- The sales at different prices must be reasonably contemporaneous. If the sales are separated by several months, this requirement is likely not satisfied.
- The sales must be by the same seller. This requirement may be satisfied where the sales are by commonly owned corporations or a parent and subsidiary.
- The sales must be of goods or commodities of "like grade and quality." Services are not covered. Physically identical goods sold under different brands are of like grade and

quality. Small physical differences or differences is the timing of delivery may render goods *not* of like grade and quality.

- The goods must be sold for use, consumption, or resale within the United States.

- There must be a reasonable possibility that the price difference will harm competition.

The competitive harm need only be potential. The impact may be felt either by the competitors of the seller (so-called "primary line" injury), or by the competitors of the buyer ("secondary line" injury) or even their customers ("tertiary line" injury). Some cases hold that a possible effect on primary line competition may be inferred from predatory intent. Other cases require a showing of the defendant's market power to establish a possible effect on primary line competition. Several courts have held that at least in secondary line cases, injury to a single competitor may satisfy the requirement of injury to competition.

To establish injury to competition in a secondary or tertiary line case, the favored and disfavored customers *or* their customers must compete with each other in the same relevant market. If the buyers are in different "lines of commerce," there is no violation. Thus, the courts have recognized that manufacturers may under certain circumstances extend "functional discounts" to wholesalers which are not afforded to retailers.

Defenses to a Section 2(a) Claim

Sections 2(a) and 2(b) of the Robinson-Patman Act allow the seller to avoid liability if it establishes that the discriminatory price:

- Was set in good faith to meet the lower price of a competitor. This defense is available even if the seller, lacking accurate information, inadvertently undercuts its rival's price.

- Was justified by differences in the cost of manufacture, sale or delivery. This defense requires specific proof that a quantity discount was cost-justified.

- Was in response to changing conditions, for example product deterioration or obsolescence.

The seller has the burden of proving these defenses.

Advertising and Promotional Allowances

One of the most dangerous and least understood provisions of the Robinson-Patman Act is Section 2(d), which prohibits a seller from granting advertising and promotional allowances to customers unless they are available to all competing customers on proportionally equal terms. This section is dangerous because (unlike Section 2(a)) it does not require proof that the discriminatory allowance will even potentially injure competition. This section applies, however, only (1) if the purchasers are actually in competition with one another, and (2) the allowance was made in connection with the resale of the seller's goods.

Buyer Liability

Section 2(f) prohibits a buyer from knowingly inducing a seller to violate section 2(a).

Damages

To recover damages for price discrimination, the plaintiff (competitor) must show that the favored purchaser used the discount to lower its resale prices or otherwise cause the plaintiff to lose profits. It is not sufficient that the favored purchaser simply retained the discount and thereby earned greater profits than the plaintiff.

Antitrust Compliance Policy

To avoid paying damages or suffering criminal penalties, your company should adopt

and follow an antitrust compliance policy. An example of such a policy is set out below.

• • •

XYZ Company Antitrust Compliance Policy

XYZ Company's policy is strict compliance with the antitrust laws of the United States.

Overview of the Antitrust Laws

There are several ways in which the antitrust laws affect persons engaged in sales. Section 1 of the Sherman Act broadly prohibits agreements between two or more competitors to fix prices, allocate customers, or allocate sales territories. The Robinson-Patman Act prohibits price discrimination (selling the same product to competing customers at different prices), and promotional allowances which are not extended to all customers on proportionally equal terms.

There are legal defenses to charges that these laws have been violated, but it is best to avoid conduct which may result in charges of illegality. When in doubt, inquire of the Company's legal department [or counsel knowledgeable about the antitrust laws].

Key Antitrust Concepts

An *agreement* between competitors does not have to be formal or written. It does not require a handshake or even the words "I agree" or their equivalent. Responding to pressure from competitors to change prices, to stay away from certain customers, or to stay out of certain sales territories can be evidence of an agreement. Exchange of price information by itself may support a charge of price-fixing. Meeting with competitors and just talking about prices can also be evidence of a conspiracy to fix prices. Avoid conduct which might give the appearance that an agreement exists.

Agreements between competitors to fix prices, allocate customers, or allocate sales territories are *per se* illegal. This means that the agreement, in and of itself, is illegal. Once a court has determined that an agreement is *per se* illegal, it will not allow any defense, justification, or excuse for such an agreement.

Price Agreements with Competitors

It is *per se* illegal to agree with a competitor to raise, lower or keep prices the same or within certain limits. It does not matter whether an exact or uniform price is agreed upon. Agreeing upon formulas to calculate prices, upon price differentials among products, or upon elements of price, terms of credit, amount of discounts, inclusion of freight charges, etc. is *per se* illegal. *Therefore, never discuss prices or pricing policy with a competitor.*

- **Do not exchange price lists or pricing information with competitors.**
- **Price lists may be obtained from customers but not for the purpose of facilitating agreement between competitors on prices.**
- **Note the date and source of all price information on the face of the material.**
- **The only exception to the rule against communications with competitors about price is in connection with a good faith purchase from or sale to a competitor.**

Price Agreements with Customers

An agreement with a customer concerning the resale price of a product is *per se* illegal. The XYZ Company may suggest resale prices but it must be clear that the customer is free to accept or reject the suggestion.

- **Never agree with a competitor to sell or refrain from selling in any area.**
- **Never agree with a competitor to sell or refrain from selling to any customer or class of customers.**

- **Never agree with a competitor to divide or share sales to a particular customer.**

Other Antitrust Violations

Other sales practices may violate the antitrust laws under particular circumstances. These practices include:

- **Selling at different prices to customers who compete with each other.**
- **Granting promotional allowances to some customers that are not offered on equal terms to customers who compete with them.**
- **Agreeing with a customer that it will buy a product only from us, or that we will sell a product only to it.**
- **Restricting the customers or territory a distributor or dealer may serve.**
- **Requiring customers who want to buy one of our products also to buy another product they do not want.**

Because the law is complex and depends on an analysis of particular competitive conditions, you should consult the Company's legal department [or counsel experienced in antitrust issues] before engaging in any of these practices.

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Paper Not Available In Time For Publication

Theoretical Considerations in Pulse Reverse Plating

Dr. Ned Mandich, CEF, HBM Electrochemical & Engineering Corp., Lansing, IL

Theoretical aspects of pulse reverse plating will be presented. Limiting rates of deposition, effect of anodic pulses on limiting current density, effect of periodically changing rates on morphology of deposits, maximum deposition rates and amplification of surface irregularities, among others, will be discussed with respect to current.

For copies of this paper please contact:

Ned Mandich, CEF
HBM Electrochemical & Engineering
2800 Bernice Road
Lansing, IL 60438
708/895-7710

CHARACTERIZATION OF ELECTRODEPOSITED ZINC COATINGS

Nicholas M. Martyak
Atotech USA
Somerset, NJ

and

Richard J. Nichols
Atotech Deutschland GmbH
Berlin, Germany

Zinc electrodeposits from additive-free and additive-containing acid solutions were characterized using electrochemical methods such as linear sweep, cyclic voltammetric and controlled current studies. Scanning electron (SEM) and atomic force (AFM) investigations revealed the surface morphology of zinc deposits and the role of additives on the surface structure. The surface structure of various chromate coatings (black, blue, green and yellow) were also studied using SEM and AFM. Corrosion properties of the zinc-chromate systems were studied using Tafel and linear polarization and galvanostatic methods. Surface studies were also made on the chromate films and zinc coatings after corrosion testing.

INTRODUCTION

Metals are electrodeposited for both decorative and functional applications. Zinc is a unique metal in that it may fulfill both requirements serving as a decorative coating due to its high surface reflectivity and acting as a functional coating protecting the substrate. The influence of additives on the structure of electrodeposited coatings is well documented. Decorative zinc coatings are due in part to the role of grain refiners and addition agents in solution. Addition agents are commonly added to plating solutions to produce levelled, lustrous deposits. Fischer details most of the work on addition agents prior to 1954[1]. More recently, Plieth discussed the role of additives on the electrocrystallization processes[2]. Specifically, additives for zinc plating have been investigated for the past few decades and several bright zinc formulations have been developed[3].

Zinc deposits for functional applications include steel strip and wire and fasteners. Zinc is often deposited on ferrous materials to act as a sacrificial anode. However, zinc metal is thermodynamically unstable in the presence of water[4] and tends to dissolve with the evolution of hydrogen. Because of the large overpotential of zinc for hydrogen evolution ($i_o = 10^{-10}$ A/cm^2) this reaction is often slow. In contact with a metal of lower hydrogen overvoltage (Pt), zinc dissolution occurs rapidly. Chromate coatings are applied to zinc deposits to further protect and increase the corrosion resistance of the zinc

electrodeposits[5,6]. The chromate layers produce a variety of colors and different levels of corrosion protection which is dependent upon the composition of the chromate solutions and immersion times.

This study was undertaken to study the influence of additives and brighteners on the structure and corrosion behavior of zinc electrodeposits. Zinc deposits from additive-free and solution containing grain refiners were also chromated to produce coatings with different levels of corrosion protection. The nature of the chromate coating was studied using scanning electron and atomic force microscopy. Corrosion behaviors were studied *in situ* and the protective nature of the chromate layers determined.

EXPERIMENTAL

Zinc was deposited from an acid chloride solution containing 40 g/L Zn, 200 g/L KCl, 25 g/L H_3BO_3 operated at 26°C and pH 5.3. Zinc was deposited to a thickness of 6 μm on a low carbon steel substrate. Additives and grain refiners (brighteners) were added to produce a lustrous deposit[7].

Electrochemical studies were performed using a PAR 273 potentiostat. The working electrode was a Pt rotating disk electrode with an area of 0.197 cm^2. A Pt gauge was the counter electrode. All potential were measured against a SCE. Linear sweep voltammetry was performed by sweeping the potential from 0.0 V to -2.5 V at 20 mV/sec. Rotation rates for mass transfer studies varied from 0 - 5000 RPM. Cyclic voltammetric studies were done by scanning anodically from, 0.0 V to +1.0 V then reversing the potential to -2.5 V and ending at 0.0 V. The scan rate was 20 mV/sec. Controlled current studies were done by stepping the current from 5 mA to 100 mA and recording the potential.

For surface analysis and corrosion studies, zinc was deposited on low carbon steel. After zinc plating, the samples were triply rinsed in distilled water and immersed in chromate conversion coatings. Immersion times for deposits plated from zinc solutions containing additives in the black, hexavalent blue, olive drab and yellow chromate solutions were 60 seconds, 15 seconds, 30 seconds and 30 seconds, respectively. Deposits plated in additive-free solutions required considerably longer immersion times in the chromate solutions, 300 seconds, 120 seconds, 300 seconds and 240 seconds for the black, blue, green and yellow coatings, respectively.

Various electrochemical corrosion studies of the zinc and chromated coatings were done. Corrosion studies were performed in 4% NaCL at pH 6.8 - 7.0. The solution was sparged before use but stagnant during testing. Galvanostatic studies were performed by stepping the current from 1 mA to 100 mA and recording the potential. Plots of potential vs. time were recorded. Tafel plots were made by scanning from -250 mV of the open circuit potential (E_{oc}) to + 250 mV of E_{oc}. Tafel slopes and corrosion currents were measured. Linear and cyclic polarization scans were also made of the zinc and chromate coatings.

SEM analysis of zinc deposits plated from solution containing no additives and solutions containing grain refining agents was done using a Cambridge 360 Steroscan. Chromated zinc deposits were analyzed in a similar manner. All samples were gold coated prior to SEM analysis. AFM analysis of the surface was done using a Digital Instruments Nanoscope III. The scanning head was capable of 125 µm scans. Samples were analyzed before and after corrosion testing.

RESULTS

Linear sweep voltammetry of an acid zinc solution shows zinc deposition occurs at approximately -1.05 V vs SCE (-0.808 V vs NHE), Figure 1a. Survey scans show no zinc deposition at potential more noble than -1.05 V. Further cathodic polarization decreases the deposition current, Figure 1b. Continued polarization further increases the cathodic current, Figure 1c. Visible signs of hydrogen gas were seen on the cathode at potentials more negative than -1.6 V vs SCE.

Controlled current studies in a boric acid-free solution, Figure 2, show a transition time of about 30 seconds. The potential increases from -1.150 V to -1.65 V. Oscillations are seen in Figure 2. The diffusion coefficient for this system is 8.31 E-6 cm^2/sec. In a solution containing boric acid, the potential remains constant at -1.10 V.

Acid zinc deposits from additive-free solutions is shown in Figure 3. The grains appear hexagonal and vary in size from 2 -20 µm. AFM analysis also reveals the third dimension of Figure 3. The size of the grains in Figure 4 are 5 - 20 µm in length and vary in height from 0.2 - 2.0 µm. The average surface roughness is 0.6 µm. AFM analysis of deposits plated from solutions containing grain refiners is shown in Figure 5. Grain size analysis shows the grains are approximately 0.7 µm in size; roughness measurements reveals a smooth surface with an R_a of 0.01 µm.

Chromating bright zinc deposits changes the surface feature of the zinc coatings. Optical analysis of chromated zinc coatings deposited from additive-free solutions exhibit a rough surface, characteristic of the bare zinc coating. Optical microscopy shows cracks in the black, green and yellow chromated films deposited from zinc solutions containing additives. SEM and AFM analysis of the zinc and chromate layers shows very fine structure in all the chromate films. Cracks are seen in the black, green and yellow chromate layers; no cracks are seen in the blue chromate coatings. An AFM image shows the black chromated zinc consisted of a network of cracks, Figures 6a and 6b. The fine structure of the blue chromate layer is seen in Figure 7.

Sectional analysis of the microcracks indicates the thickness of the green, yellow or black chromate layers is on the order of 0.5 µm. The width of the cracks is approximately 0.2 µm wide. The thickness of the blue chromate layers could not be determined.

Roughness analysis of as-deposited zinc coatings plated from additive solutions

reveals a mean roughness of about 0.005 μm. After immersion in the blue chromate solution, the average surface roughness remains about 0.005 μm. Immersion in the black, green or yellow chromate solution increases the surface roughness; 0.01 μm for the green chromate.

Corrosion tests of zinc and chromated zinc coatings shows the protective nature of the chromium layers. Tafel plots for zinc deposits plated from solutions containing no additives and subsequent black chromate, Figure 8, shows the increase in corrosion resistance due to the chromate film. The anodic branch for the zinc deposit without a chromate film so no signs of passivity; the black chromate causes the cathodic branch of the Tafel plot to intersect the anodic branch in a passive domain. Similar studies show the greatest corrosion protection from the green chromate film followed by the black and yellow. The blue chromate film offered little enhanced corrosion protection compared to the bare zinc coating.

Tafel studies show the corrosion protection is greater for zinc deposits plated from additive-free solutions, Figure 9. The passive region for the black chromate-additive-free deposit occurs at a smaller critical current density than does the black chromate-zinc deposit plated from solutions containing the grain refiners.

Galvanostatic studies offer a qualitative means of studying the corrosion protection of the zinc layers as seen in Figure 10. The current was step 1 mA/cm^2. Galvanostatic studies show an iron substrate acquired a potential of -0.53 V vs SCE after 200 seconds in the chloride medium. All deposits and chromate layers start at a cathodic potential which becomes more anodic with time. Eventually, the potential is seen to rise to a limiting value of approximately -0.51 V vs SCE. Stepping the current to either 10 mA/cm^2 or 100 mA/cm^2 required a considerably shorter times to reach the limiting potential.

DISCUSSION

The results of LSV and cyclic voltammetric studies showed zinc deposition occurring at -1.05 V vs SCE. This is in accord with the thermodynamic plots of E-pH[4] indicating the kinetics of zinc deposition are fast. The effects of solutions components using the rotating disk electrode shows zinc is under mass transfer limitation. Rotating disk electrode studies can be modelled to the Levich Equation. Cyclic voltammetric studies also show the amount of zinc deposited on the rotating disk electrode is greater at slower sweep speeds. The Levich equation shows for a mass transfer limited process, the amount of zinc deposited (obtained by integration of the area under the CV peak) should be greater at the lower sweep rates.

One of the more interesting components of the zinc electrolyte is boric acid and often made the determination of the zinc diffusion coefficient hard to calculate. Diffusion coefficients were more readily determined from controlled current studies. Controlled current experiments show a transition time for zinc deposition in solutions containing no

boric acid, Figure 2. The transition time is due to the reduction of zinc at the applied current step. The potential changes as the zinc is deposited on the electrode and thus varies with time and moves to values characteristic of the Zn^{+2}/Zn couple. At some point in time, the flux of zinc ions to the electrode surface is too slow to accept the flux of electrons transversing the electrode surface. At this point, the potential jumps to a new value where a new reduction reaction occurs, reduction of water. The diffusion coefficient from the zinc electrolyte is calculated from the transition time by employing the Sand. equation[8]. In the presence of boric acid, there is no true transition time. Apparently, the flux of zinc ions is sufficient for continued zinc deposition. Most theories postulate that boric acid acts as a buffer in the system. Boric acid may also be acting as some type of "electron-bridge" thus facilitating zinc deposition.

Zinc deposits plated from additive-free solutions were matte gray. The grains are indicative of uninhibited growth. The use of grain-refining additives to produce bright deposits has been the subject of numerous investigations[9,10,11]. Most studies believe that organic addition agents decompose and are adsorbed on the cathode surface. Such foreign species block kink sites preventing the lateral spreading of atomic layers. As new layers are deposited on the ones underneath, they can only spread laterally as the underneath layers. This leads to three dimensional structures. The shape of the three dimensional epitaxial crystallites[11] usually have surfaces of a low-index crystal plane. The foreign substance can also cause repetitive nucleation of new grains resulting in a very fine-grained electrodeposit. Several studies have shown that the addition agent or its decomposition products must be uniformly distributed over the entire surface or crevices develop and hence dull deposits are obtained. The bright deposits in this study are due to a decrease in the grain size as shown in Figures 3 - 5.

The chromate coatings changes the surface structure as shown by SEM and AFM studies. SEM analysis of the chromate layers reveals a fine structure in all cases and the presence of cracks in the thicker chromate films. One of the problems encountered with SEM analysis of these films is beam damage. Although the samples were gold coated prior to analysis, the incident electron beam caused damage to the surface structure. AFM overcomes the problems encountered with SEM. Figures 6 and 7 show the advantages of AFM studies over SEM. In addition to providing information about the fine structure, it is possible to quantify the third dimension of the surface feature. Cracks sizes (e.g., widths and depths) are determined from AFM studies and yield information about the thickness of the chromate layers. Coupled to electrochemical studies, the role of chromate thickness on corrosion prevention is readily attained.

The use of AFM obviates the need for gold coating the samples so information about corrosion products and changes in surface features is directly obtained. Very high resolution of small areas is possible with AFM which may be impossible with conventional surface science techniques.

Electrochemical atomic force microscopy allows for the study of electrochemical process in-situ. Studies are planned for monitoring changes in surface structure in aqueous media[12].

The corrosion behavior of the zinc deposits and chromate films is complex. Figure 8 shows zinc corrodes in the chloride medium. The cathodic branch indicates some type of diffusion-limited reduction process, possibly the reduction of oxygen. The corrosion of zinc is shown by the anodic branch. The corrosion rate for zinc is approximately 55 mils per year (mpy). Addition of a blue chromate to the zinc deposits has little effect on the shape or position of the Tafel curve. This indicates that a blue chromate offers little corrosion protection to the zinc coating. This is in accord with the AFM results which shows little change in the surface roughness after immersion in the blue chromate solution. Because of the small differential in surface roughness after chromating, is likely that the blue chromate layer is thin.

The effect of the black chromate layer on corrosion protection is also shown in Figure 8. The cathodic branch doesn't show the same type of diffusion limited reduction reaction as did the bare zinc coating. Anodic polarization shows the critical current density is significantly less then the unprotected zinc and a passive film is present on the surface. The corrosion rate calculated from the critical current density is about 5 mpy, an order of magnitude less than the zinc coating. The corrosion rate may be less then the 5 mpy due to the passive surface film. It is likely that the sample is still corroding due to anodic polarization but at a slower rate then the zinc alone. The Tafel plots for the green and yellow chromate films were similar in shape to that seen in Figure 8 for the black chromate film. The critical current density was similar for the black, green and yellow film indicating enhanced protection offered by these coating.

The effect of chromating zinc deposits plated from additive-free and additive-containing solutions is shown in Figure 9. The black chromate on the zinc deposit plated from an additive-free solution appears to have better corrosion resistance then the black chromate on the bright zinc deposit. The enhanced corrosion protection may be due in part to a thicker black chromate coating on the rough zinc deposit. Recall, the immersion time in the chromate solution was considerably longer for zinc deposits from the additive-free solution, 300 seconds, compared to zinc deposits plated with grain-refining additives, 60 seconds. The longer immersion time undoubtedly imparted a thicker chromate layer on the zinc. As mentioned above, it is difficult to calculate the corrosion rates from Tafel plots of samples with a passive film. The Tafel plot does reveal the presence of a passive film and thus the added benefit of the chromate layers.

Galvanostatic studies shown in Figure 10 is another method to show the added benefit of the chromate layers. The transition times reveal the relative protection of the zinc coating and chromated layers. The iron substrate acquires a potential of -0.54 V as soon as the current is stepped. This potential lies in the $Fe_3O_4/Fe(OH)_2$ domain[4]. The iron is thus corroding in the chloride medium. The zinc coating has an initial potential of about -0.94 V which lies on the $Zn/Zn(OH)_2$ line of the Pourbaix diagram[4]. This E-pH diagram is in the absence of chloride ions; calculations for the zinc system in chlorides moves the domain of metallic zinc more cathodic and the zinc hydroxide to higher pH values. This now puts the E-pH coordinate in the $Zn^{+2}/Zn(OH)_2$ domain indicating the zinc is corroding forming $ZnCL_2$ (e.g. white rust). After approximately 5000 seconds, the potential jumps to a value similar to that of the iron substrate. Optical microscopy shows

the sample has both white and red rust, Figure 11. Because of zinc corrosion. the iron substrate is now exposed to the chloride medium and is corroding in a manner similar to the unprotected iron substrate. The chromate layers extend the transition time before the onset of red rust. The longest transition time was recorded for the green chromate followed by the yellow, black and blue. The E-pH coordinate (-0.93 V; pH 6.9) for the chromated zinc coatings lies in the $Cr(OH)_3$ domain. The passive film observed in the Tafel studies is likely to be a mixture of chromium hydroxide and zinc hydroxide.

The corrosion of zinc appears to be general. Optical microscopy of zinc deposits and blue chromated zinc examined after polarization in the chloride medium shows white corrosion over the entire area. No specific areas could be identified as the origin of corrosion. The black, green and yellow chromate films all show that corrosion starts at the cracks of the chromate film, Figure 11. This appears likely in that at the bottom of the crack is exposed zinc. Corrosion probably starts at the bottom of the crack. The enhanced corrosion protection of the black, green and yellow chromates may be due to several reasons. Firstly, the crack is sites for zinc dissolution and therefore anodic. The adjacent area may be cathodically protected. Second, the chromate film may swell in an aqueous medium. If corrosion occurs in the base of the cracks, the chromate film may become gelatinous[3] and seal the crack forming a continuous protective layer. This would be particularly true for the thicker chromate coating (e.g., black, green and yellow).

CONCLUSION

The structure of zinc and chromate layers was investigated using SEM and AFM. Grain refiners reduce the surface roughness an thus impart luster to the zinc coating. Blue chromate conversion coatings are thin, continuous and change the surface structure of the zinc layers only little. Black, yellow and green chromate layers are considerably thicker than the blue coating. Cracks are present in the thicker coatings. Corrosion appears to start at the cracks of the chromate layers and propagate throughout the film. Green chromate coatings offer the best corrosion protection. Thicker chromate layers further increase the corrosion resistance. Electrochemical methods provide a fast and convenient means for qualitatively ranking the effectiveness of the chromate coating for corrosion protection.

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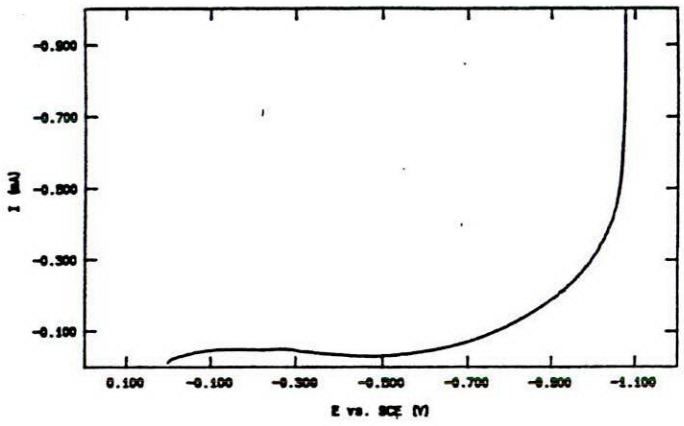

Figure 1a. LSV of Zinc Solution Containing no Additives Showing Onset of Zinc Deposition

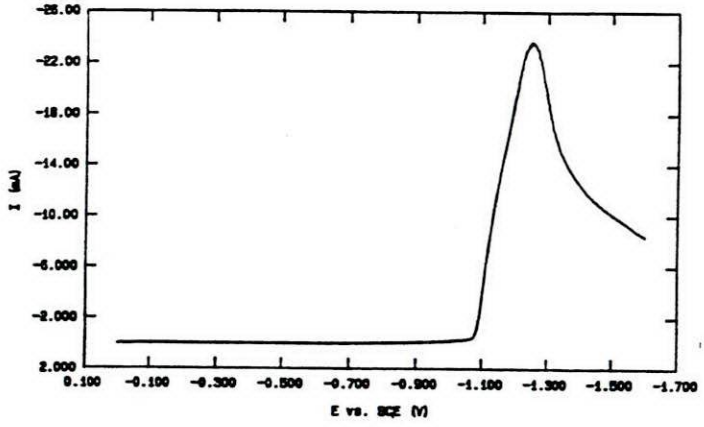

Figure 1b. LSV Showing Decrease in Cathodic Current

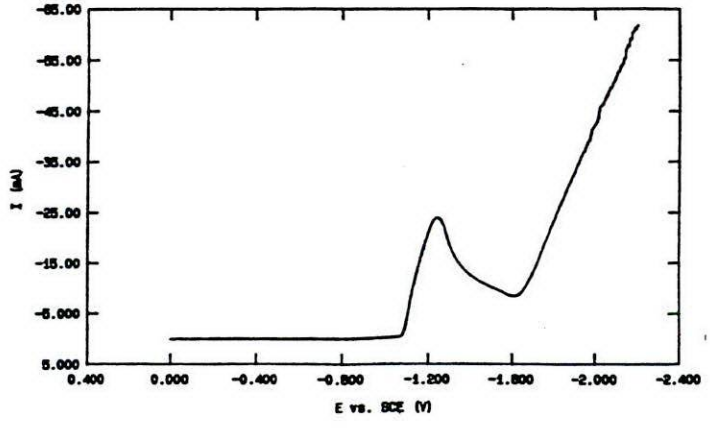

Figure 1c. LSV of Zinc Deposition and Hydrogen Evolution

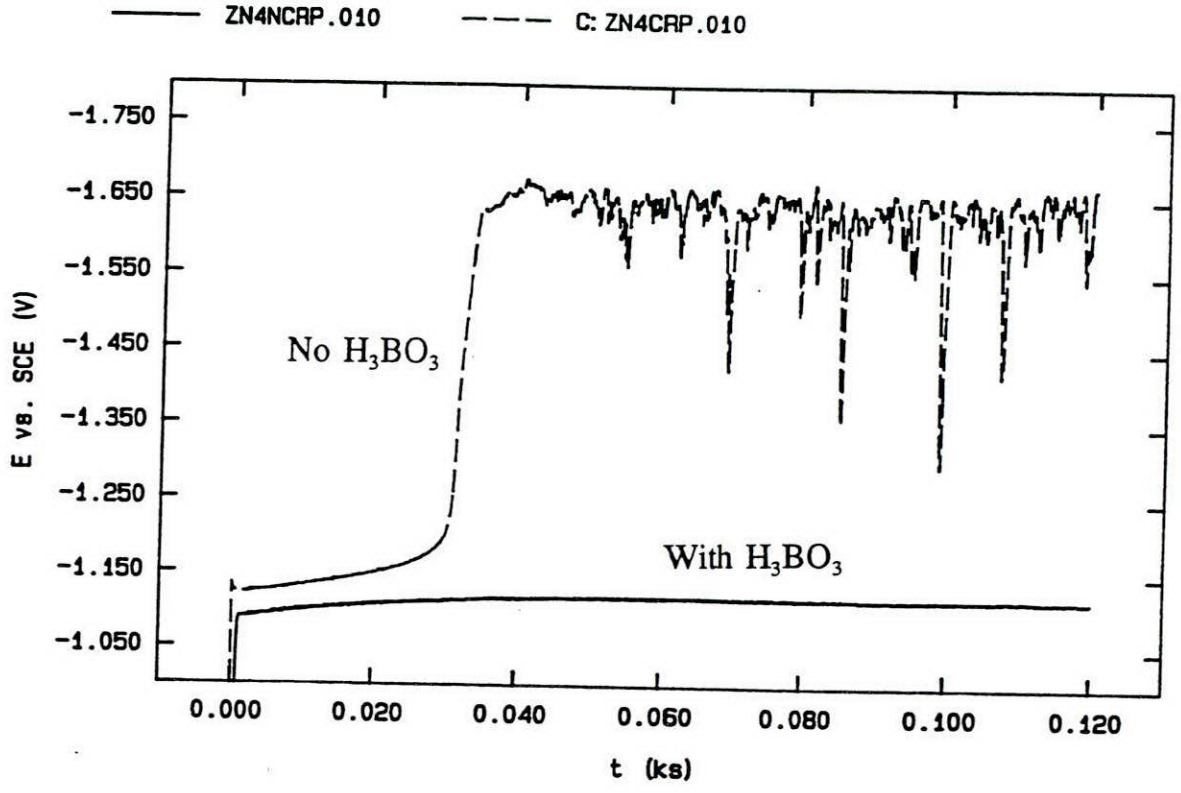

Figure 2. Controlled Current Plots for Zinc Deposited in Absence and Presence of Boric A

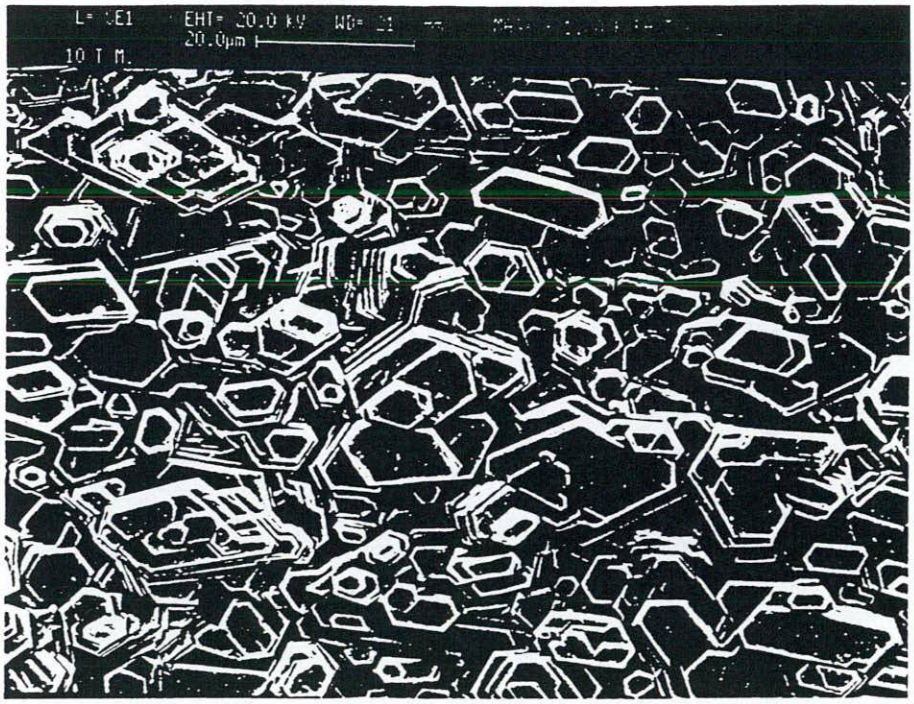

Figure 3. SEM of Zinc Deposit Plated from Additive-Free Solution

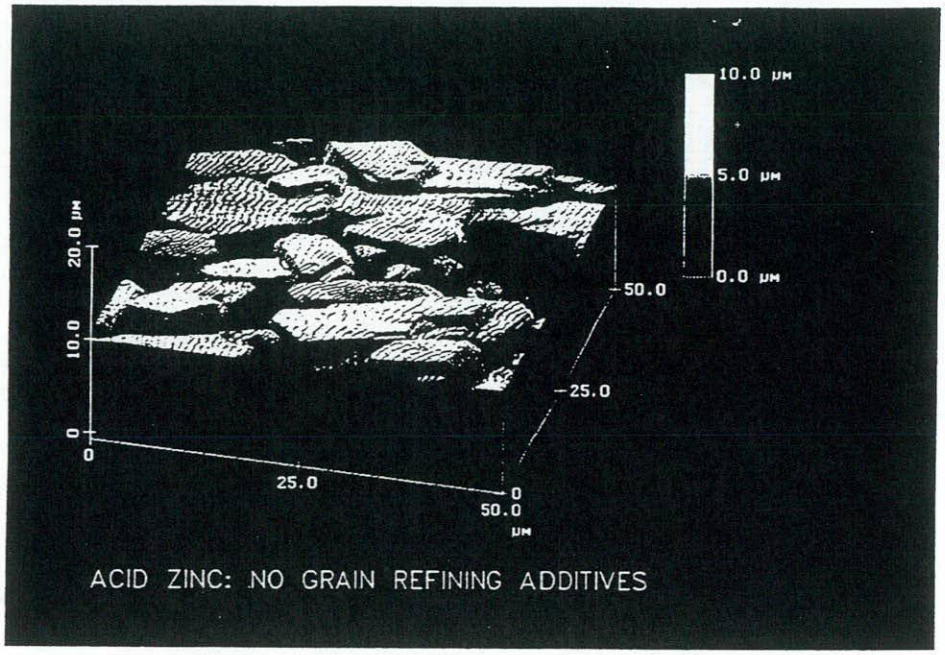

Figure 4. AFM of Zinc Deposit Plated from Additive-Free Solution

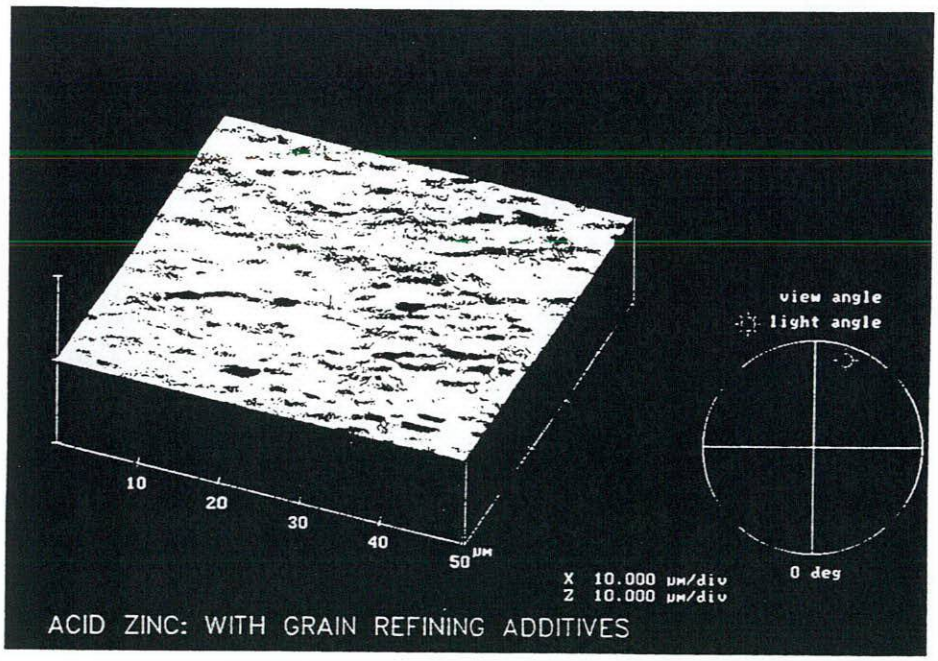

Figure 5. AFM of Zinc Deposit Plated from Zinc Solution Containing Grain Refiners

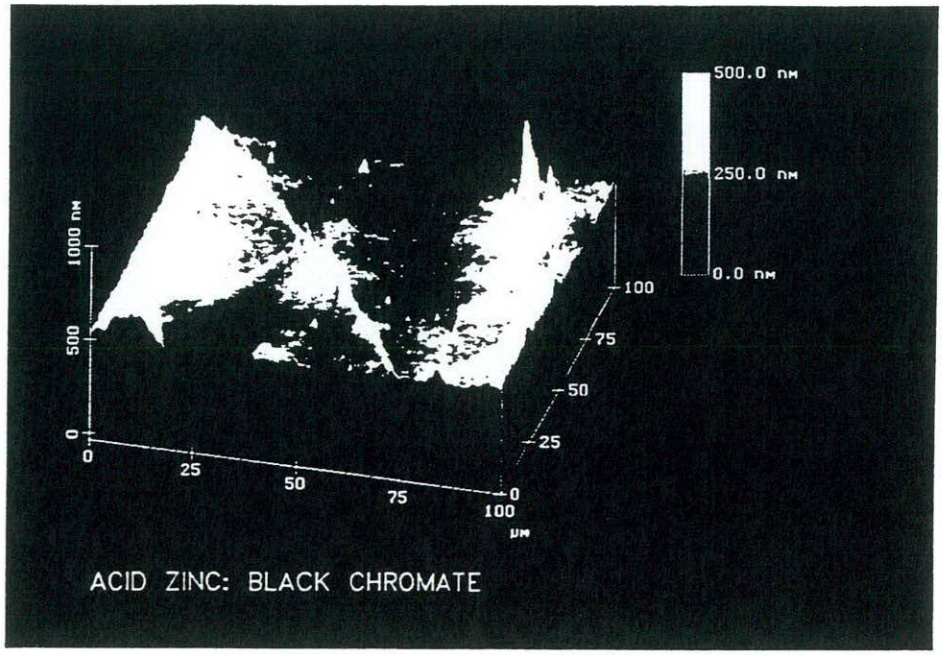

Figure 6a. AFM Image of Black Chromate

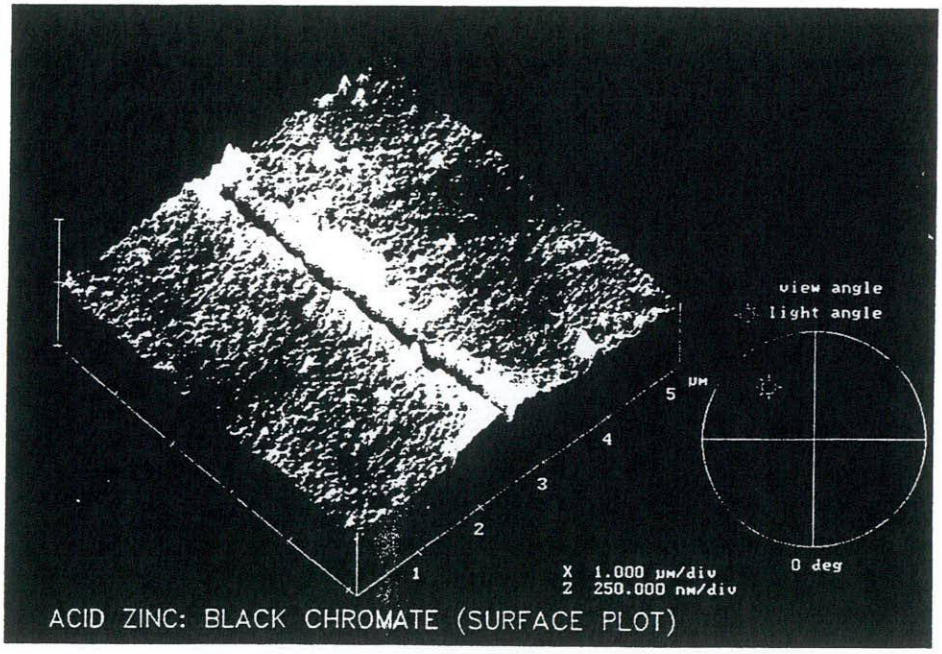

Figure 6b. AFM Image of Black Chromate Coating Showing a Crack

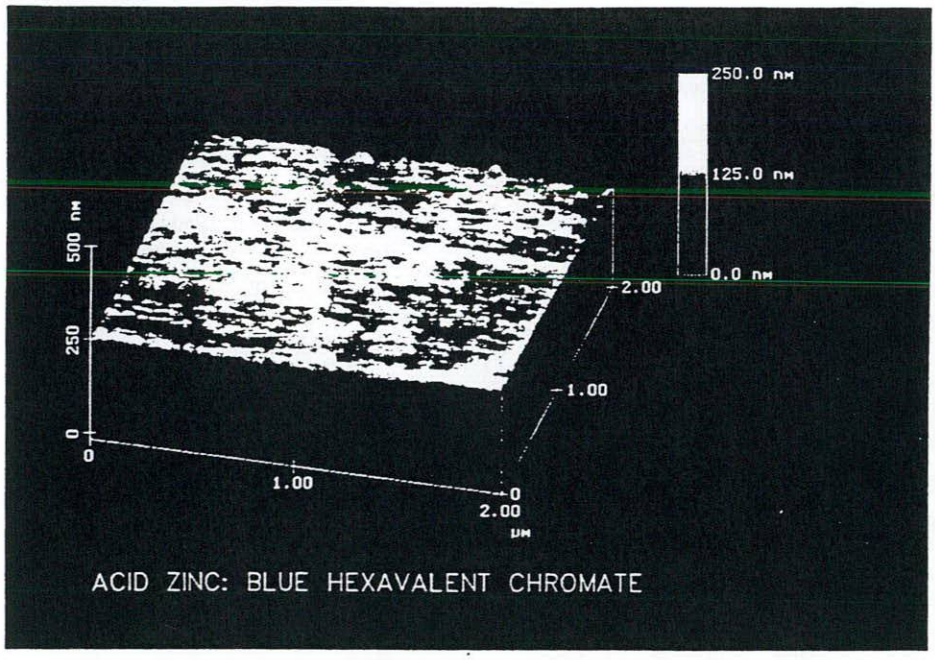

Figure 7. AFM Image of Blue Chromate

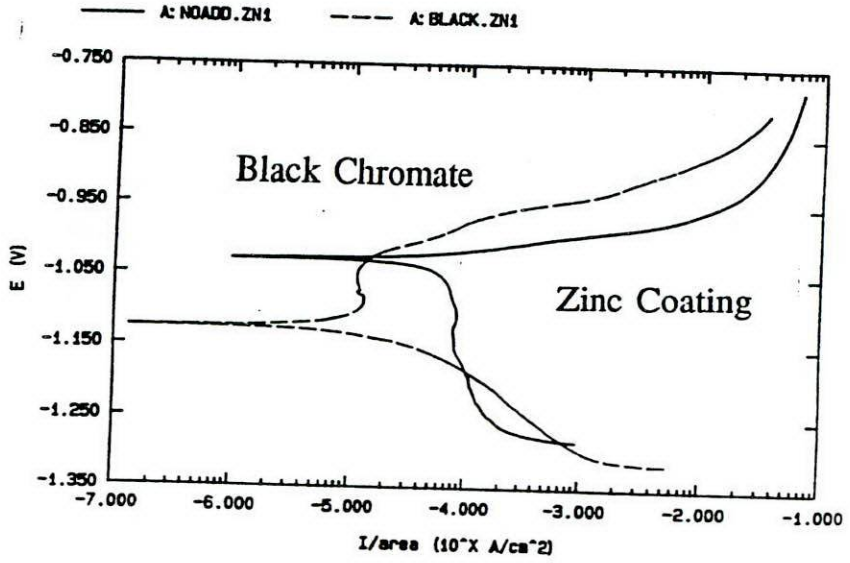

Figure 8. Tafel Plots of Zinc Deposit and Black Chromated Zinc Deposit (Both Additive-Free Zinc Deposits)

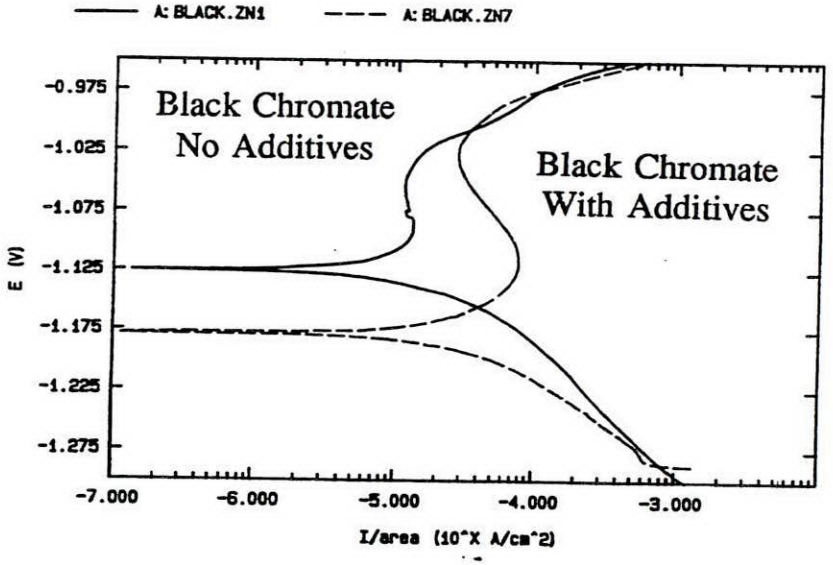

Figure 9. Tafel Plots of Black Chromated Zinc Deposits

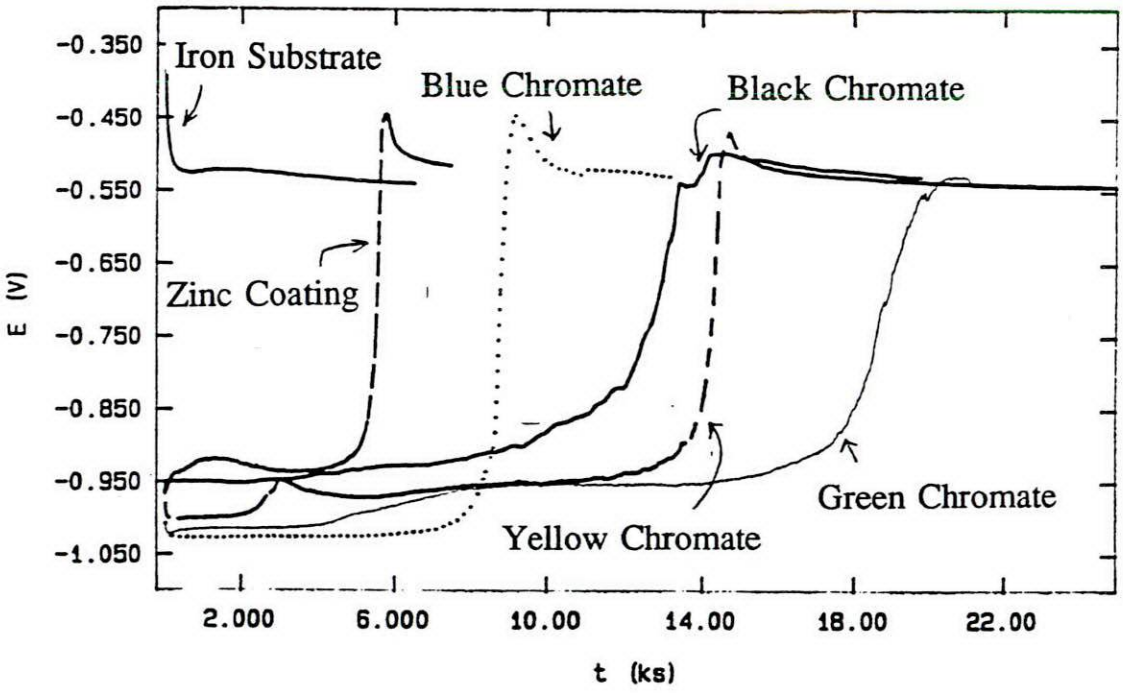

Figure 10. Galvanostatic Plots Showing Relative Corrosion Protection of Zinc and Chromate Films

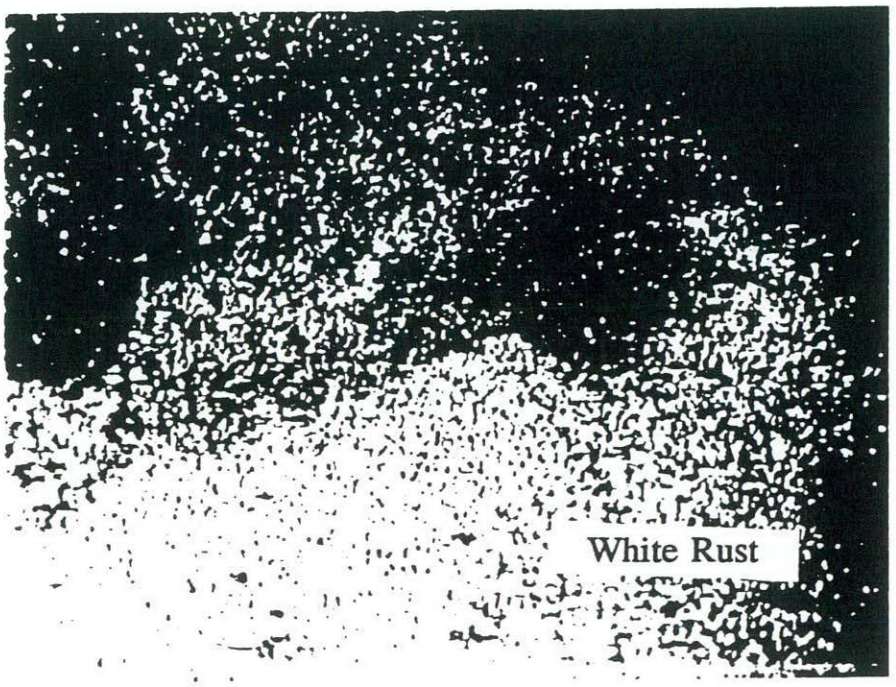

Figure 11a. Optical Image of Zinc Coating After Corrosion Testing

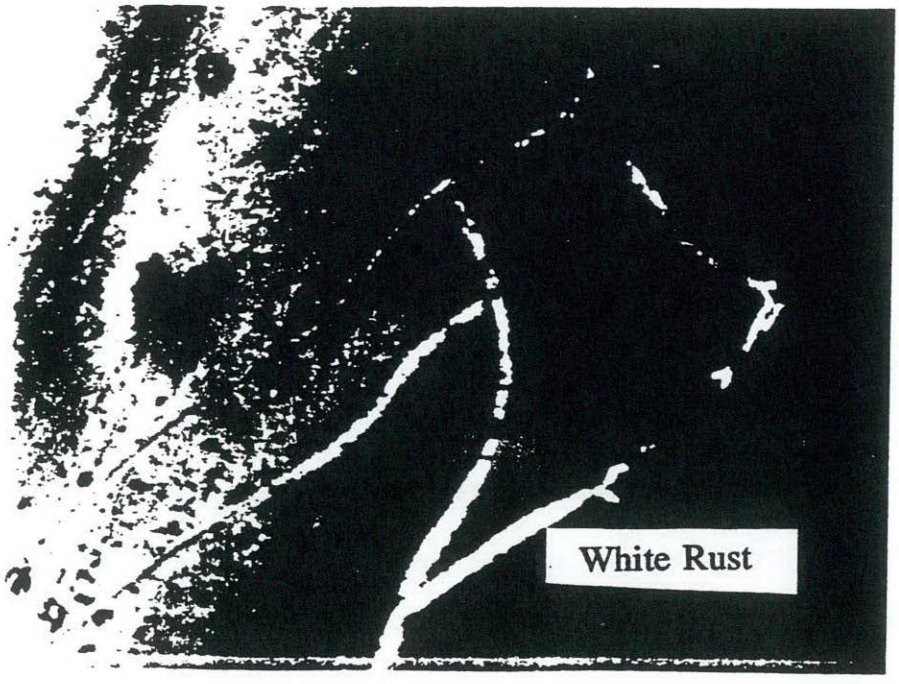

Figure 11b. Optical Image of Green Chromate Coating After Corrosion Testi

Non-Hexavalent Chromium Plating Solution
A Russian Viewpoint

V. N. Kudryavtsev
E. G. Yinokurov
Mendeleyev University
Moscow, Russia

S. R. Schachameyer
Eaton Corporation
Milwaukee, WI

Chromium deposits are used in many industrial fields and for a number of purposes, such as: protective and decorative, corrosion resistance, wear-resistance, hard and heat-resistant coatings. Chromium plating is the fourth most plated metal after Zn, Ni and Cu in terms of total surface area covered in Russia. Only toxic electrolytes based on chromium (VI) salts are used for chromium plating in Russia up to now.

Electrolytic chromium deposits were first obtained from solutions based on chromium (III) compounds in the middle of the last century [1]. In 1860-1910, the predominate number of studies were dedicated to the chromium electroplating from solutions of chromium (III) salts. However, in 1905, when the catalytic effect of sulfate anions on chromium electrodeposition from chromic acid solutions was found in the work supervised by Prof. V. Bancroft, Cornell University, USA [2], the studies of trivalent electrolytes virtually ceased for some time, with all attention being focused on chromic acid solutions. Sargent's studies in 1909-1914's, also directed by Prof. V. Bancroft, allowed the development of chromium plating electrolytes [3] which is used as a basis up to now. In Germany, independently from Sargent, but almost at the same time, chromium plating was studied by A. Libreich. Moreover, the principal Libreich patent [4] was publicized a month before G. Sargent's paper.

In the 20th century, virtually simultaneous but independent development and industrial implementation of chromium plating technologies took place in America and Europe. In the USA, it was mostly a protective and decorative chromium plating, and as a hard chromium plating in Germany.

Chromium plating, in particular wear-resistant uses, has found wide utility in Russian industry too. It is exemplified by the fact that a book dedicated to practical chromium plating from hexavalent electrolytes was written in Russia in 1932 [5].

Some of the first research of trivalent electrolytes in Russia was conducted under the direction of Prof. A. V. Pamfilov [6].

He studied chromium electroplating from sulfate solutions. Prof. V. I. Lainer, who studied chromium plating from a bath containing $KCr(SO_4)_2$, and reached a conclusion that trivalent baths are not promising. He wrote in his book [5] that electrolytes based on the chromium (III) compounds and the coatings obtained from these baths have a number of drawbacks preventing the possibility of their practical usage.

After the World War II Russian scientists returned to the study of trivalent chromium plating electrolytes. In the 50-70's, Professors N. T. Kudryavtsev and A. I. Falicheva made a major contribution to the study of chromium plating solutions based on chromium (III) compounds in Russia.

The influence of chromium (III) compound modifications on the electrodeposition from solutions based on chromium sulfate or perchlorate and containing urea, formaldehyde, monoethanolamine and other additives was studied by A. I. Falicheva et al. [7]. They found, that it was impossible to obtain bright chromium deposits from baths, containing the "violet" modification of chromium (III) compounds, which corresponds to the "simple" $[Cr(H_20)_6]^{3+}$ ions. The chromium deposits have a gray color, were brittle and easily delaminated from a substrate. Bright chromium deposits, but at a low C. E. (<10%) were obtained from electrolytes containing the "green" modification of chromium salts, representing complexes of chromium with OH^- and $S0_4^{-2}$ ions. A peculiar ratio of chromium (III) compounds having "violet" (about 70%) and "green" (about 30%) modifications was needed to obtain deposits of a good quality. New procedures for chromium solutions preparation was suggested. A prolonged electrolyte aging, dummy electrolysis or addition of Cr^{2+} compounds were recommended to accelerate the modification reactions of chromium compounds and to obtain the optimum ratio of "green" and "violet" forms of chromium salts.

In-depth studies on chromium plating and on the electrodeposition of Cr-Ni, Cr-Fe and Cr-Co alloys from chromium (III) solutions were conducted under the direction of N. T. Kudryavtsev [8]. N. T. Kudryavtsev was one of the first who studied electrolytes containing chromium glycerin complexes. It was revealed that an increase of glycerin concentration in the solution decreases chromium C. E. but produces chromium deposits of a better quality. The suggested chromium plating bath has the following composition: $Cr_2(S0_4)_3 \cdot K_2S0_4 \cdot 24H_20$ 340 g/l, NH_2CH_2C00H 150-250 g/l, pH 1.9-2.9; T-20-30°C, C.D. 30-40 A/dm_2; graphite anodes, C.E. = 14-17%. Fe, Ni, or Co salts incorporated into the bath allowed deposition of chromium alloys with these metals.

Baths of a more simple composition were developed in Kudryavtsev's laboratory in addition to complex chromium plating baths. For example, the following electrolyte was recommended for a "milky" Cr-(10%)Fe alloy plating in moles/liters(M/L): $Cr_2(S0_4)_3$ 0.5, $(NH_4)_2S0_4$ 2.5, $FeS0_4 \cdot 7H_20$ 3-10, pH 2.3-2.7, T-40°C, C.D. 8-10 A/dm^2, magnetite anodes, C. E. was up to 30%.

Professors B. L. Zabotin, A. T. Vagramyan, and R. J. Agladze should be noted amongst other Russian scientists who made contribution to the development of chromium (III) plating.

A number of Institutes continued the investigation of the trivalent electrolytes in 70-80's. At that time about 3 to 5 papers, dedicated to a trivalent chromium plating, were published in Russia a year. Now, the research in this field is carried out mainly in four Russian scientific centers: in Moscow's Mendeleyev University; Karpov Physical Chemical Institute; Metallurgical Institute and in the Kazan Technological University.

In the above work, attempts were made not only to study Cr electroplating conditions, but also to discover the mechanisms of Cr electrodeposition from Cr (III) electrolytes.

On the basis of this research work, the difficulties in Cr plating from Cr (III) bath were identified. They are: low pH chromium hydroxide formation and low electrolyte buffering capacity; the formation of great variety of complex ions differentiated in chemical composition, stability, reactivity, etc., which complicates the electroplating of Cr. The other drawbacks of the Cr (III) bath in comparison with the Cr (VI) bath are: more complicated bath composition, lower thickness of coating, more expensive chromium salts (in Russia), more sensitivity to accidental admixture ions, lower conductivity of the electrolyte and therefore a higher necessary electrolysis voltage. The oxidation of Cr^{3+} to Cr^{6+} at the anode is very undesirable, because Cr^{6+} ions upset the cathode process, lowers the C.E. and deteriorates the surface appearance of the coating.

There are some other reasons that could help to explain the situation with Cr (III) electrolyte research, development and implementation in the Russian plating industry. Many people know that Cr (III) plating process is more complicated than Cr (VI) in operation. One of the main problems which keeps industry from applying the process is the necessity to operate the bath with cathode and anode separation by using separate electrode compartments. Russian plating shops do not like to deal with this complication.

Baths which could be used without electrode separation have also drawbacks. These electrolytes contain both ammonia and chloride ions. Ammonia forms very strong complexes with heavy metals. This complicates to a very large extent the waste treatment of rinse waters. Secondly, such electrolytes are very aggressive. Russians also are very cautious to implement new processes which are not operated somewhere in the country before. Continuous slow-down of industrial production in the last three years in Russia also does not encourage any widespread implementation of new or unknown processes. Because of these difficulties related to Cr plating from Cr (III) bath most Russian electroplaters don't believe the process could be operated in our plating industry successfully. Therefore, there is only one Cr (III) plating bath operated now in the Russian plating industry.

Only some weighty reasons could compel industry to use new processes. There is a new reason today in Russia - a sharp rise of government environmental requirements. This forces the plating industry, not only to improve and install new environmental equipment but also look for and implement the new environmentally safe processes. Therefore we believe that today or very soon the Russian plating industry will seek and want new processes. One of the new processes will be Cr plating from Cr (III) bath.

The advantages of trivalent baths should be decisive if it could be possible to overcome their main shortcomings. The advantages of trivalent solutions are: The electrochemical equivalent is twice as large as that for Cr(VI) baths; higher C.E. and deposition rate; higher throwing and covering power; lower chromium concentration in a solution. And, lastly, presence of chromium in a bath only in the non-toxic trivalent state is the one of the major advantages of the trivalent bath over the toxic hexavalent bath.

Electrodeposition of relatively thick, wear-resistant coatings having microhardness comparable with that of a coating from hexavalent baths - is one of the main problems that must be solved in the future.

In our earlier work [9] it was shown that amorphous Cr-P alloys having extremely high corrosion resistance (especially in hydrochloric acid) are deposited from hypophosphite-containing chromium (III) electrolytes.

When studying trivalent electrolytes we addressed the two main goals: 1) to become closer to understanding the chromium electrodeposition mechanism; 2) to develop a bath without ammonia and chloride ions which allows deposition of hard wear-resistant coatings with a thickness up to 10μ.

In the present work, which is a part of these studies, the influence of electrolysis conditions on the phosphorus content of the alloy, deposit microhardness, wear-resistance, surface morphology and on the limiting thickness for good quality Cr-P coatings were studied. This work was done jointly by Mendeleyev University (Russia) and Eaton Corporation (USA).

The initial bath was of the following composition (g/l): $Cr_2(SO_4)_3$ $6H_20$-250; $Al_2(SO_4)_318H_20$ -120; Na_2SO_4 - 60; $NaH_2PO_2 \cdot H_20$ -20; $CO(NH_2)_2$ - 70; pH 1,5; C.D. 45 A/dm^2,t 35°C. All parameters are maintained constant while only one was varied for a parametric study.

Influence of bath composition and electrolysis conditions on the alloy composition and limiting thickness of a coating.

Variation of the current density influences the concentration of P in the alloy and C.E. to a great extent. It could be seen in Fig. 1 that the phosphorus content of alloy drops from 17 to 9 wt. %, and C. E. for the alloy increases from 7 to 16% when the C.D. increases from 32 to 60 A/dm^2. Cr-P alloys containing from 7 to 16% of phosphorus have an amorphous structure. Desirable quality coatings (bright and semi-bright) are deposited over a wide range of C.D. from 20 to 60 A/dm^2.

However, the quality of deposits obtained from the above-mentioned bath deteriorates with growth of the deposit thickness, especially at high C.D. Influence of the aluminum sulfate concentration, pH, and C.D. on the limiting thickness for good quality deposits was studied to optimize a bath composition and electrolysis conditions.

The limiting thickness (l_{Lim}) of the deposit depends on the concentration of aluminum sulfate in electrolyte. pH and C.D. were also studied. The results are shown on Fig. 2. As can be seen (l_{Lim}) increases with rising aluminum sulfate concentration in the bath (Fig. 2a), decreases with pH and increases with C.D. (Fig. 2b, curves 1 and 2 respectively). The following facts should be considered to explain the observed dependencies.

It is known [10] that chromium deposition from a Cr (III) bath occurs with simultaneous increase of the pH of the solution layer in the vicinity of the cathode up to a pH value for chromium hydroxide formation (pH ~4). The superfluity of the hydroxide concentration in the vicinity of the cathode results in the formation of a film consisting of hydroxide compounds. We believe that existence of the film is an essential condition for the electrodeposition of chromium from Cr (III) bath as well from Cr (VI) bath.

The pH for aluminum hydroxide formation is 3.0, which is less than for chromium hydroxide (pH~4). It therefore is very much likely that in the electrolyte with aluminum sulfate, the hydroxide film contains not only chromium hydroxide but aluminum hydroxide as well. In this case, the properties of the hydroxide films in the electrolytes with and without aluminum sulfate would be different. We believe that the quality and properties of chromium deposit depend on the hydroxide film composition and properties of it. In this connection one of the possible explanations of the dependencies shown on Fig. 2a and 2b could be related to changing of the hydroxide film composition and its properties with the changing of the aluminum sulfate concentration in the electrolyte.

We are not able to directly investigate the hydroxide film composition itself. But we know that constituents of hydroxide film are included in the coating during electrodepositon of chromium. Therefore, in making qualitative and quantitative analyses of the inclusions in the coating which depend on electrolyte composition, we can make conclusions about the hydroxide film composition.

In our particular case we have studied the amount of aluminum in the coating which depends on C.D., pH, aluminum and urea concentration in the electrolyte. We did this study with the application of the JSM-35 X-ray microanalysis unit.

Experimental data for the influence of C.D., concentration of urea, aluminum sulfate and pH on the aluminum content of the coating are shown in Table 1. It is evident that aluminum content of the deposit greatly depends on the above-mentioned parameters: aluminum content of deposit increases with concentration of aluminum sulfate in the electrolyte and decreases with urea concentration, C.D. and pH increase.

Taking into consideration the formation of a cathodic film and variation of the composition and properties of the latter depending on the above mentioned conditions, the results obtained can be explained in the following way.

Increase of the aluminum concentration in the electrolyte should give rise to the growth of aluminum hydroxide compounds in a cathodic film and, consequently, to the increase of the amount of aluminum included into the deposit.

Under the same electrolysis conditions, the greater the pH value of the bulk solution, the higher will be pH of the solution layer adjacent to a cathode surface (near-cathode layer). It is believed that the increase of the pH of the near-cathode layer should increase the cathode-film content for a metal having high pH value of hydroxide formation; that is, chromium. The quantity of hydroxide aluminum compounds in the film are bound to become lower thus resulting in a decrease of aluminum inclusions into deposits.

There are two possible reasons for the decrease of aluminum inclusions with the increase of the current density. In the first place, increase of the C.D. is accompanied by the increasing pH value of the near-cathode layer, thus lowering the aluminum inclusions which can be explained by the scheme shown above. Secondly, it seems quite possible that inclusion of impurities into the coating is controlled by a absorption-diffusion mechanism. In this case, the impurity content of deposits should decrease with current density by the law of the diffusion kinetics [11].

The decrease of the aluminum content of a deposit with an increase of urea concentration can only be related to an aluminum - urea complex formation. An increase of urea concentration increases the fraction of the complexes and give rise to the change of their structure. It could lead to the increase of pH value for aluminum hydroxide formation resulting in lowering the aluminum concentration both in the near-cathode layer and in the coating.

Good correlation between factors influencing (i_{Lim}) and the amount of aluminum in the deposit is evident from Table 1. The interrelationship of (i_{Lim}) vs. aluminum amount in the coating was plotted using the above-mentioned results (Table 1 and Fig. 2). Aluminum in the coating was varied by changes of aluminum and urea concentration in the electrolyte, current density and pH (Table 2). It is obvious from these results that the change of any parameter resulting in the growth of aluminum concentration in the coating is accompanied by increase of (i_{Lim}), the latter being directly proportional to the aluminum amount in the deposit. From our point of view, these results provide rather strong evidence of a cathode "film" existence and of the influence of its composition on the process of chromium electrodeposition from Cr (III)-electrolytes. The correlation coefficient for the relationships presented on Fig. 3 is 0.91, this value being well over the critical one measuring 0.53 (the significance level is 0.05).

Table 1

Influence of aluminum sulfate and urea concentration in a bath, C.D. and pH on Al content in the coating.

$Al_2(SO_4)_3.18H_2O$g/l	Urea, g/l	C.D., A/dm^2	pH	Al wt.%
0	70	46	1.3	0.0
60	70	46	1.3	0.29
120	70	46	1.3	0.50
180	70	46	1.3	0.41
120	0	46	1.3	0.51
120	3b	46	1.3	0.43
120	70	46	1.3	0.50
120	105	46	1.3	0.32
120	140	46	1.3	0.18
120	70	32	1.5	0.85
120	70	39	1.5	0.66
120	70	46	1.5	0.54
120	70	53	1.5	0.32
120	70	60	1.5	0.33
120	70	46	1.1	1.03
120	70	46	1.3	0.50
120	70	46	1.5	0.54
120	70	46	1.7	0.27

SURFACE MORPHOLOGY

The surface morphology of a Cr-P alloy coating was studied on the SEM. The surface was cleaned prior to analysis. The surface of the coating was found to contain microcracks, pores and micro-spheroids (nodules). The number and size of micro-spheroids were shown to increase when the C.D. rises (Table 2) and the physical appearance of the coating changes deposits from bright to matt.

TABLE 2

Influence of C.D. on the number (N) and size (d) of nodules: Coating thickness 3μm, t=35°C.

I, A/dm	N, nodules/cm	d, μm
40	60	0.25-0.33
46	105	0.33-0.50
55	175	0.50-0.66
62	225	1.16-1.33

The number and size of modules also depends on the electrolyte temperature. By way of example, the size of the nodules are 0,3-0,5 μm at 35°C 0,8-1,0μm at 25°C, all other plating conditions remaining the same. The number of nodules increases when the temperature is decreased. The phenomena for the formation of nodules on the chromium

alloy coating surface is known and from the surface appearance standpoint there are no defects. The physically visible surface usually does not change when nodules begin to emerge, but coating properties could be changed to some extent.

Microcracking of deposits was determined microscopically at the magnification x400. It was shown that the number of microcracks per unit length increases with deposit thickness (Fig. 4) and reaches the value about 90 cracks per mm (deposit thickness of 4-7μm). The microcracking of chromium coatings obtained from hexavalent electrolytes is about 1-2 cracks/mm [12] at the deposit thickness of 20-25μm. Consequently, the chromium-phosphorus alloy deposits is much more microcracked compared with conventional chromium coatings.

MICROHARDNESS

A standard Russian hardness measuring device was used to study chromium microhardness. Hardness was determined by forcing a diamond pyramid (loading weight 50g) into the coating and measuring the size of the indentation.

The thickness of coatings which can be obtained in our bath of the optimum composition (without ammonia and Cl) is less than 10μm. As is well known, reliable results can not be obtained when measuring hardness of thin coatings by forcing a diamond pyramid normal to the surface. Thus, comparison hardness measurements were done both on the deposit surface (for deposits of various thickness) and on deposit cross-sections.

Fig. 5 gives microhardness results obtained on the deposit surface. As illustrated in Fig. 5 the microhardness values do change with deposit thickness: microhardness rises from 460 to 570 kg/mm^2 (curve 1) when thickness of deposits increases from 1.8 to 8 microns. Similar dependence is observed after deposit heat treatment too; deposit microhardness being increased after the heat-treatment.

Microhardness data obtained on the deposit cross-sections are presented along the x-axis. Microhardness of Cr-P alloy deposited at 25 A/dm^2 is about 910 ± 80 kg/mm^2. Deposit hardness increases by a factor of 1.3-1.4 (up to 1200-1300 kg/mm^2) after heating at 350 ± 10°C for 45 min. (Figure 5, curve 2).

Microhardness data obtained on the coating surface and on the cross-sections vs. current density are shown on Fig. 6. It is evident that microhardness measured on the deposit cross-sections is much higher than that on the surface of the coating: microhardness increases from 910 to 1000 kg/mm^2 as the current density changes from 25 to 35 A/dm^2 (curve 1).

WEAR RESISTANCE

There is almost no data in the literature on wear resistance of chromium and chromium alloys from Cr (III) electrolytes. We have carried out comparative investigations of the wear resistance of chromium coatings from CrO_3 electrolyte (C.D. = 50 A/dm^2, t = 50°C) and from Cr (III) electrolyte (t = 35°C, pH=1.3, C.D. = 35 A/dm^2).

Parameters of wear experiments were the following: dry wear, contact pressure 0.6 MPA, rotation speed 100.0 cycles/min. Mass loss of Armco-Fe samples with coating was a criterion of coating wear resistance.

Results of experiments are shown on the Figure 7. As can be seen the base material shows the lowest wear resistance - the biggest mass loss (curve 1). Chromium and chromium alloys coatings do exhibit lower wear. Mass loss of plated samples is much less than unplated samples (Figure 7, curves 2, 3).

However, as can be seen from the comparison of curves 2 and 3 wear resistance of Cr-P alloy is almost one-half that of pure chromium. Results obtained show that there is no direct correlation between coating hardness and wear resistance when testing under conditions of dry friction. The wear-resistance of chromium deposits is higher than that of Cr-P alloy in spite of the higher microhardness of Cr-P deposits (about 1000 kg/mm^2 compared with microhardness of chromium coatings (about 900 kg/mm2). The higher microcracking of Cr-P alloys (Figure 4) is likely one of the reasons for lower wear resistance in the Cr-P coating. Presence of microcracks causes destruction and erosion of the metal deposit during dry friction. The particles resulting from wear of a damaged coating play the role of an abrasive promoting more rapid wear of a deposit. Local temperatures increase during testing which can bring about the increase of the microhardness of Cr-P alloy deposits (Figure 5) and of the wear particles playing the role of an abrasive. This also can lead to the increase wear of deposits.

CONCLUSIONS

The present state of the art of studying and promoting of trivalent chromium plating baths in Russia was provided. The main difficulties hampering the promotion of trivalent chromium plating electrolytes (one of these difficulties is a low thickness of good quality deposits) are considered. It was shown that the condition (state) and/or properties of the cathodic film are the main factors controlling the limiting thickness of Cr-P deposits. It was established that deposits of higher thickness can be obtained by increasing the concentration of aluminum sulfate in the solution and by lowering the buck solution pH and current density. The above-mentioned changes of these factors are accompanied by enrichment of a cathodic film by aluminum hydroxide compounds, probably, resulting in changes of film properties so that electrodeposition of more thick deposits becomes possible.

The electrodeposited Cr-P alloy coatings are characterized by having microhardness compared with chromium deposits from the standard chromium bath. Cr-P alloy deposits have a highly developed network of microcracks. The wear-resistance of these coatings under dry friction wear is somewhat lower than that of Cr (VI) deposits. The Cr-P alloy deposits of a good quality with a thickness of 8-9 μm may be obtained from a bath containing 120-160 g/l of aluminum sulfate at current density up to 40 A/dm^2 and pH of the solution of 1.4.

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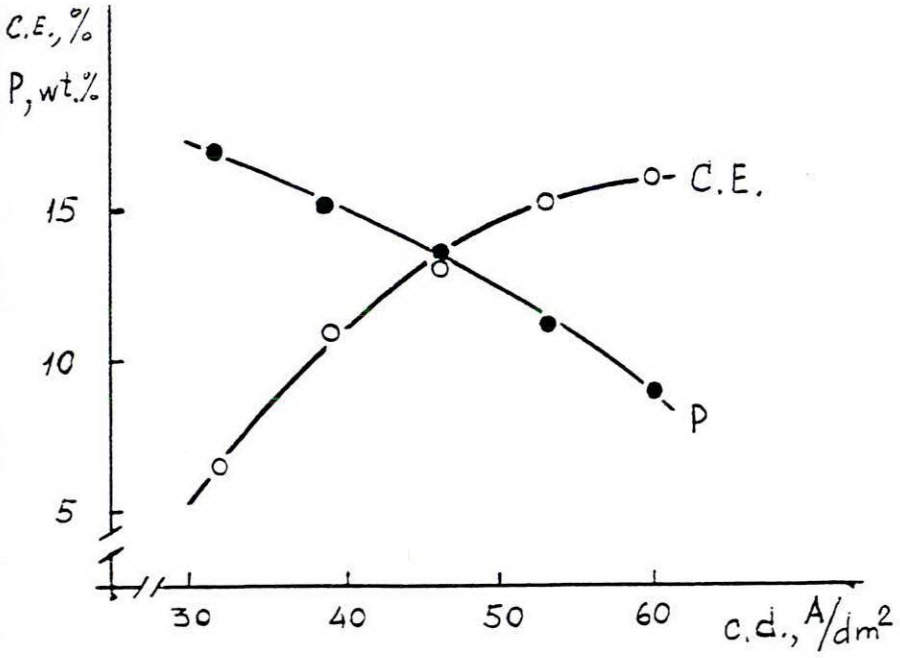

Figure 1
Dependence of the alloy composition and current efficiency on the current density.

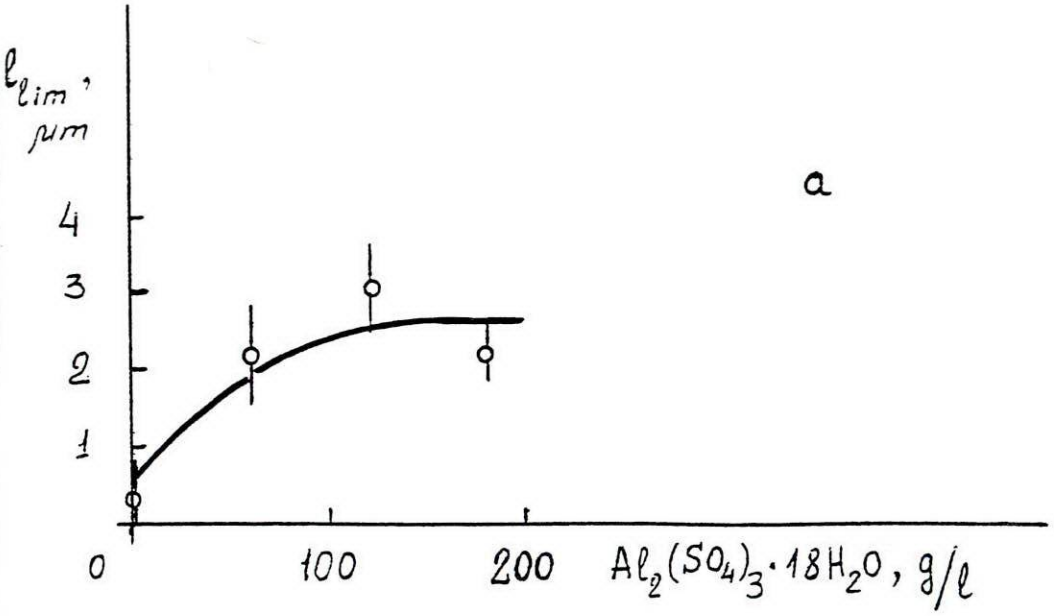

Figure 2(a)
Dependence of limiting thickness for good quality deposits (l_{Lim}) on the aluminum sulfate concentration.

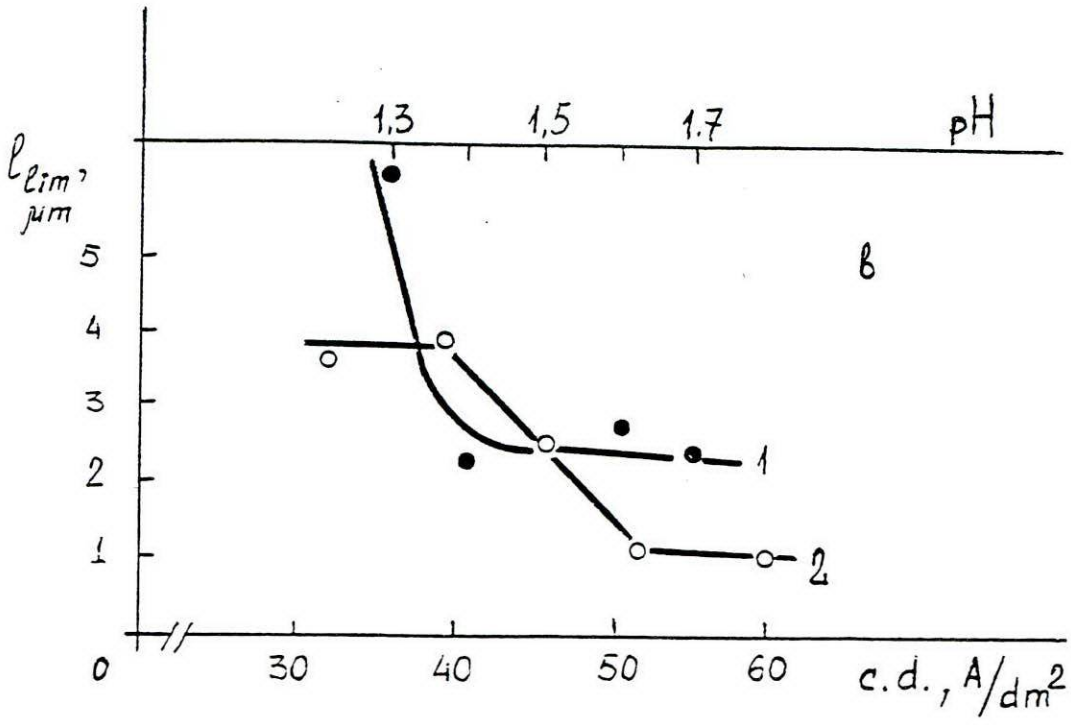

Figure 2(b)
Dependence of limiting thickness for good quality deposits (l_{Lim}) on pH of the bath (1) and current density (2).

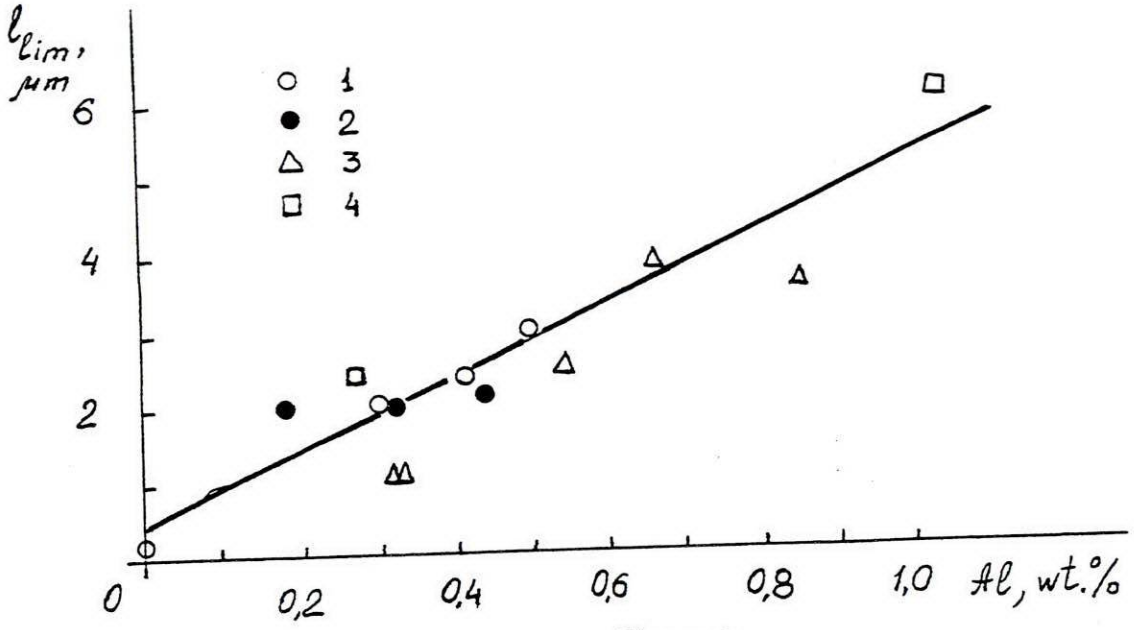

Figure 3
Dependence of limiting thickness for good quality deposits (l_{Lim}) on the aluminum content of the coating at various concentrations of aluminum sulfate (1), urea (2), current density (3) and pH of the bath (4).

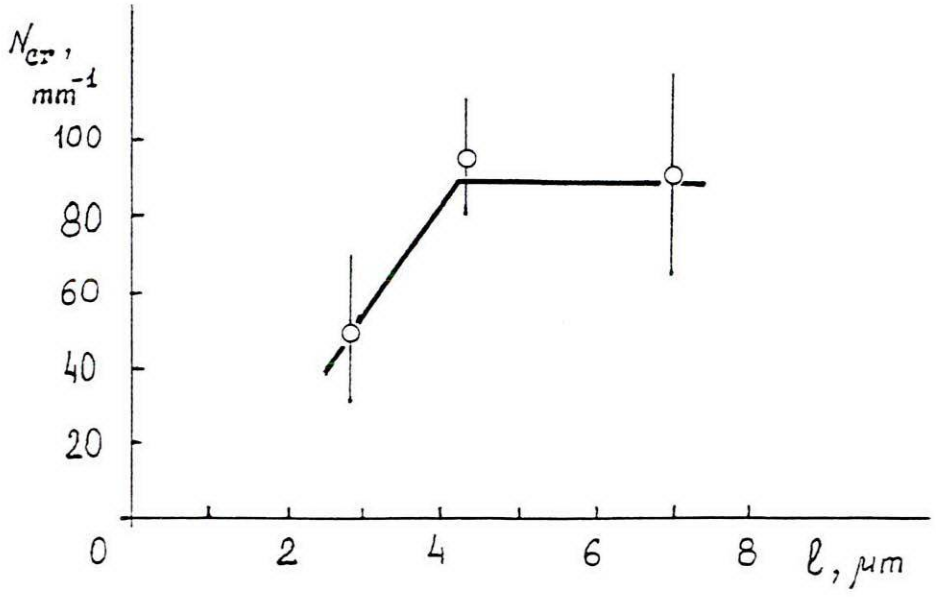

Figure 4

Microcracks number per unit length (N cr) vs. deposit thickness of the Cr-P alloy (temperature 35°C, pH 1.3, current density 25 A/dm^2).

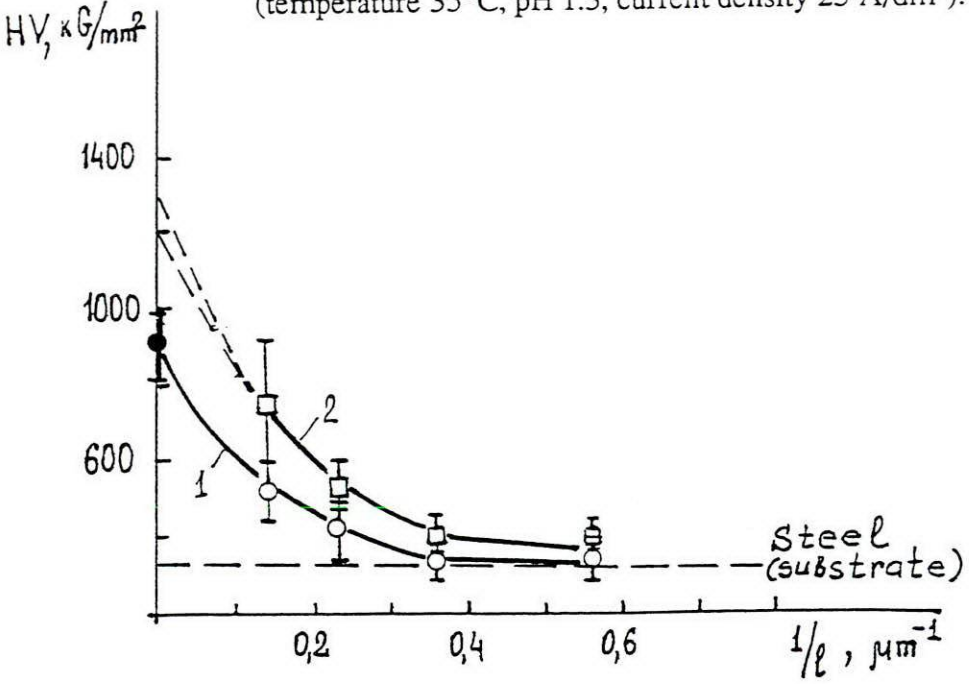

Figure 5

Microhardness of Cr-P alloy deposits (Hv) vs. the inverse deposit thickness before (curve 1) and after (curve 2) heat treatment (temperature 350°C, 45 min.). The crosshatched circles corresponds to microhardness values obtained on the cross-sections.

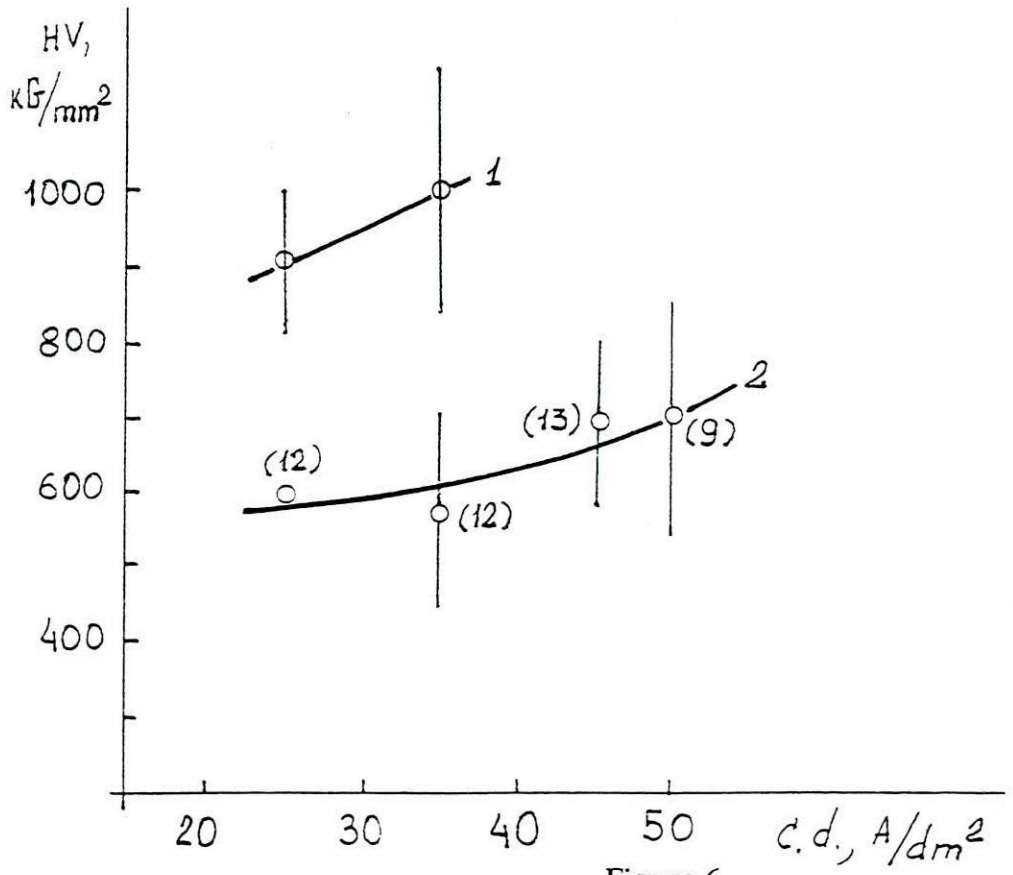

Figure 6

Dependence of Cr-P alloy microhardness on the current density determined on the cross-sections (1) and on the deposit surface (2). Deposit thickness (μm) is indicated by the numbers near circles. Electrolyte temperature 35°C, pH 1.3.

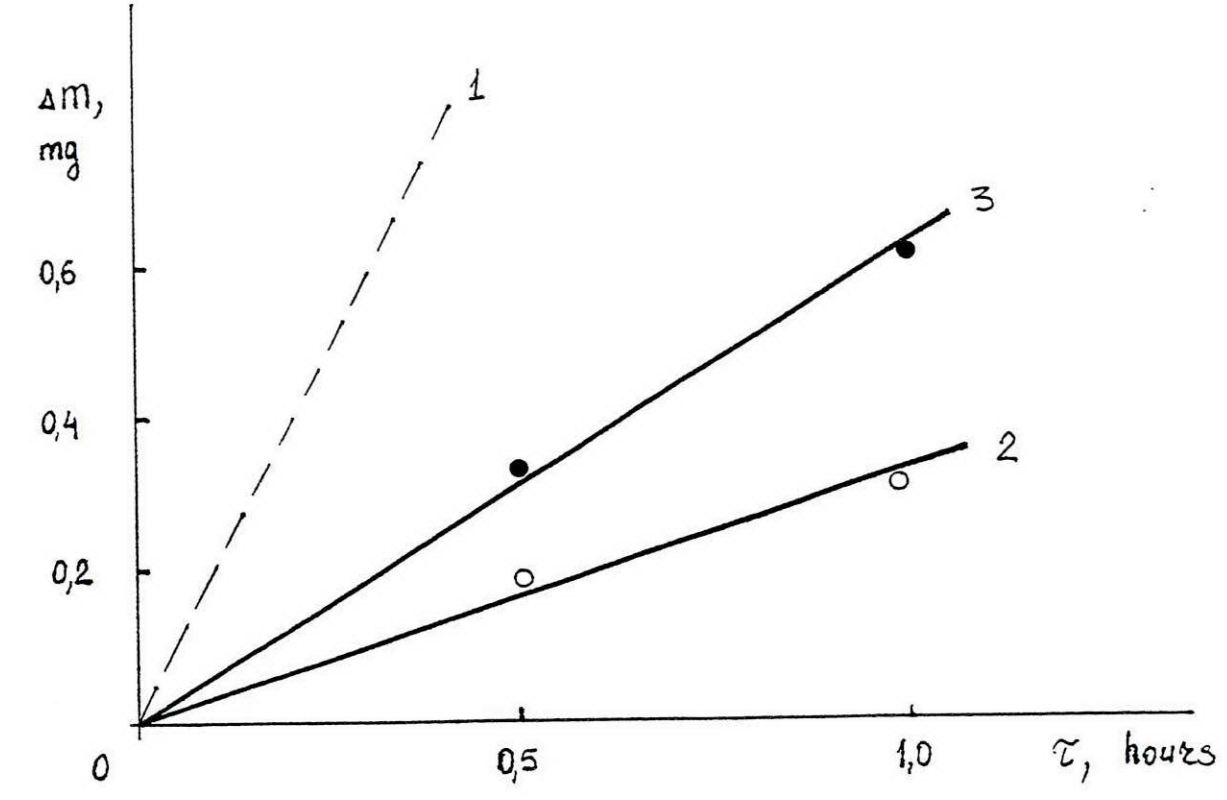

Figure 7

Mass loss Fe-Armco without coating (1), with coating (2) and with Cr-P coating (3) at dry friction vs. time.

Paper Not Available In Time For Publication

Study of Different Processes for Protection & Finishing of Electroplated Parts in the Automotive and Related Industries

Louis Candeil, L. C. Systems, Cugnaux, France

This paper will concern the improvement of corrosion resistance on classic zinc with special finishing by different black passivation and finishing methods. A variety of zinc alloy deposits, such as zinc-iron, zinc-cobalt and zinc-nickel were studied for the effects of thermal shock. The effect of special finishes on these zinc alloy deposits regarding salt spray resistance will be presented. Other physical parameters were also measured, such as gritting oils resistance.

For copies of this paper please contact:

Louis Candeil
General Manager
L.C. Systems
Zone Industrielle Die Casque
20 Rue Aristide Berges
Cugnaux, France 31270
610 76126
FAX: 610 76814

ELECTROLESS GOLD DEPOSITION IN A NON-ALKALINE, CYANIDE FREE BATH

Anne Sullivan, Ajay Patel and Paul A. Kohl
School of Chemical Engineering
Georgia Institute of Technology

ELECTROLESS SESSION
AESF SUR/FIN '94

ELECTROLESS GOLD DEPOSITION IN A NON-ALKALINE, CYANIDE FREE BATH

Anne Sullivan, Ajay Patel and Paul A. Kohl
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Autocatalytic electroless deposition of gold has been investigated in a cyanide free, non-alkaline bath. The bath consisted of sodium gold (I) thiosulfate and sodium L-ascorbic acid. At pH = 6.42, 30 °C, gold is deposited at rates up to 1.5 μm/hr, depending on the bath concentrations of gold thiosulfate and ascorbic acid. However, stability is presently a problem at high deposition rates. At lower deposition rates, bath stability is improved. Cyclic voltammetry is used to explain the characteristics of the gold plating bath.

INTRODUCTION

In the production of multichip modules, electroless plating is a common approach to filling level to level via connections. Electroless deposition is also used for plating of gold in electrical contacts. Conventional electroplating requires an external current source and a contiguous ground plane of metal. Electroless plating uses a galvanic deposition reaction making the contiguous ground plane unnecessary. Since electroless plating selectively deposits metal on catalytic surfaces, the expense and waste is less than unselective physical vapor deposition techniques.

An autocatalytic electroless deposition of gold has been investigated in non-basic, non-cyanide media at near room temperatures. Electroless methods of depositing gold typically operate at pH > 13 and necessitate the use of cyanide as a complexing agent[1-6]. Polymeric materials used in multilayer structures degrade at pH > 10. The presence of cyanide ions in solution is unfavorable because it inhibits the oxidation of many reducing agents and forms HCN in acidic media. This investigation focuses on developing a bath using gold thiosulfate as the gold complex and L-ascorbic acid as the reducing agent.

Electroless gold deposition consists of a chemical reduction of a gold complex coupled with a catalytic chemical oxidation reaction. The electroless plating of gold must occur autocatalytically on the initial and deposited gold surfaces to produce sufficient layer thickness, without homogeneously producing gold throughout the solution. Other considerations in developing an electroless gold plating bath include the bath stability and the deposition rate for various bath conditions.

BACKGROUND

Electroless plating proceeds as two simultaneous reactions on the gold surface: the reduction of the gold complex to gold and the oxidation of a reducing agent.

Oxidation reaction: $R \rightarrow R^{+n} + ne^-$

Reduction reaction: $AuL_m^n + e^- \rightarrow Au + mL^{(n-1)/m}$

R is the reductant, R^{+n} is the oxidized species and AuL_m^n is the gold (I) complex with $L^{(n-1)/m}$ being the ligand. The overall deposition reaction can be explained using these partial reactions and the mixed potential theory. The mixed potential theory states that the partial reactions occur simultaneously at the same electrochemical potential. In order to use the mixed potential theory to predict autocatalytic deposition, the redox potential of the reductant must be more negative than the reduction potential of the metal deposition and that the oxidation must proceed catalytically. If the redox potential of the reductant is more positive than the reduction potential of the gold complex, no deposition of gold occurs. If the reducing agent is not catalytically oxidized on gold, gold is homogeneously reduced throughout the solution.

At the mixed potential, the anodic current of the reducing agent, in the absence of the metal ions, equals the cathodic current of the metal deposition, in the absence of the reducing agent, and corresponds to the theoretical deposition rate. The mixed potential theory predicts the deposition potential and rate of deposition if the rate determining step and the catalytic properties of the electrode surface do not change over the potential range of interest and are identical to the catalytic properties of the gold substrate used in the electroless baths.

The redox potential of the oxidation and reduction reactions are a function of pH and bath composition. The partial reaction rates are limited by the concentration of the electroactive species, mass transport, kinetic limitations and the temperature of the solution. Cyclic voltammetry is the technique used to investigate the partial reactions involved in the electroless gold deposition. Results from the voltammogram comparisons confirm ascorbic acid as the best reducing agent for gold thiosulfate. Cyclic voltammetry is also used to determine the effect of pH, concentration of reactants and reduction products on the

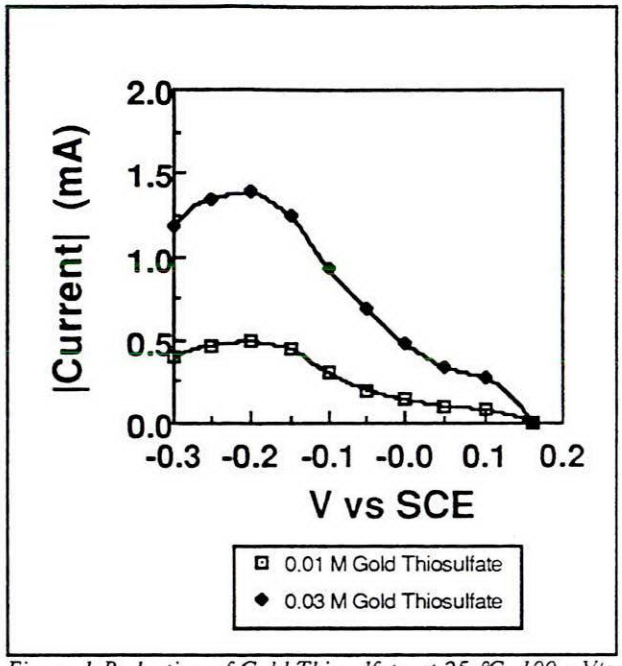

Figure 1-Reduction of Gold Thiosulfate at 25 °C, 100 mV/s, on Au Electrode.

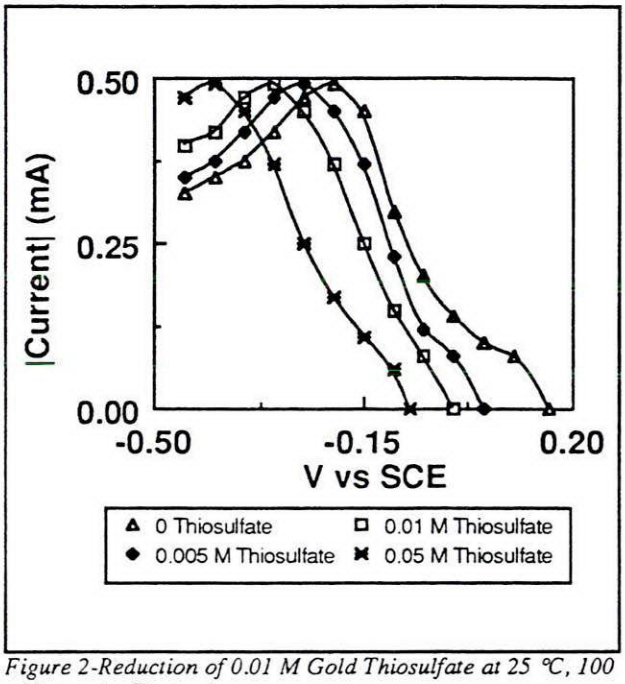

Figure 2-Reduction of 0.01 M Gold Thiosulfate at 25 °C, 100 mV/s, on Au Electrode.

reduction of gold thiosulfate and the oxidation of ascorbic acid.

SELECTION OF GOLD COMPLEX

Gold electroplating and electroless plating baths commonly use potassium gold (I) cyanide, $KAu(CN)_2$, as the gold complex[1-6] because of its high stability and solubility.

$Au^+ + 2\,CN^- \leftrightarrows Au(CN)_2^-$ $K_{st} = 10^{39}$ (7)

These baths have cyanide ions present in solution, which inhibit the oxidation of many common reducing agents[1, 3]. A cyanide free gold complex with reasonable stability and a reduction potential more positive than the reduction potential of $Au(CN)_2^-$ is preferred. Gold thiosulfate is soluble and highly stable in solution[7].

$Au^+ + 2\,S_2O_3^{-2} \leftrightarrows Au(S_2O_3)_2^{3-}$ $K_{st} = 5 \times 10^{28}$

According to the Nernst equation, a gold complex with a higher stability constant is more difficult to reduce than a gold complex with a lower stability constant. Therefore, gold thiosulfate reduces at a potential more positive than gold cyanide[8, 9].

$Au(S_2O_3)_2^{3-} + e \rightarrow Au + 2S_2O_3^{2-}$ $E^0 = 0.153$ V vs NHE

These characteristics of gold thiosulfate fulfill the desired criteria for the autocatalytic deposition of gold in non-basic and non-cyanide media.

REDUCTION OF GOLD THIOSULFATE

The voltammogram of the gold thiosulfate reduction is shown in Figure 1. Gold thiosulfate is reduced within the potential range of 0.15 V and -0.3 V vs SCE. The cathodic current increases with the gold thiosulfate concentration. Since the pKa's of thiosulfate[10] are 0.6 and 1.6 and the investigated pH region is between 4 and 10, the gold thiosulfate reduction is independent of pH, unlike the gold cyanide reduction. The voltammograms shown in Figure 1 are for a 9.2 pH buffered solution, but are characteristic of the gold reduction reaction for all pH's investigated. Electroless reduction of gold thiosulfate at the pH's investigated is limited to the potential range of 0.15 V to -0.3 V vs SCE.

By the use of a rotating ring disk electrode, the reduction products have been identified as two thiosulfate ions for every one gold thiosulfate ion reduced. The accumulation of thiosulfate ions adversely effects the gold thiosulfate reduction by shifting the electroreduction to more negative potentials. Figure 2 shows the reduction moving 0.04 volts negatively when the thiosulfate concentration doubles. If the concentration is increased by ten, the reduction shifts 0.12 volts in the negative direction. The ultimate effect of this thiosulfate accumulation is the inhibition of the autocatalytic reduction in the electroless bath. In other words, as the thiosulfate concentration increases the deposition rates will decrease.

SELECTION OF REDUCING AGENT

Several reducing agents have been used in conjunction with gold cyanide in electroless gold

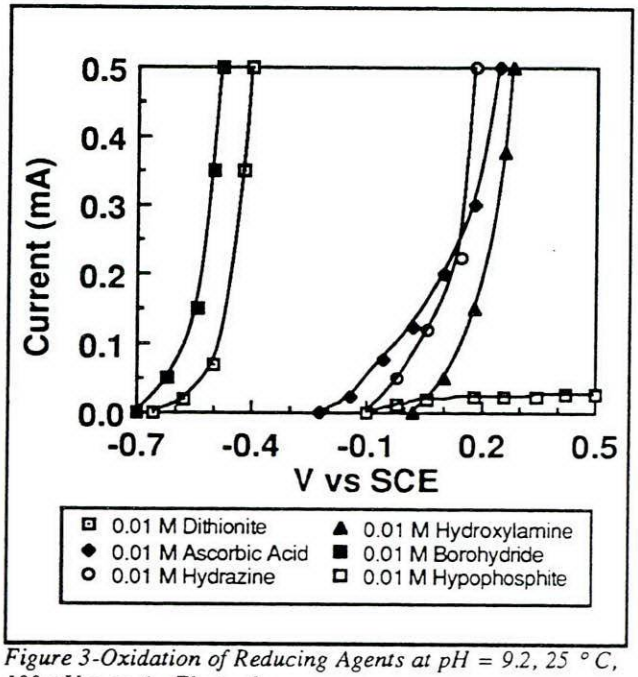

Figure 3-Oxidation of Reducing Agents at pH = 9.2, 25 °C, 100 mV/s, on Au Electrode.

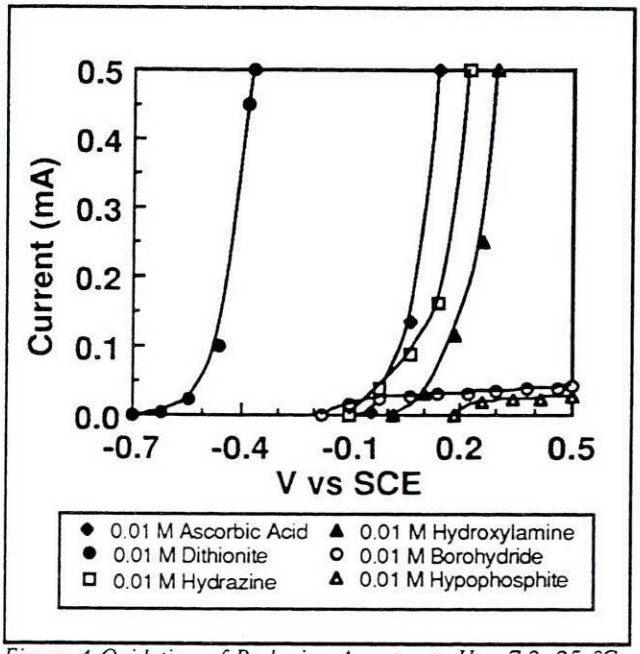

Figure 4-Oxidation of Reducing Agents at pH = 7.2, 25 °C, 100 mV/s, on Au Electrode.

plating baths. Borohydride, dimethylamine borane, hydrazine and hypophosphite have been used as reducing agents for the autocatalytic reduction of gold (I) cyanide and gold (III) cyanide complexes in electroless gold baths[1-3, 5-6]. However, all of these baths operate at high pH. Other baths using borohydride, dimethylamine borane and hypophosphite with $Au(SO_3)_2^{3-}$ or $AuCl_4^-$ have been developed, but also operate at high pH[2]. Hydroxylamine reduces gold (I) cyanide on Ni and n-GaAs surfaces at low pH, but the reduction is not autocatalytic[2, 4-5]. Thiourea, dithionite and ascorbic acid have also been proposed as strong reducing agents for gold[5, 11]. However, only ascorbic acid oxidizes catalytically on gold in the potential region defined by the gold thiosulfate reduction.

Cyclic voltammograms of the anodic behavior of several reducing agents at pH = 9.2 are compared in Figure 3. The strongest reducing agents, dithionite and borohydride, oxidize at potentials more negative than the gold thiosulfate reduction potential region. When the reducing agent oxidizes this easily, reduction occurs homogeneously rather than heterogeneously. The slow oxidation of hypophosphite is characteristic of a weak reducing agent. Hydroxylamine, hydrazine and ascorbic acid oxidize on gold in the gold thiosulfate reduction potential region. However, hydroxylamine is not a strong reducing agent and may not reduce gold thiosulfate at significant rates.

As the pH decreases, the borohydride species responsible for electroless gold reduction is consumed in a hydrolysis reaction, weakening the borohydride's reducing strength. Figure 4 illustrates this weak anodic behavior of borohydride at pH = 7.2. At pH = 7.2, dithionite oxidizes at potentials too negative for heterogeneous gold reduction. Hydroxylamine does not have sufficient reducing strength. Both hydrazine and ascorbic acid have the anodic characteristics of being reducing agents for gold thiosulfate.

The predicted electroless bath behavior for these reducing agents and gold thiosulfate are confirmed with observations of actual electroless baths. The deposition rates are measured over a two hour period and the observed type of gold thiosulfate reduction for each reducing agent are summarized in Table I. At pH = 9.2 and 7.2, dithionite homogeneously reduces gold thiosulfate. Borohydride homogeneously reduces gold thiosulfate at pH = 9.2, but does not reduce gold thiosulfate at pH = 7.2. Hypophosphite does not reduce gold thiosulfate at either pH. Hydroxylamine heterogeneously reduces gold thiosulfate at both pH = 9.2 and 7.2, but at a very slow rate. Hydrazine catalytically reduces gold thiosulfate at slightly higher rates. However, the deposition rates for both pH's are highest for ascorbic acid. The strong catalytic reducing characteristics displayed in the oxidation voltammograms and electroless bath results establish ascorbic acid as an excellent reducing agent for gold thiosulfate.

OXIDATION OF ASCORBIC ACID

Ascorbic acid oxidizes electrochemically to

Table I.

Electroless Bath Results for Different Reducing Agents

REDUCING AGENT	DEPOSITION RATE (kÅ/hr)		COMMENTS
0.01 M	pH = 7.2	pH = 9.2	
Dithionite	0	0	Homogeneous production of Au at pH=7.2 and 9.2
Borohydride	0	0	Homogeneous production of Au at pH=9.2, No Au production at pH=7.2
Hypophosphite	0	0	No Au production at pH =7.2 and 9.2
Hydroxyl-amine	1.42	1.65	Heterogeneous production of Au at pH=7.2 and 9.2
Hydrazine	1.88	2.25	Heterogeneous production of gold at pH=7.2 and 9.2
Ascorbic Acid	3.32	5.33	Heterogeneous production of gold at pH=7.2 and 9.2

produce dehydroascorbic acid and two electrons[12-13].

$$AA \text{ -----> } DHA + 2e^-$$

where AA is ascorbic acid, DHA is dehydroascorbic acid. Ascorbic acid has two dissociated states[13].

$$H_2A = HA^- + H^+ \qquad pKa = 4.12$$

$$HA^- = A^{2-} + H^+ \qquad pKa = 11.34$$

where H_2A is the fully protonated form of ascorbic acid, HA^- is the monoprotonated form ofascorbic acid and A^{2-} is the fully dissociated form of ascorbic acid. Between pH = 4.12 and 11.34, the monoprotonated form of ascorbic acid dominates. The oxidation of ascorbic acid in different pH buffered solutions is shown in Figure 5. As the pH decreases, the oxidation shifts to more positive potentials and the anodic current decreases. A comparison of this anodic behavior with the cathodic reduction of gold thiosulfate is also shown in Figure 5. Applying the mixed potential theory, the deposition rate should increase with pH. The mixed potential moves positively and the current at the mixed potential decreases with pH. The theoretical deposition rates for the 0.05 M ascorbic acid/0.03 M gold thiosulfate electroless bath are: 18.4, 14.6 and 11.6 μm/hr at pH = 9.2, 6.4 and 4.6, respectively.

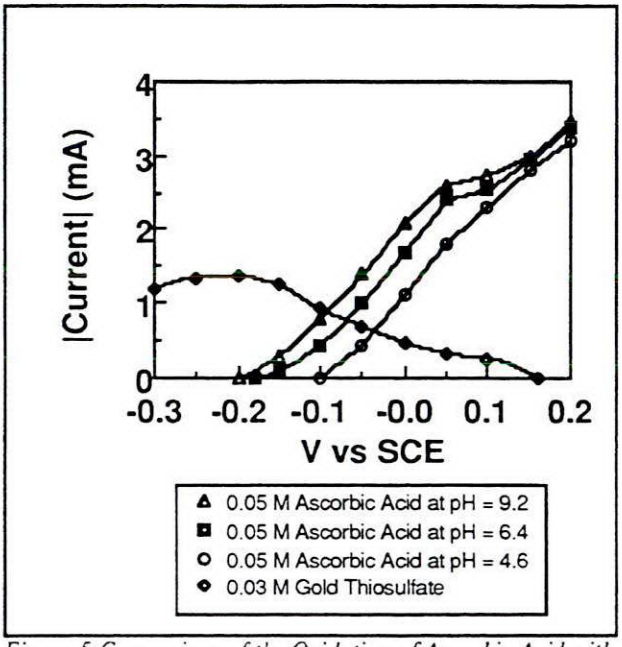

Figure 5-Comparison of the Oxidation of Ascorbic Acid with the Reduction of Gold Thiosulfate at 25 °C, 100 mV/s, on Au Electrode.

Ascorbic acid in its monoprotonated and diprotonated form react with oxygen homogeneously[14-15]. The rate of the homogeneous oxidation is faster for the diprotonated ion[14-15]. Therefore, the consumption of ascorbic acid via this side reaction increases as the pH increases. This auto-oxidation is also catalyzed by various metal ions and metal complexes[12-13, 15-23]. If catalyzed by gold thiosulfate ions, the auto-oxidation must be examined more closely.

The oxidation voltammograms of ascorbic acid used to predict deposition rates are representative of a nearly constant concentration equal to the initial bulk concentration of ascorbic acid. In actuality, ascorbic acid is gradually consumed in the electroless bath. In addition, the gold thiosulfate reduction voltammograms do not show the accumulation effect of the reduction product, thiosulfate. Therefore, the deposition rates predicted by the mixed potential do not account for any side reactions depleting the reactant concentration or any changes in the reduction characteristics of the gold thiosulfate complex.

ELECTROLESS DEPOSITION OF GOLD

The actual deposition rates are a function of time and pH, as shown in Figure 6. The bath at pH = 9.2 has the highest initial deposition rate, as predicted. This deposition rate drops rapidly with time. Since the auto-oxidation of ascorbic acid is slower at the lower pH's, the decrease in deposition rates for pH = 6.4 and 4.6 is less pronounced. At pH = 6.4, ascorbic acid is a

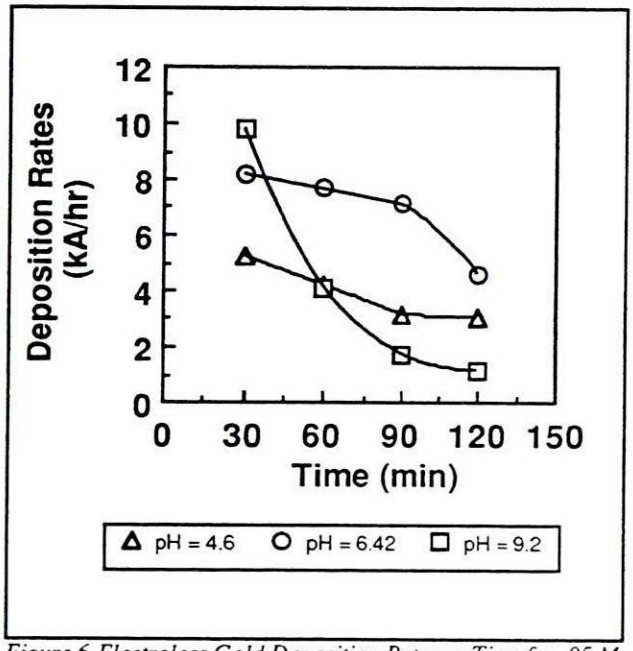

Figure 6-Electroless Gold Deposition Rates vs Time for .05 M Ascorbic Acid, 0.03 M Gold Thiosulfate at 30 °C, in air.

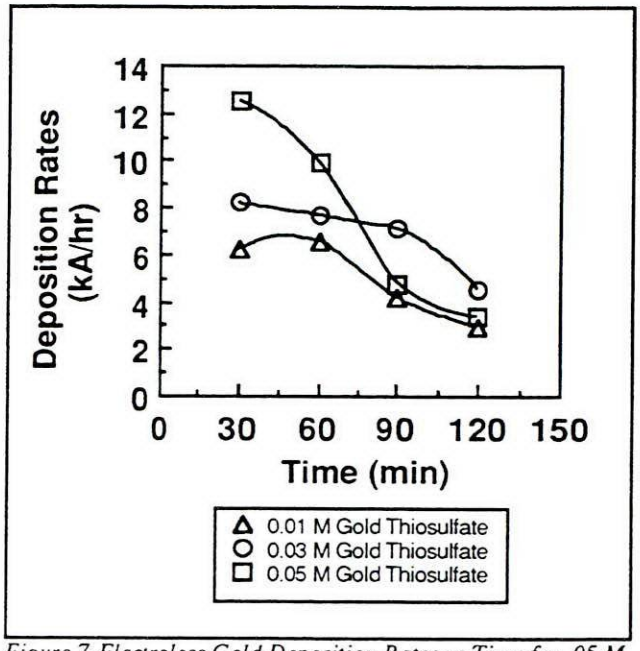

Figure 7-Electroless Gold Deposition Rates vs Time for .05 M Ascorbic Acid at pH = 6.42, 30 °C, in air.

stronger reducing agent and heterogeneously reduces gold thiosulfate faster than at pH = 4.6, Figure 6.

Increasing the concentration of gold thiosulfate in the electroless bath increases the heterogeneous reduction rate, Figure 7. If the gold thiosulfate concentration increases beyond a critical point, gold thiosulfate is homogeneously reduced. Homogeneous production of gold is catastrophic for two reasons. First, the homogeneous reaction depletes the reactant concentration and competes with the heterogeneous reaction. Secondly, the precipitate formed by the homogeneous reaction further catalyzes the heterogeneous reduction of gold thiosulfate on the gold seed. This unfavorable autocatalytic reaction competes with the favorable gold deposition reaction on the desired substrate. The critical concentration is dependent upon the operating time of the electroless bath. When the electroless bath is operated for two hours, the critical concentration of gold thiosulfate is 0.05 M for the 0.05 M ascorbic acid bath. Homogeneous reduction of gold thiosulfate occurs after 38 minutes in the 0.05 M ascorbic acid/0.05 M gold thiosulfate electroless bath.

The 0.05 M ascorbic acid/0.05 M gold thiosulfate bath deposition rates are compared to the deposition rates of the 0.03 M ascorbic acid/0.05 M gold thiosulfate bath to show the effect of ascorbic acid concentration, Figure 8. At the lower ascorbic acid concentration, the rate of deposition decreases, especially in the first hour. The deposition rates in the second hour approach the deposition rates of the 0.05 M ascorbic acid bath since gold thiosulfate is not homogeneously reduced.

Electroless baths with 0.01 M ascorbic acid and 0.01 M gold thiosulfate were performed in air and in a nitrogen atmosphere. The comparison of deposition rates time show the effect of the atmospheric oxygen, see Figure 9. Gold thiosulfate was homogeneously reduced within a half hour of being

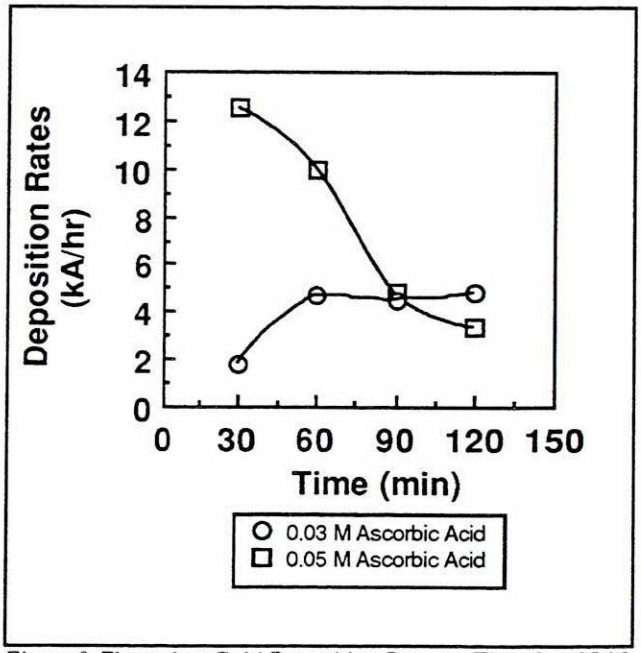

Figure 8-Electroless Gold Deposition Rates vs Time for .05 M Gold Thiosulfate at pH = 6.42, 30 °C, in air.

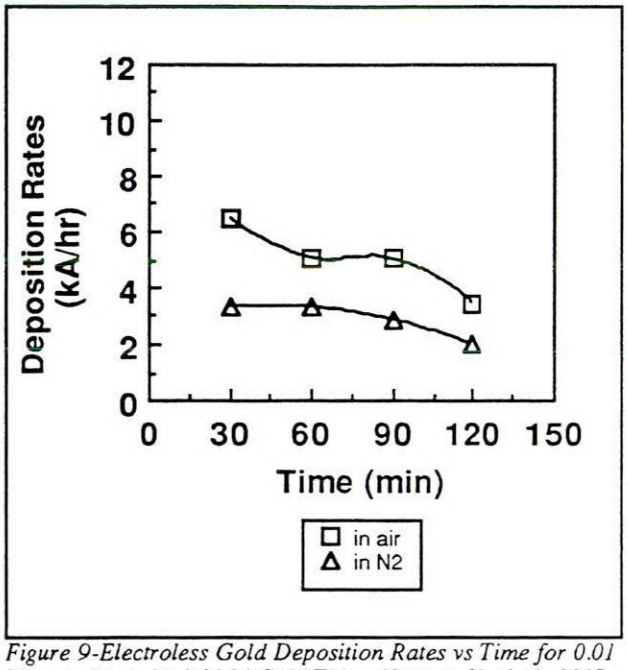

Figure 9-Electroless Gold Deposition Rates vs Time for 0.01 M Ascorbic Acid, 0.01 M Gold Thiosulfate at pH=6.42, 30°C.

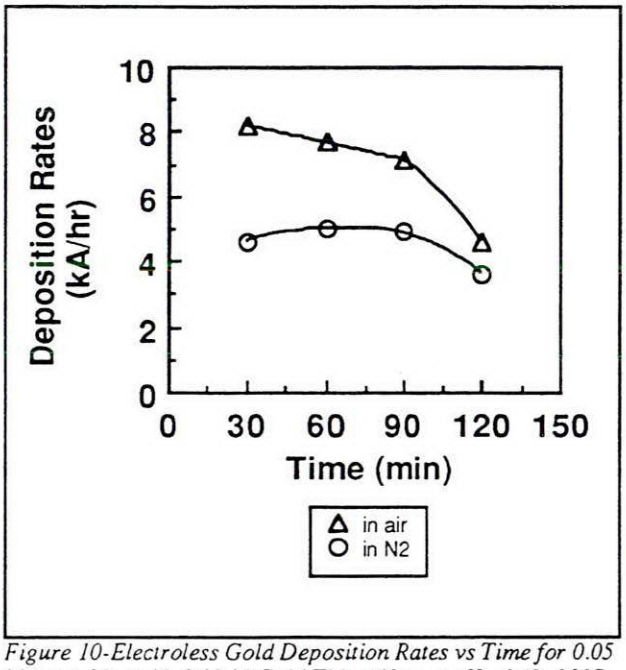

Figure 10-Electroless Gold Deposition Rates vs Time for 0.05 M Ascorbic Acid, 0.03 M Gold Thiosulfate at pH=6.42, 30°C.

exposed to atmospheric oxygen. In the oxygen free atmosphere, the homogeneous reduction does not occur during the two hour bath, but the rate of the autocatalytic reaction is reduced.

A multiple step process can explain this observed behavior in nitrogen. Ascorbic acid auto-oxidizes in air to produce dehydroascorbic acid and hydrogen peroxide[12-13]. Hydrogen peroxide is not produced by the reaction between ascorbic acid and gold thiosulfate. Therefore, hydrogen peroxide is not present in the bath performed in an oxygen free environment. In the case of hydrogen peroxide production, a second reaction occurs between hydrogen peroxide and thiosulfate, the reduction product[24-25]. This side reaction retards the accumulation rate of thiosulfate. As a result, the thiosulfate accumulates faster in the nitrogen atmosphere and inhibits the autocatalytic reaction more significantly. The lower deposition rates for electroless baths in nitrogen are a qualitative measure of this thiosulfate accumulation effect. To illustrate this point, an electroless bath, which does not have homogeneous reduction in open air, is repeated in a nitrogen atmosphere. The deposition rates of this 0.05 M ascorbic acid/0.03 M gold thiosulfate bath remained relatively constant in both atmospheres, Figure 10. Yet, the deposition rates in nitrogen are significantly lower.

To find the critical concentration of ascorbic acid in a nitrogen atmosphere, electroless baths with higher concentrations of ascorbic acid are compared to the 0.01 M ascorbic acid/0.01 M gold thiosulfate bath, Figure 11. The deposition rates increase significantly with ascorbic acid concentration. At 0.1 M ascorbic acid, homogeneous reduction occurs within an hour, and thereafter, the deposition rate drops rapidly. At 0.075 M ascorbic acid, gold is not produced homogeneously during the two hours observed. However, the deposition rate does decrease with time at an unfavorable rate.

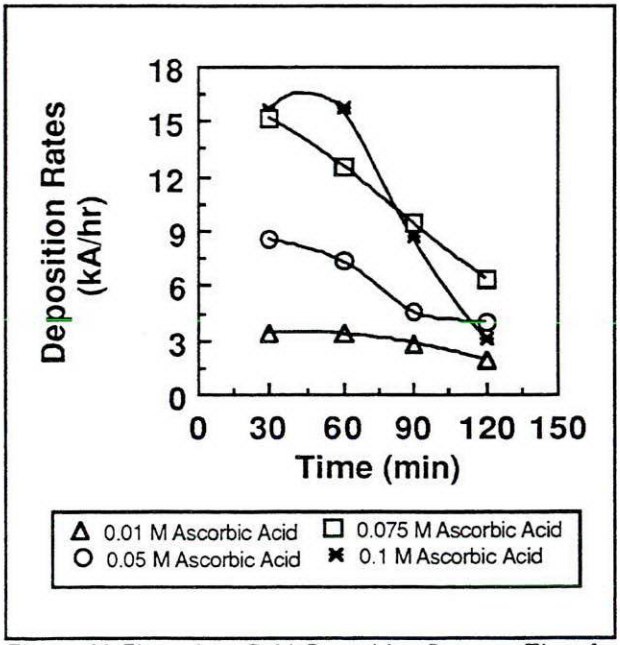

Figure 11-Electroless Gold Deposition Rates vs Time for 0.01 M Gold Thiosulfate at pH = 6.42, 30 °C in nitrogen.

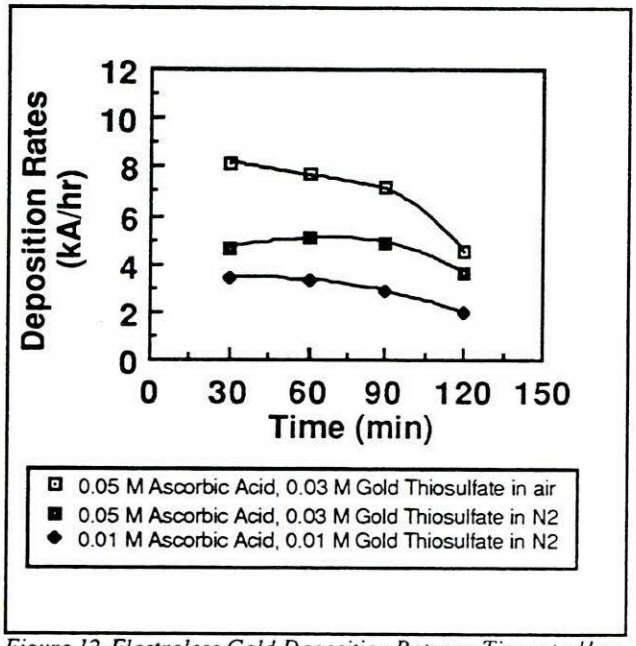

Figure 12-Electroless Gold Deposition Rates vs Time at pH = 6.42, 30 °C.

Of the electroless baths presented here, only three maintain fairly constant deposition rates without homogeneously reducing gold thiosulfate, Figure 12. The 0.05 M ascorbic acid/0.03 M gold thiosulfate bath exposed to air has an average deposition rate of 7.6 kÅ/hr. The same bath operated in a nitrogen atmosphere has a slightly lower average deposition rate of 5 kÅ/hr. The 0.01 M ascorbic acid/0.01 M gold thiosulfate bath operated in nitrogen has the lowest average deposition rate of 3 kÅ/hr.

CONCLUSIONS

Cyclic voltammetry and the mixed potential theory predict that ascorbic acid is a reasonable reducing agent for gold thiosulfate and that the best buffered pH solution at room temperature is the 6.4 pH citric acid buffer. Actual electroless baths confirm that ascorbic acid autocatalytically reduces gold thiosulfate at sufficient deposition rates. The bath with the highest and most stable deposition rates over a two hour period and with no homogeneous reduction is the 0.05 M ascorbic acid/0.03 M gold thiosulfate electroless bath operated in air at 30 °C. The overall deposition rate for this electroless bath is 7.6 kÅ/hr.

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New techniques to use electrochemical measurements in the process control

Dr. A. R. Zielonka, Prof. Dr. Ch. J. Raub

Forschungsinstitut für Edelmetalle und Metallchemie
D 73525 Schwäbisch Gmünd
Katharinenstr. 17
Germany

The constantly increasing demands on the quality of the electroplated coatings as well as on the stability of the electrolytes applied require new methods for the process control as well as for the regeneration of the electrolytes. Besides the control of the basic electrolyte composition, the maintenance of the efficiency of the applied organic additives represents an essential prerequisite for the determined deposition of functional coatings. Beyond the application of chemical analytical processes which are used for the determination of individual components of the different electrolytes and additives, the electrochemical measurement and analytical methods are becoming more and more important for the process control of electroplating processes.
A substantial advantage of the electrochemical methods consists in the fact that, besides the determination of the concentration of the different electrolyte-components, it is possible to make statements about the influence of the individual electrolyte components under deposition conditions. Because electrolyte additives are mainly multiple component mixtures (brighteners, levelers, wetting agents, stabilisers, etc.) a chemical analysis is often dissatisfactory, if not impossible. Furthermore, even when an analytical registration of the concentration of the additives is possible, their mere presence in the electrolyte does not yet allow a direct conclusion as to their effectiveness, especially in the interaction with other electrolyte components, as the mechanism of the interaction of the different additives has not yet been fully explained. The experiences in the application of voltametric and polarographic measurement methods have shown that the measured curves, when they are registered under defined conditions, allow substantial

statements about the electrochemical processes, and thus can be applied as a sensitive indicator of the function of an electrolyte. A problem in the application of current density potential curves for the process control is the unsatisfactory reproducibility of the measurements. A fundamental reason for the unsatisfactory reproducibility of the measurements is the alteration of the measurement electrode surface during the registration of the current density potential curves. Thus, a task of the present research work consisted in developing measurement equipment that guarantees a good constancy of the measurement electrode surface, even for a long time period of investigation, that allows a defined variation of the hydrodynamic conditions on the measurement electrode and that permits the analysis of an electrolyte in a wide current density range.

These requirements could be fulfilled by a fluid dynamic cell with coaxial electrode configuration. A very good constancy of the measurement electrode surface is achieved in the applied test cell by using a wire cathode which is continuously lead into the test cell. Thus, also for a long time period of analysis, an influence of the alteration of the cathode surface on the measurement results can definitely be excluded. The structure of the test cell applied is shown in the following figure.

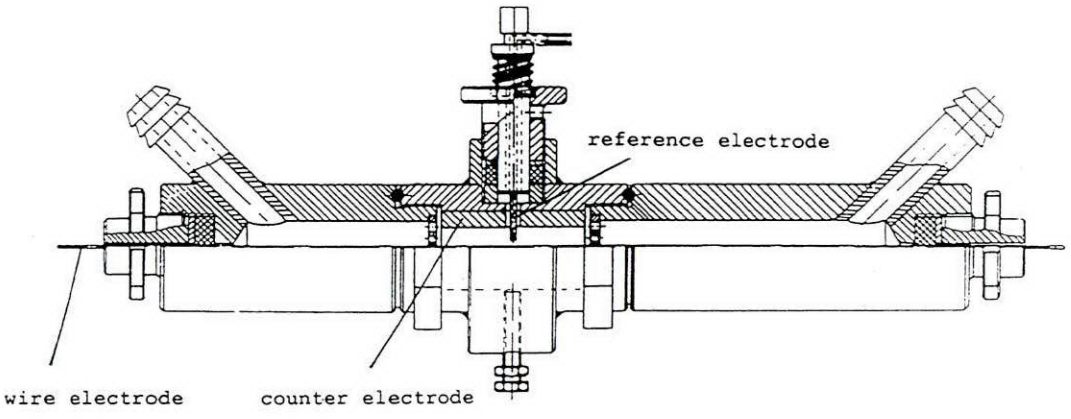

Fig. 1 electrochemical measurment cell

The measurement of the potential ensues by means of a capillary which is applied radially to the measurement electrode. The test cell is part of a measurement installation which consists of a thermostatic electrolyte container, a pump and a fluid-flow meter.

For the measurement of the current density potential curves, a computer-controlled potentiostat is used. After previous experiments with potentio- and galvanodynamic measurements, the galvanodynamic measuring method turned out to be the most appropriate for the proof of the effectiveness of electrolyte additives.

Within the scope of the analyses, the following test parameters were varied:
- current density
- scan rate of current density
- hydrodynamic conditions
- electrolyte temperature
- wire moving velocity

By the variation of the different test conditions, the ability to make statements on the otherwise two dimensional current voltage measurements is substantially increased.

In the presentation, it will be reported on the application of the described measuring equipment for the analysis of alloy-electrolytes, especially with regard to the applied organic additives.

Metal Analysis Using Anodic Stripping Voltammetry and Microelectrodes

R. P. Renz, C.-D. Zhou, D.R. Veach, and E.J. Taylor
Faraday Technology, Inc.
3155 Research Blvd.
Dayton, OH 45420

Abstract

We are developing an electrochemical transducer based on anodic stripping voltammetry and microelectrode technologies. This transducer would be used in the printed circuit board industry for process control and compliance verification, Specifically, we are developing an accurate, rapid, and simultaneous metal analysis methodology for low metal concentrations (~20 ppb). We initially conducted tests in high purity water to demonstrate the analysis of single component mixtures of copper and lead, and copper, lead, and tin. Also included are the results of actual waste water from a printed circuit board plater.

Introduction

Anodic Stripping Voltammetry (ASV) is a well established electroanalytical technique for measuring trace metals in water or other liquid matrices, with its roots dating back to the invention of polarography by J. Heyrovsky in (1922). ASV metal analysis typically consists of three steps as shown in Figure 1: 1) deposition of a mercury film onto an electrode, 2) deposition of the trace metals in solution into the mercury to form an amalgam, and 3) stripping or dissolving the metals out of the amalgam. The mercury film serves as a substrate for the subsequent amalgam formation with the copper.

Typically, ASV is conducted using Hanging Mercury Drop Electrodes (HMDE) or Rotating Disc Electrodes (RDE). With these electrode configurations, several obstacles to on-line instrumentation exist. Namely, accuracy is limited by interference from organics or dissolved oxygen in the sample solution. Consequently, the organic interferants are "digested" in a pressure bomb at elevated temperatures for one to eight hours prior to analysis. The dissolved oxygen is removed by bubbling nitrogen through the sample solution prior to analysis. However, these procedures are not consistent with the requirements of a real-time/on-line monitor. Ultramicroelectrodes and microelectrodes with diameters of 5 to 50 microns and less offer a solution to these problems.

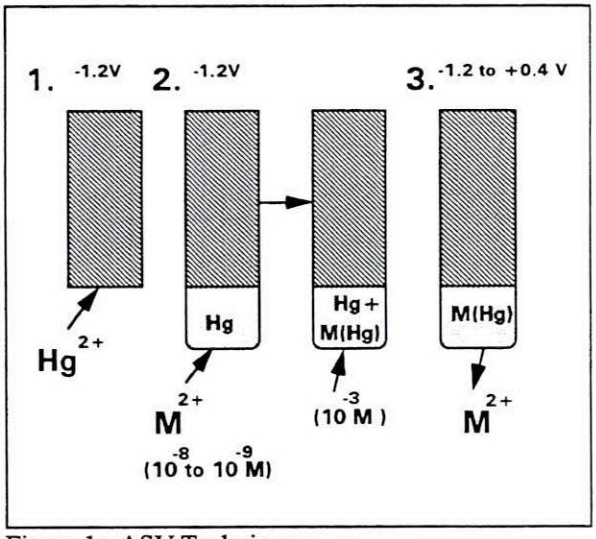

Figure 1: ASV Technique

Although Laitinen and Kolthoff (1941) conducted voltammetric experiments on a platinum "microwire" 50 years ago, significant research in this area began in the 1970s. Pioneering research by Fleischmann (et al.,1987), Wightman (1988), and Wrighton (White et al., 1985) and their coworkers provided the basis for the development of microelectrode sensors. The benefits are attributed to the small dimensions of the microelectrode leading to spherical diffusion and rapid steady state operation.

For example, the time dependent current at an infinite planar electrode is given by the Cottrell equation

$$i(t) = nFAD^{(1/2)}C(\pi t)^{(-1/2)} \qquad (1)$$

where "n" is the number of electrons in the reaction, "F" is the Faraday constant, "A" is the electrode area, "D" is the diffusion coefficient, "C" is the reactant concentration, and "t" is the time. The time dependent current at a sphere is given by

$$i(t) = nFADC[(D\pi t)^{(-1/2)} + r^{-1}] \qquad (2)$$

where "r" is the radius of the sphere. The case of spherical diffusion contains a time-dependent "Cottrellian" term and a time-independent term. At small "r", the time-independent term dominates. For example, for r = 5 microns and D = 10^{-5} cm^2/sec, the time-independent current is ten times the time-dependent "Cottrellian" current after only 0.8 sec. Consequently, steady state current is essentially attained in real time.

Fabrication of microelectrodes with a disc geometry is more easily attainable than the sphere or hemisphere geometry. For a microdisc electrode, the time-dependent current is approximated by (Wightman and Wipf, 1989)

$$i(t) \cong nFADC[(D\pi t)^{(-1/2)} + a/r] \qquad (3)$$

where "a" is empirically determined as 3 to 6 (Oldham, 1981). The main point, however, is that the current consists of a "Cottrellian" time-dependent term and a time-independent term. This is true for other geometries, such as very narrow band electrodes. Consequently, for narrow band widths, the time-independent term dominates the time-dependent Cottrellian term. Band electrodes are important for the development of a practical instrument.

In addition, since the currents at microelectrodes are small, two electrode electrochemical cells may be used instead of the traditional three electrode cell. That is, one microelectrode serves as both the counter and reference electrode and the other serves as the sensing electrode. Finally, since the area of the microelectrodes is small, the capacitive currents due to "charging" from adsorption of interferant species is minimal. Consequently, one can obtain high signal to noise ratios . Low concentrations of Cd and Pb were detected in nondeoxygenated solution using a carbon fiber microelectrode (Baranski, 1987).

In summary, several characteristics of microelectrodes are relevant to our in-line metal monitoring (Lafleur et al., 1990):

- enhanced signal to interferant current
  ===> leading to improved sensitivity
  ===>eliminating the need to deoxygenate the sample
- steady state operation
  ===>eliminating the need for complicated input signals such as differential pulse
  ===> resulting in rapid real-time response

Experimental Results

Single Component Studies

Experiments were carried out to measure copper, lead, and tin in high purity water (HPLC grade from Fisher Scientific) with a carbon microelectrode. Ten ASV experiments were conducted per concentration and the average value of peak charge was used for the calibration.

Copper in HPLC Water

A 30 second cleaning potential of +800 mV was applied prior to co-depositing mercury and copper at -1200 mV vs. Ag/AgCl reference for 150 seconds. These experiments were conducted using a solution containing 50 ppm mercury. Copper was stripped from the mercury coated electrode by sweeping the electrode potential at 400 mV/s from -1200 mV to 400 mV vs. Ag/AgCl. We ran varied concentrations of copper from 20 ppm down to 20 ppb and found that copper concentration was indeed linearly proportional to the peak charge (the area under the peak), as tabulated in Table 1 and depicted by Figure 2.

Table 1: Cu(II) data (Figure 2)

Conc. (ppb)	Potential (mV)	Standard Deviation	Charge (μC)	Standard Deviation
20000	200	0.01453	23.69	0.036337
2000	132.3	0.01427	2.718	0.022467
200	85.8	0.04456	0.2438	0.007613
20	40.2	0.03671	0.053	0.048717

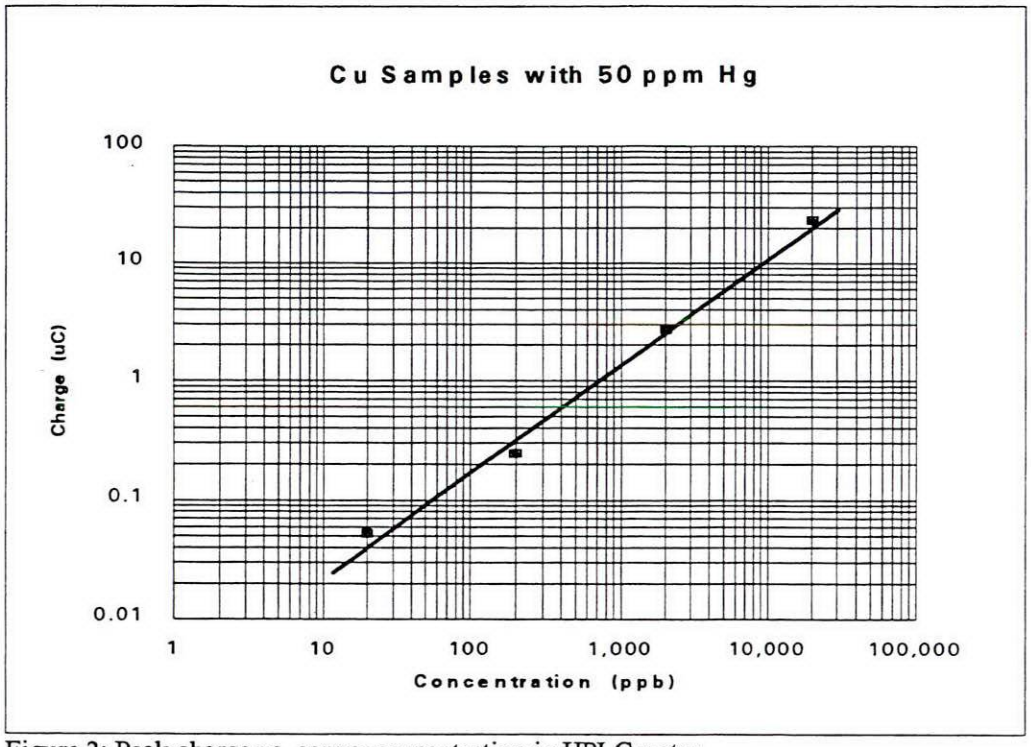

Figure 2: Peak charge vs. copper concentration in HPLC water.

Lead in HPLC Water

Lead was tested in a similar manner as copper. The electrode was cleaned at +800 mV for 30 seconds, then lead was co-deposited with 50 ppm mercury at -1200 mV. Lead was stripped from the mercury coated electrode at 400 mV/s from -1200 mV to 300 mV vs. Ag/AgCl. Figure 3 shows the charge-concentration linearity over a 20 ppb to 20 ppm lead concentration range. Table 2 tabulates this data.

Table 2: Pb(II) data (Figure 3)

Conc. (ppb)	Potential (mV)	Standard Deviation	Charge (μC)	Standard Deviation
20000	-360.5	-0.00476	9.58	0.033301
2000	-360.5	-0.00476	0.968	0.031485
200	-329.9	-0.01191	0.0966	0.007613
20	-425.3	-0.01499	0.008	0.083333

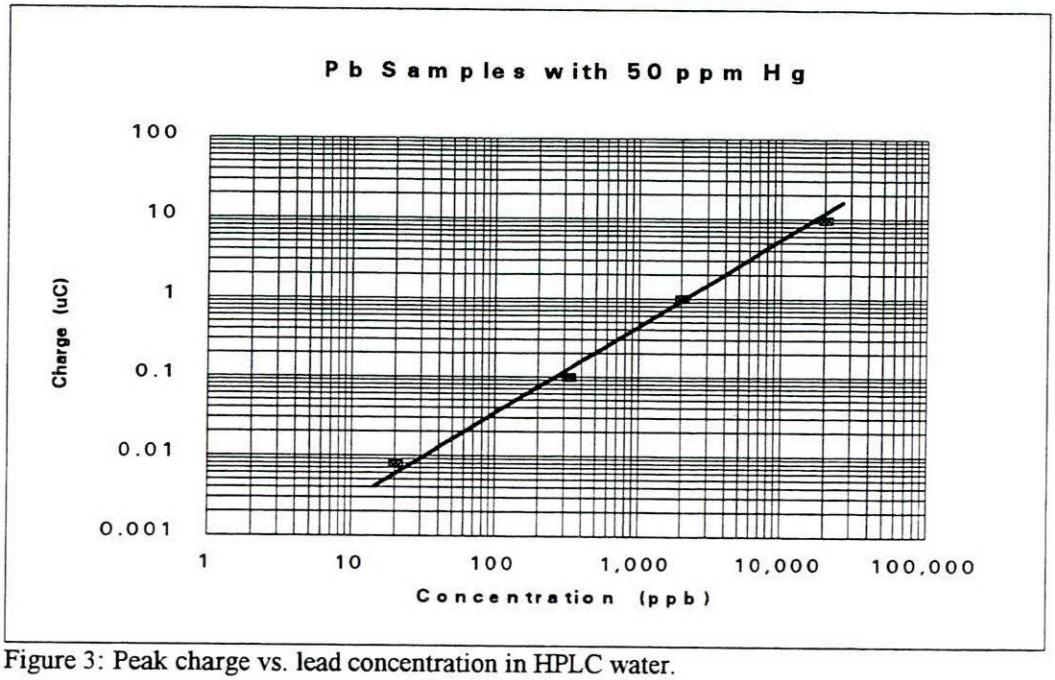

Figure 3: Peak charge vs. lead concentration in HPLC water.

Tin in HPLC Water

Tin was tested in a similar manner as copper and lead. The electrode was cleaned at +800 mV for 30 seconds, then tin was co-deposited with 50 ppm mercury at -1200 mV. Tin was stripped from the mercury coated electrode at 400 mV/s from -1200 mV to 100 mV vs. Ag/AgCl.. Table 3 tabulates the concentration data. Figure 4 shows the charge-concentration calibration.

Table 3: Sn(II) data (Figure 4)

Conc. (ppb)	Potential (mV)	Standard Deviation	Charge (μC)	Standard Deviation
20000	-410	-0.00126	6.89	0.04015
10000	-424	-0.05606	2.85	0.10349
2000	-425	-0.01338	0.13	0.04150
1000	-432	-0.00655	0.06	0.09368
500	-435	-0.0204	0.03	0.33333

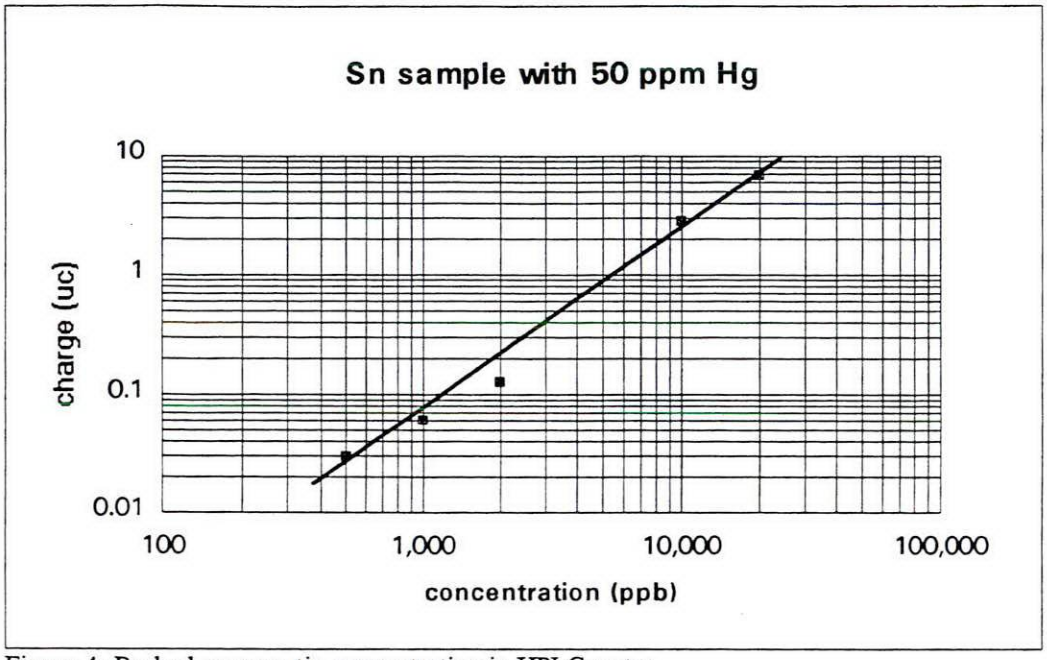

Figure 4: Peak charge vs. tin concentration in HPLC water.

Multiple Component Studies

Experiments were conducted to detect metal concentration in two component system containing copper and lead, and three component system containing copper, lead, and tin in HPLC water.

Copper and Lead in HPLC Water

A 30 second cleaning potential of +800 mV was applied prior to co-depositing mercury, copper and lead at -1200 mV vs. Ag/AgCl reference for 150 seconds. These experiments were conducted using a solution containing 50 ppm mercury. Lead and copper were stripped from the mercury coated electrode by sweeping the electrode potential at 400 mV/s from -1200 mV to 400 mV vs. Ag/AgCl. We present the data for peak charge versus metal concentration for copper and lead, in Figures 5 and 6, respectively. Table 4 summarizes the results.

Table 4: Two component data

Conc. (ppb)	Metal	Potential (mV)	Standard Deviation	Charge (μC)	Standard Deviation
20000	Cu (II)	195.3	0.015652	25.03	0.05715
	Pb (II)	-369.5	-0.005299	8.67	0.04895
2000	Cu (II)	134.4	0.015764	2.419	0.06537
	Pb (II)	-413.1	-0.004628	0.923	0.04244
200	Cu (II)	88.3	0.046862	0.1875	0.00761
	Pb (II)	-419.4	-0.009812	0.0759	0.00761
20	Cu (II)	38.1	0.075717	0.0284	0.04453
	Pb (II)	-425.3	-0.003266	0.008	0

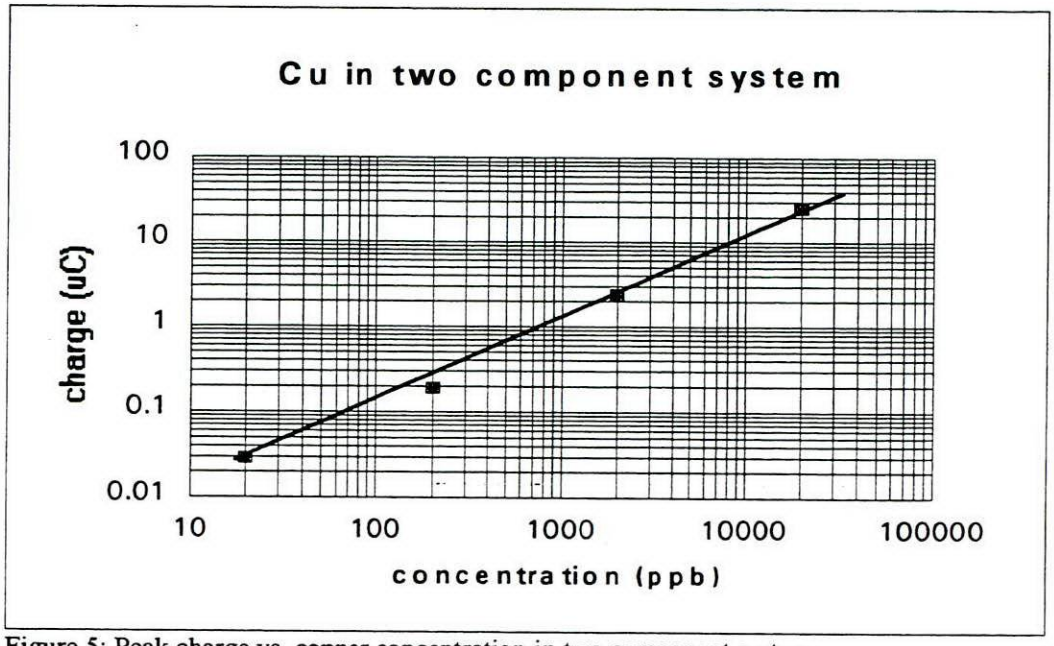

Figure 5: Peak charge vs. copper concentration in two component system.

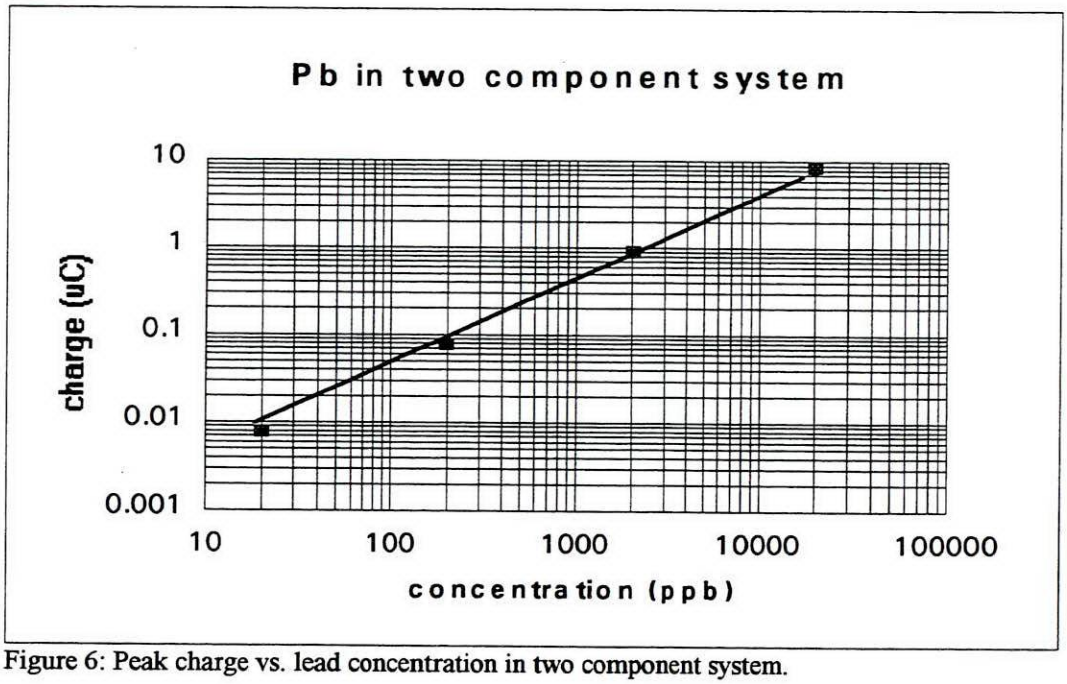

Figure 6: Peak charge vs. lead concentration in two component system.

Copper, Lead and Tin in HPLC Water

Three component system containing copper, lead and tin was tested in a similar manner as the two component system of copper and lead. The electrode was cleaned at +800 mV for 30 seconds, then copper, lead and tin was co-deposited with 50 ppm mercury at -1200 mV. Copper, lead and tin were stripped from the mercury coated electrode from -1200 mV to 400 mV vs. Ag/AgCl. Figures 7, 8, and 9 show the charge-concentration calibration for copper, lead, and tin, respectively. Table 5 tabulates the data.

Table 5: Three component system

Conc. (ppb)	Metal	Potential (mV)	Standard Deviation	Charge (μC)	Standard Deviation
20000	Cu (II)	246.4	0.017135	16.0	0.09612
	Pb (II)	-386	-0.00258	8.93	0.05092
	Sn (II)	83.3	0.040828	12.7	0.0962
2000	Cu (II)	276.2	0.003327	5.45	0.01888
	Pb (II)	-404	-0.00685	0.92	0.04032
	Sn (II)	46.1	0.00819	1.55	0.01670
200	Cu (II)	309.8	0.004138	0.21	0.06070
	Pb (II)	-414	-0.00513	0.11	0.05438
	Sn (II)	74.5	0.024711	0.22	0.03636
20	Cu (II)	38.1	0.01189	0.03	0.03333
	Pb (II)	-1019	-0.01708	0.02	0.17993
	Sn (II)	-424	-0.00327	0.01	0.01000

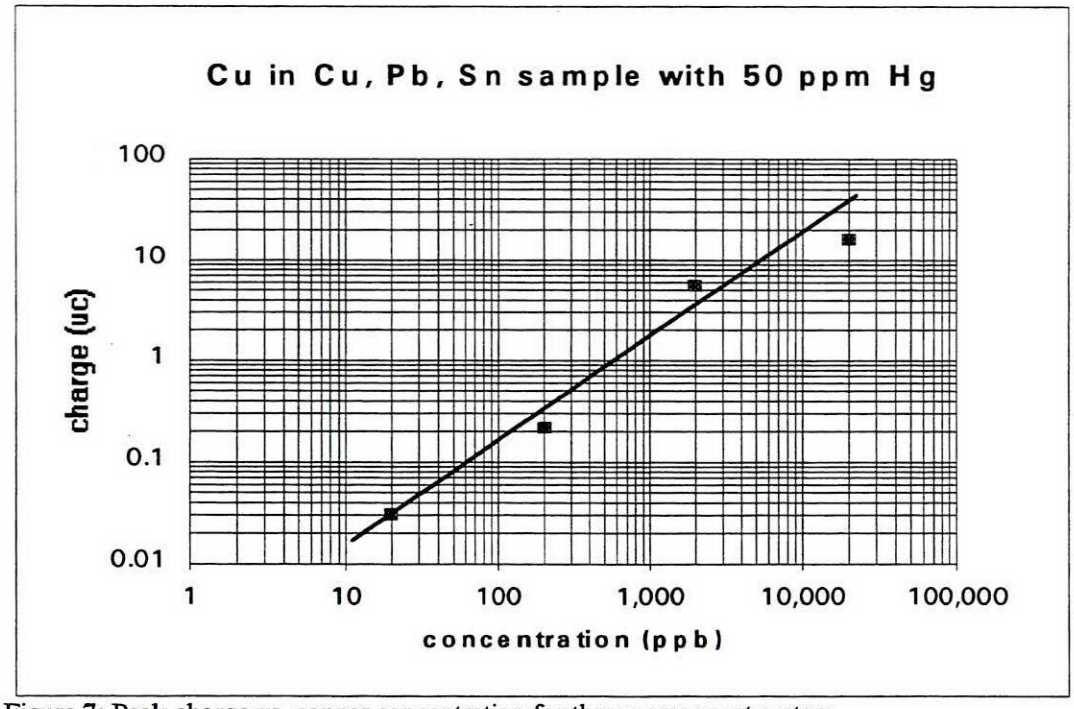

Figure 7: Peak charge vs. copper concentration for three component system.

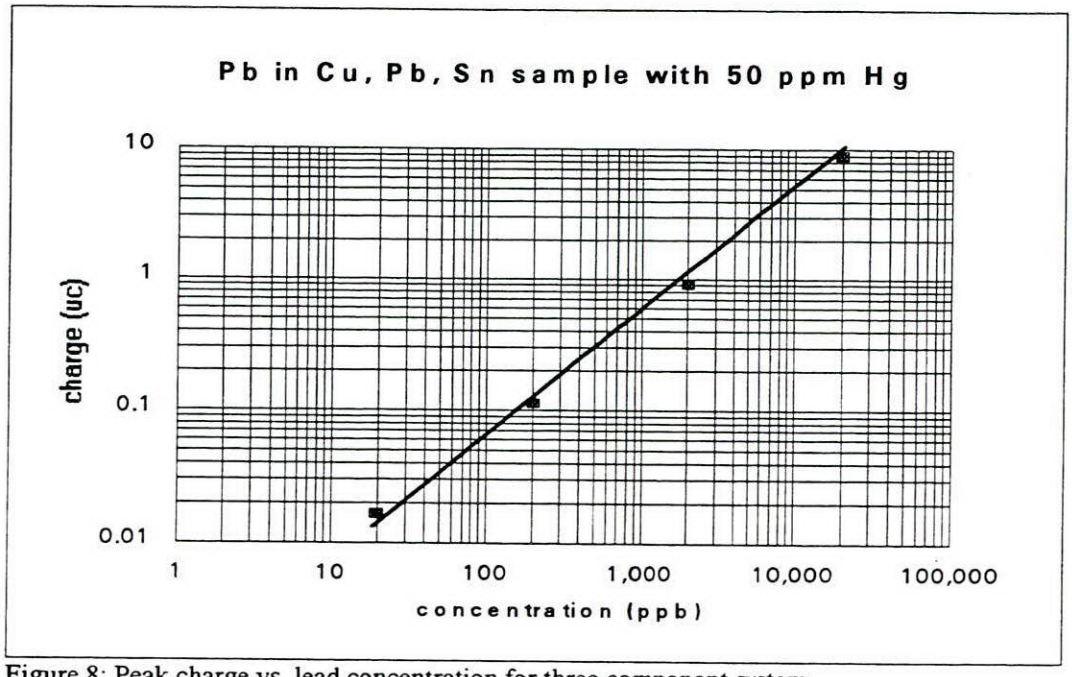

Figure 8: Peak charge vs. lead concentration for three component system.

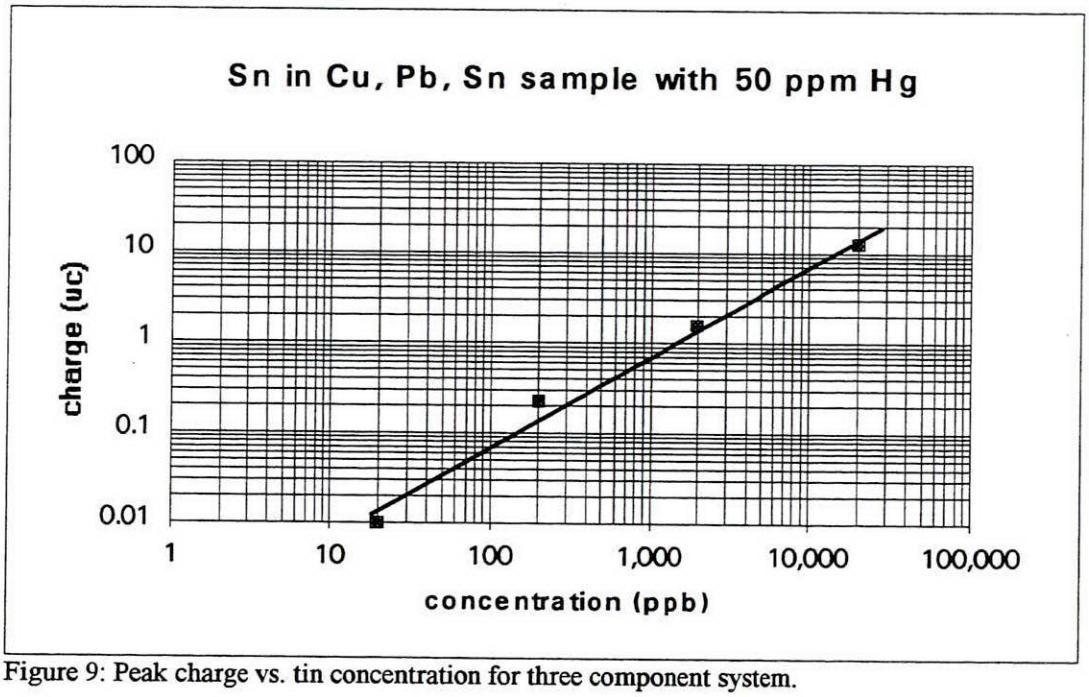

Figure 9: Peak charge vs. tin concentration for three component system.

ASV Measurement of Circuit Center Inc. Water

Three samples of Circuit Center Inc. water containing copper, lead and tin were tested in a similar manner as the three component system of copper, lead and tin in HPLC water. The experiment was carried out with the addition of 50 ppm mercury. The electrode was cleaned at +800 mV for 30 seconds, then copper, lead and tin were co-deposited with 50 ppm mercury at -1200 mV. Copper, lead and tin were stripped from the mercury coated electrode at 400 mV/s from -1200 mV to 430 mV vs. Ag/AgCl. Table 6 shows the comparison of the result obtained by ASV measurement (our result) and the result obtained by Bowser-Morner a local environmental chemistry laboratory. The copper, lead, and tin concentrations from ASV measurements were obtained from the calibration of a three component system of copper, lead, and tin in HPLC water. As shown in the table, lead concentration obtained by ASV measurement agreed well with the result obtained by Bowser-Morner because lead in Circuit Center, Inc. water also existed as a simple metal ion and no complex interfered. However, there is a difference between the ASV measurement and the Bowser-Morner measurement for copper concentration because copper existed as a complex form in Circuit Center Inc. water. Due to the complex interference for copper measurement, it is necessary to generate a calibration of copper in Circuit Center, Inc. water. Therefore, we carried out experiments to spike copper, lead, and tin in Circuit Center, Inc. water.

Table 6: Copper, lead, and tin concentration in Circuit Center Inc. water measured by ASV and Bowser-Morner

Conc. (ppm)	Sample #1		Sample #2		Sample #3	
	ASV	Bowser-Morner	ASV	Bowser-Morner	ASV	Bowser-Morner
Copper	3	5.6	2.5	3.5	2	2
Lead	0.4	0.66	0.32	0.38	0.1	≤0.1
Tin	3.5	-	2.9	-	2	-

Spiking of Copper, Lead, and Tin in Circuit Center Inc. Water

We added 2 ppm, 5 ppm, 7 ppm, and 10 ppm copper, lead, and tin to Circuit Center, Inc. water, respectively, to conduct the ASV calibration measurements in the presence of Circuit Center, Inc. complex. The test was carried out with the addition of 50 ppm mercury in a similar manner as the three component system of copper, lead and tin in HPLC water. Figures 10 and 11 show the spike of copper and lead, respectively, in Circuit Center, Inc. water for sample #1. Figures 12 and 13 show the spike of copper and lead, respectively, in Circuit Center, Inc. water for sample #2. These results are compared with the calibration of copper and lead in three component system with HPLC water. As shown in the figures, the calibration of copper and lead in HPLC water are straight lines passing through the original point. The spikes of copper and lead in Circuit Center, Inc. water are also straight lines; however, they gave positive intercepts on the x-axis, which were the background of the Circuit Center, Inc. water. Additionally, the slopes for the lead calibration curves for Circuit Center, Inc. water and HPLC water are approximately the same. This is why lead concentration in Circuit Center Inc. water measured by ASV agreed well with the result of Bowser-Morner. However, the slopes for the copper calibration curves for Circuit Center Inc. water are different from the slopes for the copper calibration in HPLC water because the complex interference existed for copper in the Circuit Center, Inc. water. Tables 7 and 8 summarize the spike result of copper, lead, and tin for Circuit Center, Inc. water of sample #1 and sample #2, respectively.

Table 7: Spike of copper, lead and tin in Circuit Center Inc. water of sample #1

Conc. (ppb)	Metal	Potential (mV)	Standard Deviation	Charge (μC)	Standard Deviation
15600	Cu (II)	282.8	0.02499	25.8	0.09132
10660	Pb (II)	-365	-0.01140	5.54	0.02436
13500	Sn (II)	95.4	0.03209	10.27	0.0454
12600	Cu (II)	265.6	0.02175	20.2	0.06000
7660	Pb (II)	- 369	-0.01466	3.38	0.08579
10500	Sn (II)	99.1	0.02446	6.27	0.1167
10600	Cu (II)	264.3	0.00565	17.9	0.07040
5660	Pb (II)	- 371	-0.01066	2.42	0.09876
8500	Sn (II)	101.7	0.020236	4.33	0.1436
7600	Cu (II)	273	0.015154	11.8	0.14987
2660	Pb (II)	- 370	-0.01534	1.07	0.15887
5500	Sn (II)	119.2	0.02158	2.54	0.15118

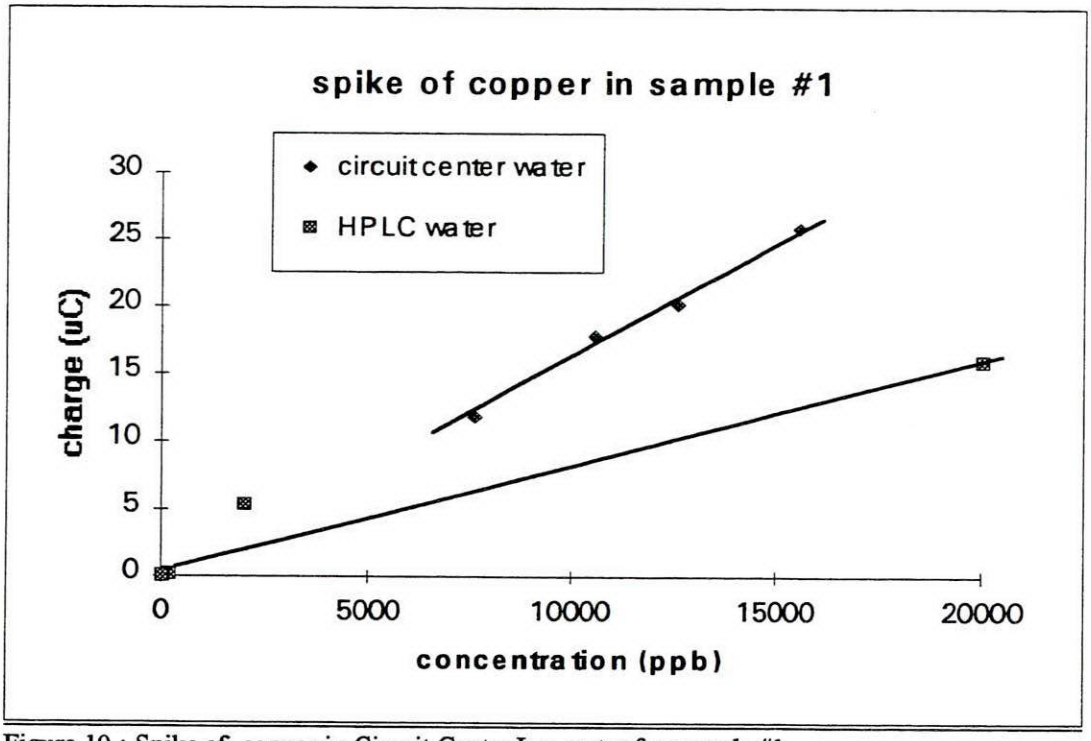

Figure 10 : Spike of copper in Circuit Center Inc. water for sample #1.

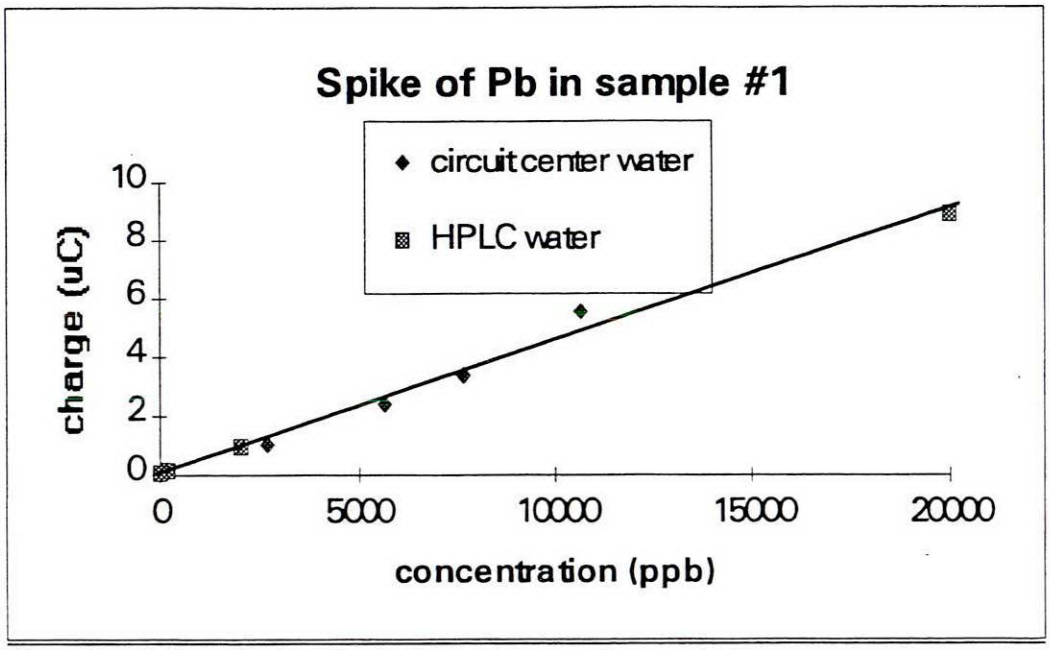

Figure 11 : Spike of lead in Circuit Center Inc. water for sample #1.

Table 8: Spike of copper, lead and tin in Circuit Center Inc. water of sample #2

Conc. (ppb)	Metal	Potential (mV)	Standard Deviation	Charge (μC)	Standard Deviation
13500	Cu (II)	256.7	0.003696	21.5	0.0792
10380	Pb (II)	-365	-0.01913	5.33	0.02664
12900	Sn (II)	92.6	0.0353	7.92	0.02714
10500	Cu (II)	258.1	0.00865	18.5	0.0214
7380	Pb (II)	- 362	-0.02407	3.76	0.03111
9900	Sn (II)	97.1	0.02085	5.98	0.07173
8500	Cu (II)	254.2	0.01199	15.8	0.08419
5380	Pb (II)	- 375	-0.0172	2.44	0.03975
7900	Sn (II)	96.3	0.03824	4.19	0.07589
5500	Cu (II)	262.8	0.008565	10.4	0.0538
2380	Pb (II)	- 373	-0.0246	1.16	0.0603
4900	Sn (II)	110.8	0.03344	2.59	0.02857

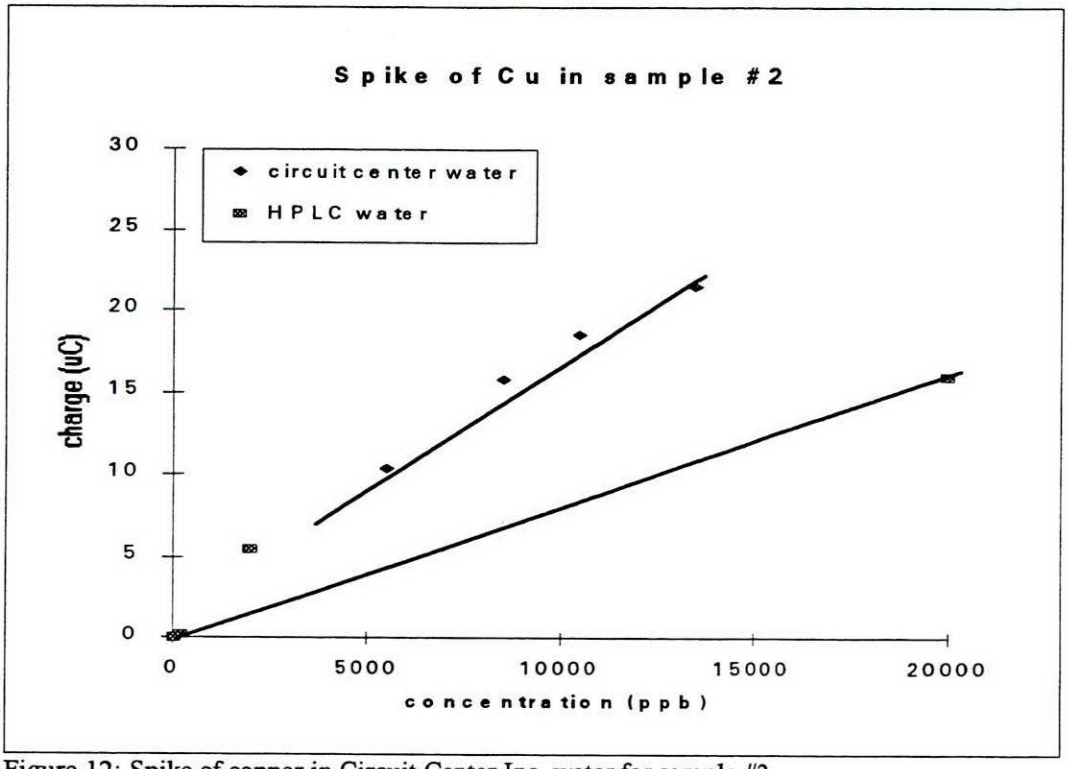

Figure 12: Spike of copper in Circuit Center Inc. water for sample #2.

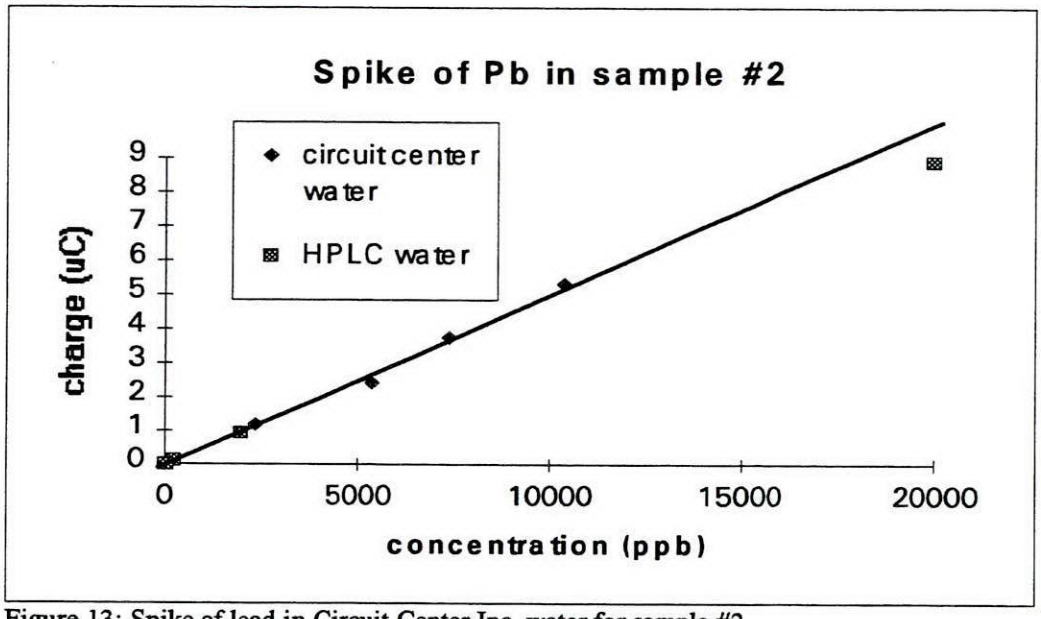

Figure 13: Spike of lead in Circuit Center Inc. water for sample #2.

Conclusions

A study has been made to demonstrate the feasibility of using anodic stripping voltammetry with microelectrode technologies to measure the amounts of metals in waste streams from 20 ppm to 20 ppb. Single component studies were made on copper, lead, and tin followed by multicomponent studies. Finally, actual waste water samples were used to measure the effects of real-world situations. Copper, lead, and tin were able to be measured in the range of 20 ppm to 20 ppb in real-world samples of waste water.

Acknowledgments

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MONITORING PLATING BATH EFFICIENCY WITH THE QUARTZ CRYSTAL MICROBALANCE

K. Keiji Kanazawa and Gary L. Borges

IBM Research Division
Almaden Research Center
650 Harry Road
San Jose, California 95120-6099

Saad Doss

IBM Corporation
5600 Cottle Road
San Jose, California 95120-6099

Cleve Hildebrand

Maxtek Corporation
2908 Oregon Court
Torrance, CA 90502

ABSTRACT

electroless plating, the utility of the Quartz Crystal obalance (QCM) had been demonstrated earlier electroless nickel plating. In the electrolytic bath, eneration of current during the deposition onto the M makes it possible to determine in-situ Faradaic ncies because both mass deposition and charge fer can be measured. The application of this CM technique in regards to plating efficiencies is ibed here for a number of electrolytic baths; ding silver/perchlorate, copper/sulfate, gold/cyanide permalloy. The dynamic measurement of the ncy suggests that this measurement can be used to tor the overall quality of the plating bath.

INTRODUCTION

ie quartz crystal microbalance (QCM) has long d in physical vapor deposition processes as a robust, le and accurate thickness and rate monitor[1]. In t years, it has also found applications in the liquid onment, bringing these same qualities to the ochemical domain [2]. In the standard usage, the al resonant frequency of the quartz disk determines perating frequency of an electronic oscillator. The deposition of material on the surface of the crystal decreases the resonant frequency in a manner that can be quantitatively described to a great precision. The frequency decrease is directly related to the mass per unit area deposited on the crystal, and the relationship applies to operation in vacuum, air or liquid. The quantitative relations connecting the frequency decrease to the deposited mass density are available for different approximations. For example, in the case of very thin elastic films, the classical relation used is that given by Sauerbrey[3] in 1959. This relation describes a linear relation between the frequency decrease and the mass density. For thicker elastic films, the acoustical properties of the film plays an increasing role and the famous "Z-Match" theory of Lu and Lewis[4] extends the range of the QCM to thicker films(although the relation is now transcendental and not linear).

This behavior suggests that this sensor can be used to monitor in-situ the deposition rate of plated materials and was shown to be capable of monitoring in situ the deposition rate and thickness for autocatalytically deposited NiP films[1]. There it was shown that the plating thicknesses measurements from the QCM were in good agreement with the standard beta backscatter measurements. In the case of electrolytic plating, the utility of QCM data is enhanced by the combination of

mass and electrical current information. The mass information with the QCM is obtained in the usual manner using the standard relations[5]. The electrical current can be integrated to determine the charge passed during deposition. Because both mass and charge are measurable during the electrolytic plating process, a comparison can be made between the actual mass deposited and the mass which would have been deposited if all the charge were effective in depositing metal. This is the concept of Faradaic efficiency. This study describes the use of a commercial plating rate monitor for measuring the Faradaic efficiency in technical baths, that is baths containing all the additives and surfactants required for effective plating.

BASICS

In use as a QCM, the quartz crystal takes the form of a circular disk having metal electrodes on both faces. These electrodes are then connected to an electronic oscillator circuit, and the quartz crystal determines the oscillation frequency. The deposition of any mass on the electrode is observed as a decrease in the frequency. In the case of electrolytic deposition, the deposition of a metal cation in solution to form an atom on the surface is accompanied by the simultaneous deposition of zq coulombs of charge, where z is the valency of the cation and q is the magnitude of the elemental electronic charge. The deposition of mass M′ of metal caused by an amount of plating charge $Q_{P'}$ is given by:

$$M' = \frac{A_W}{zqN_A} Q'_P \qquad (1)$$

where A_W is the atomic weight of the metal and N_A is Avogadro's number. M′ and Q'_P are the mass per unit area and the charge per unit area, respectively. These values have been chosen since the QCM determines the mass per unit area of the overlying film. The charge per unit area is determined by dividing the integrated current by the electrode area. The charge collected during the plating process Q′ consists of the sum of the plating current and other extraneous currents Q'_X, i.e. $Q' = Q'_P + Q'_X$. The Faradaic efficiency η is:

$$\eta = \frac{Q'_P}{Q'} = \frac{zqN_A}{A_W} \frac{M'}{Q'}. \qquad (2)$$

An interesting use of the equation above occurs in the case of the deposition of silver from a perchlorate solution onto a crystalline gold surface. The experiment consisted of a cyclical linear potential scan of the electrode, simultaneously recording the current and the frequency change,. as shown in Figure 1. The solid curve shows the current and the dashed curve shows th frequency change. The scan begins near 650 mV initially scanning positive and then reversing an scanning in the negative direction. The negative peak near 520 mV and the step at about 130 mV reflect th formation of the initial monolayer of silver on the gol surface. As the potential is scanned further cathodic, th deposition of silver on silver proceeds (the so-calle "bulk" deposition). The current is observed to abruptl peak and subsequently decay somewhat as th concentration of cations becomes limited by diffusion Upon reversal of the potential, the stripping peak for th current is observed, and then the stripping peaks for th monolayer are again observed. Concentrating now or the mass measurements, indicated by the decrease i frequency of the oscillator, note that there is a ste frequency decrease across the initial monolayer peak indicating the deposition of the silver atoms. Even in th mid-range where the current is relatively small (200-50 mV), the frequency is seen to slowly decrease, indicatin the continuation of deposition in this range. The mas deposition is seen to become very rapid in the bulk deposition regime. The details of the current and mas behavior in this regime are the subject of another study but those details do not affect the arguments presented here for the purposes of this study. Mass stripping is also evident during the anodic scan, with the stripping peaks almost mirroring the deposition peaks. To compare this data with equation (2) the mass deposited on the electrode can be calculated from the frequency decrease using the well-known Sauerbrey equation, and plotted against the charge, obtained by integrating the current. This result is shown in Figure 2. It's remarkable that the cathodic and anodic scans lie virtually atop one another, showing virtually the same behavior whether scanning negatively or positively. The dashed line in the Figure shows the slope expected for a Faradaic efficiency of unity, or 100%. The dashed line has been offset in the negative direction for clarity. The line should pass through (0,0). If this line were moved up to the correct position, the agreement in the domain of large mass density is remarkable. In the bulk deposition regime then, the behavior of the deposition is nearly ideal both with regard to slope and magnitude. But in the regime of initial monolayer formation at the lower mass densities, the behavior departs from the ideal, although reverting to ideal at the larger mass densities. This example shows the wealth of information that can be obtained from the electrochemical QCM.

DISCUSSION

While the case of silver on gold is an interesting laboratory example, it was felt that a more meaningful test for this method could be obtained by using

mercially available equipment in industrial plating s.

first test of this was provided by an acid copper which included surfactant. The commercial CPVC ing for the crystal was immersed into the bath. A inuous flow circulating pump recirculated the bath, iding a flow over the surface. A constant current of mamps was applied to the electrode, as shown by dashed line in Figure 3. The commercial plating sition monitor calculated the mass using the Lu and s formulation[4] from the frequency change of the lator and this mass is shown as the solid line in the e. The bath appears to behave in a nearly ideal ier, with the mass increasing linearly with time as cted for a constant-current deposition. Greater l is available the Faradaic efficiency is studied ing deviations from ideality which could not be rved on the mass-time plot. The Faradaic efficiency e deposition is shown in Figure 4 as the solid line. dashed line shows the 100% efficiency line. The rved efficiency is less than 100% throughout the starting at a value substantially below 100% and asing to a steady state value in the neighborhood of after 200 seconds of plating. Because the electrode needs to be known for the calculation of the daic efficiency, it is possible that errors in the area mination give rise to some of the discrepancy. In to probe this question further, the plating current manually adjusted during the plating run as shown gure 5 in a series of increasing steps. The Faradaic eny resulting from these current steps is shown in re 6. At the lowest current used (1.4 ma), the ency appears to be nearly 100%. Thus, we feel that uncertainty in the true electrode area did not ibute more than a few percent to the discrepancies. interesting to observe that the efficiency drops with asing current from about 97% down to 89%. It is hat this is due to the increasing importance of other daic processes occurring at the electrode, such as ogen evolution.

his contrasts with the behavior of a gold/cyanide in which a similar stepped current experiment was ucted. In this case, as shown in Figure 7, the ency is low at small currents and increases toward % at the higher current densities. The efficiency at r currents could not be plotted because of the sive noise in that regime.

another example of the use of the efficiency monitor technical bath occurs in the case of permalloy sition. In this case, the current steps were increased ually in sufficiently small intervals that the efficiency l be plotted in a quasi-continuous fashion as shown gure 8. It is seen that the efficiency is substantially below 100% throughout the current range, being very small at low currents and increasing with increasing current to values in the neighborhood of 87%. This is consistent with the notion of additional current required for the formation of surfce hydroxides.

The permalloy bath used a paddle as agitation, and the effects of the paddle on the deposition are illustrated in Figure 9. An increase in the plating rate when the current is turned off is clearly seen when the agitation is turned off at about 470 seconds and on again at about 720 seconds. Another interesting feature occurring during this run took place after the plating current was reduced to zero just past 800 seconds. The deposition rate not only decreases, but actual stripping of the deposit is clearly observed.

Because the permalloy experiment provided a vehicle to learn how to manually increase the current in incremental steps, we returned to the silver-perchlorate bath to study the efficiency for this bath as a function of current. These results are plotted in Figure 10 and the efficiency is seen to be reasonably high throughout the range of currents studied. Unfortunately, noise in the environment caused a less than desired signal to noise ratio. Again, the noise contributions at low current levels were sufficiently large that data are not included in the plot here.

SUMMARY

The determination of Faradaic efficiencies in industrial electrolytic plating baths using commercial instrumentation has been shown to be feasible and informative. The behavior of the electrochemical QCM monitor with the silver/perchlorate bath and the permalloy bath shows the usefulness of the technique for analytical purposes. While the sensitivity of these measurements suggests the electrochemical QCM can be used to monitor, in great detail, the overall effectiveness of most any industrial plating bath.

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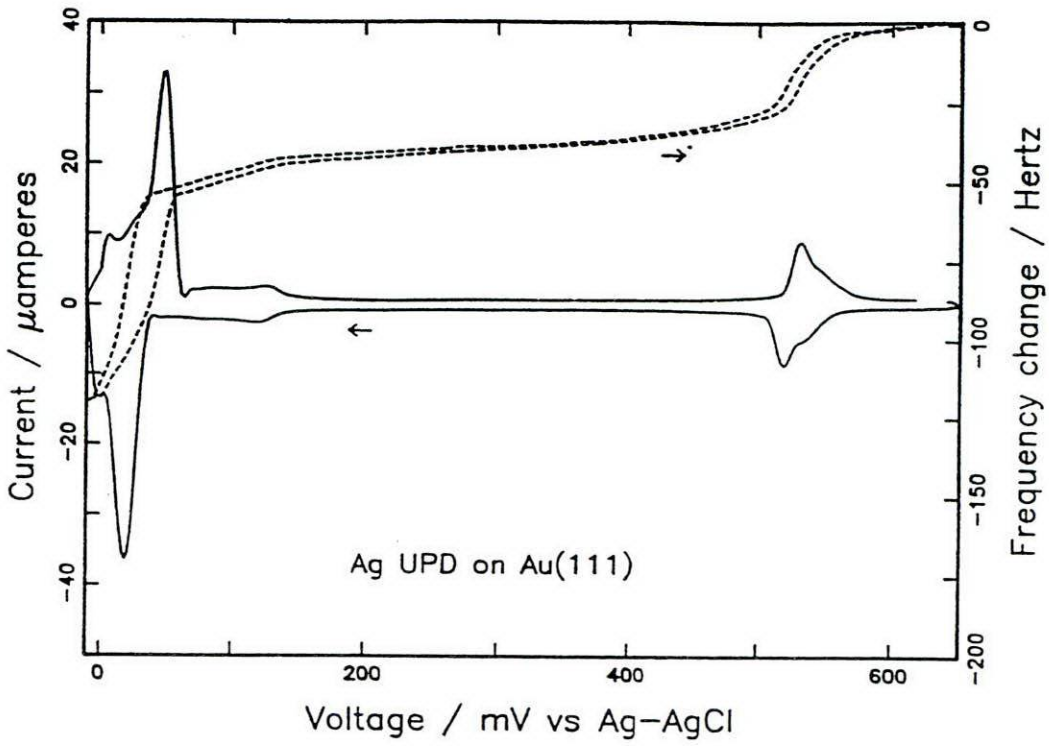


Figure 1. Current(solid) and frequency change(dashed) during the deposition of silver on an initial Au(111) surface.

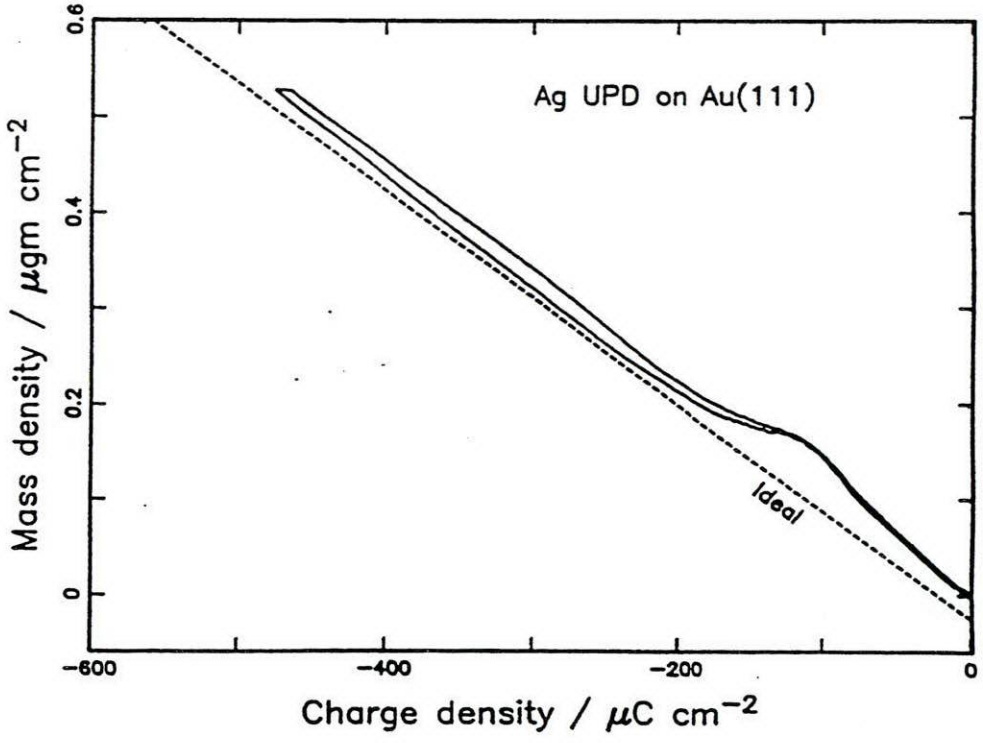


Figure 2. The calculated mass density plotted as a function of charge density for comparison with equation (2).

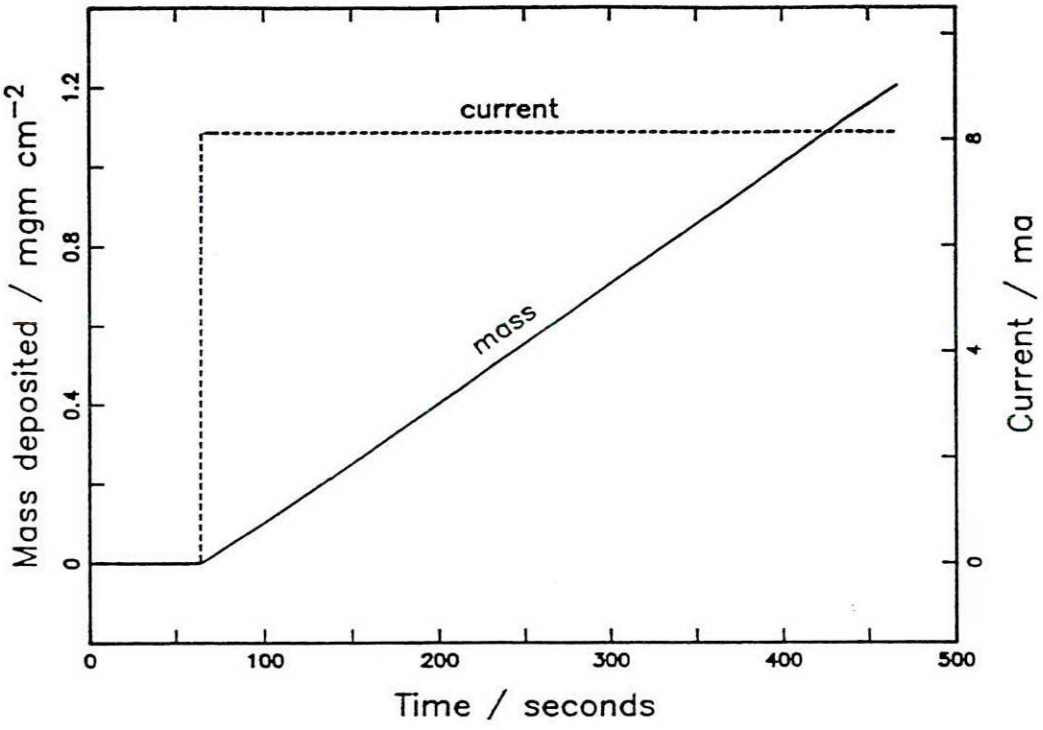


Figure 3. The current profile(dashed) during copper deposition and the corresponding mass increase.

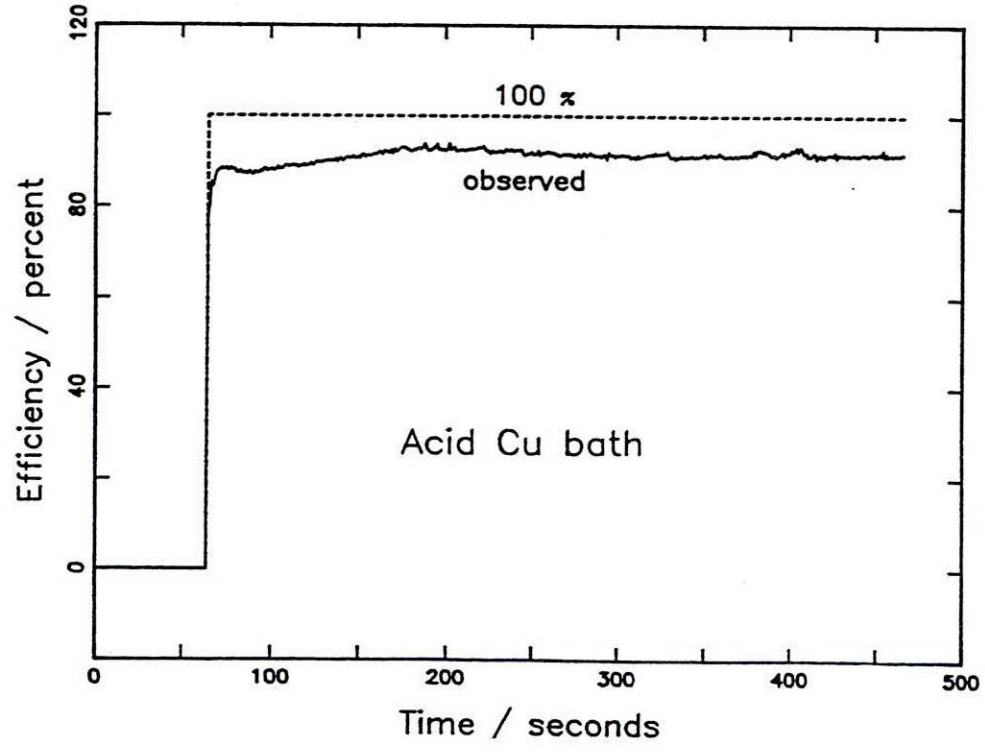


Figure 4. Details in the copper plating data of Figure 3 revealed by the Faradaic efficiency.

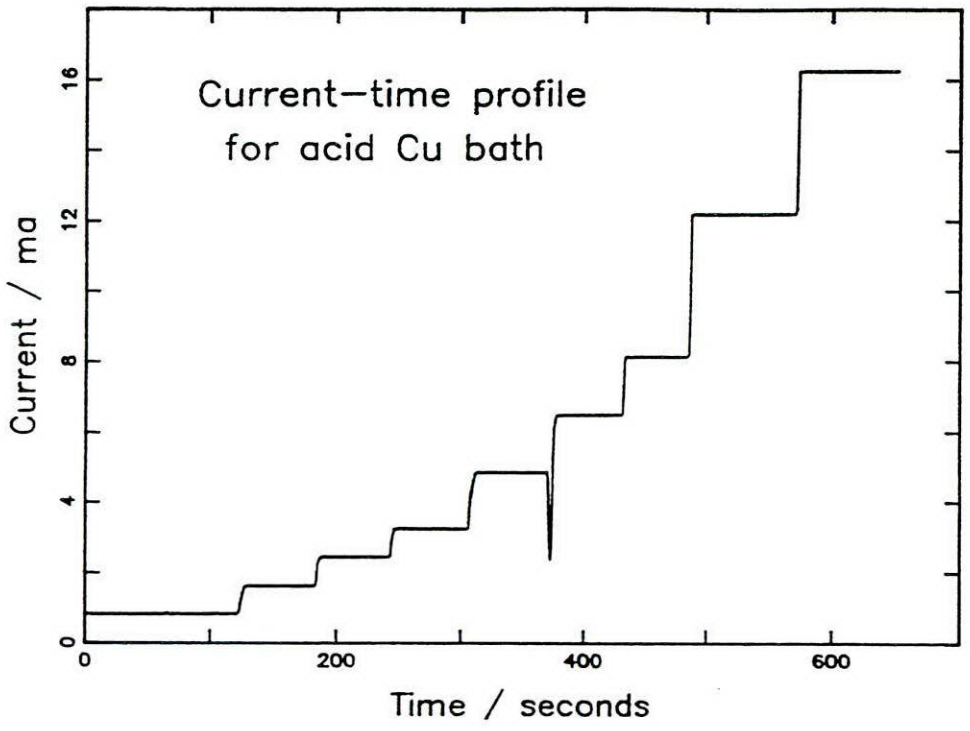


Figure 5. The current-time profile for the stepped current study to examine the effects of current density on efficiency.

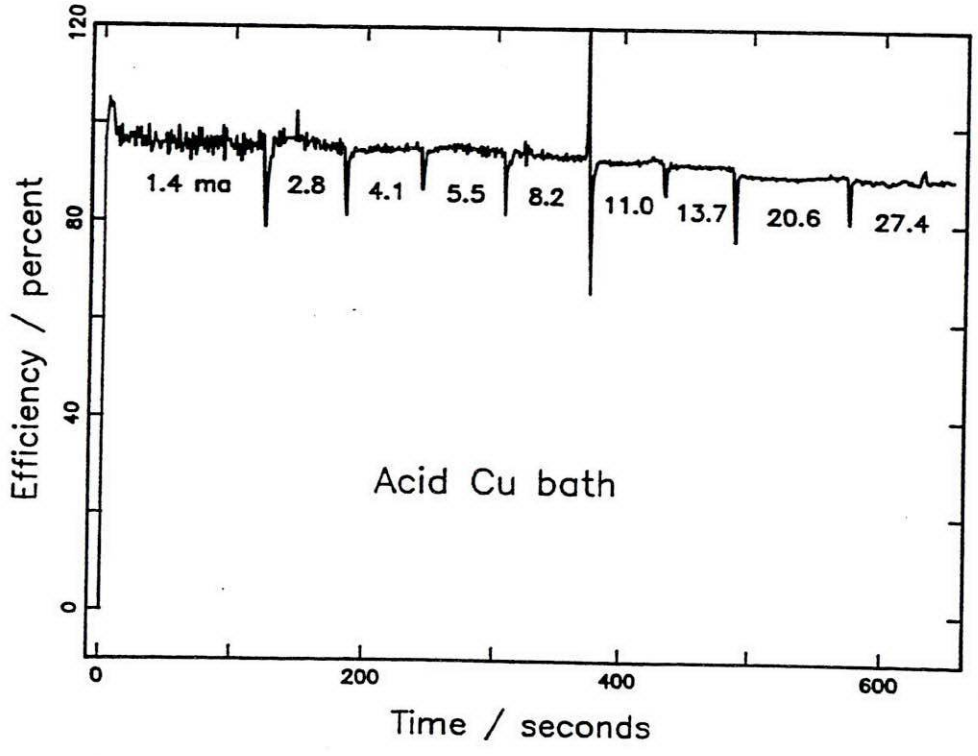


Figure 6. The decrease in the copper plating efficiency as a function of current to the electrode.

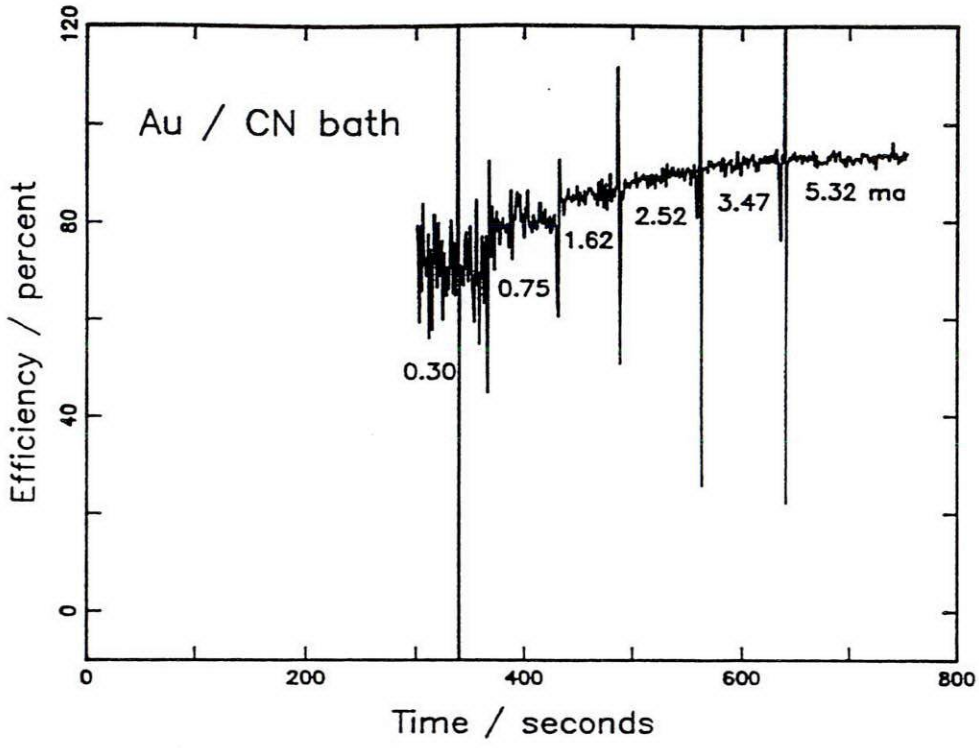


Figure 7. The efficiency of the gold/cyanide bath increases with increasing current.

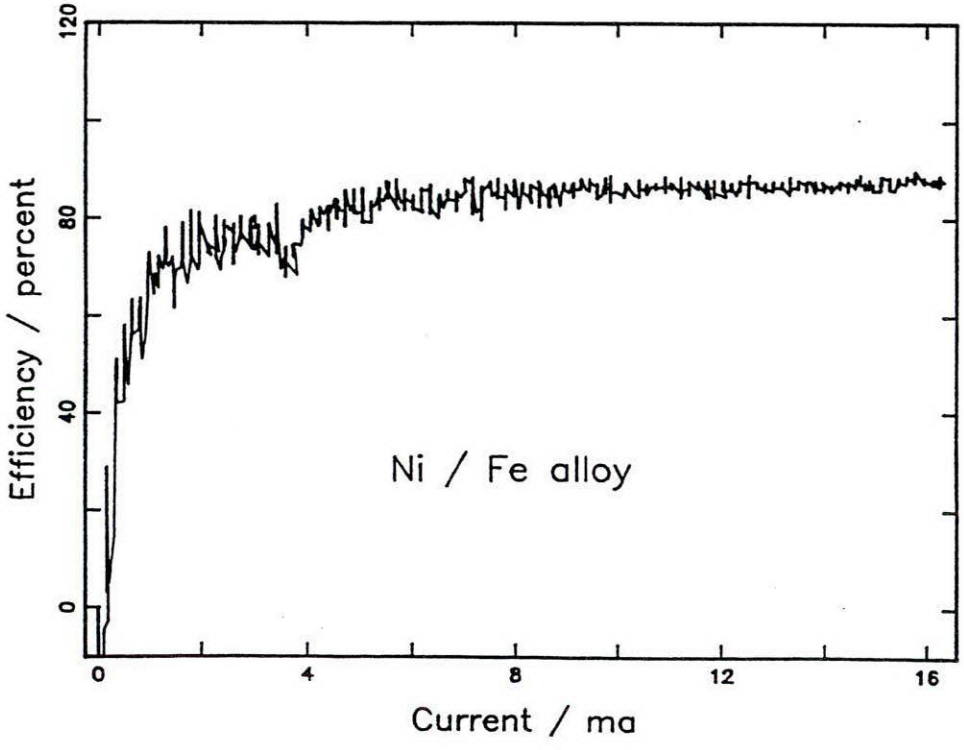


Figure 8. A quasi-static presentation of the dependence of the Faradaic efficiency on the electrode current for permalloy plating.

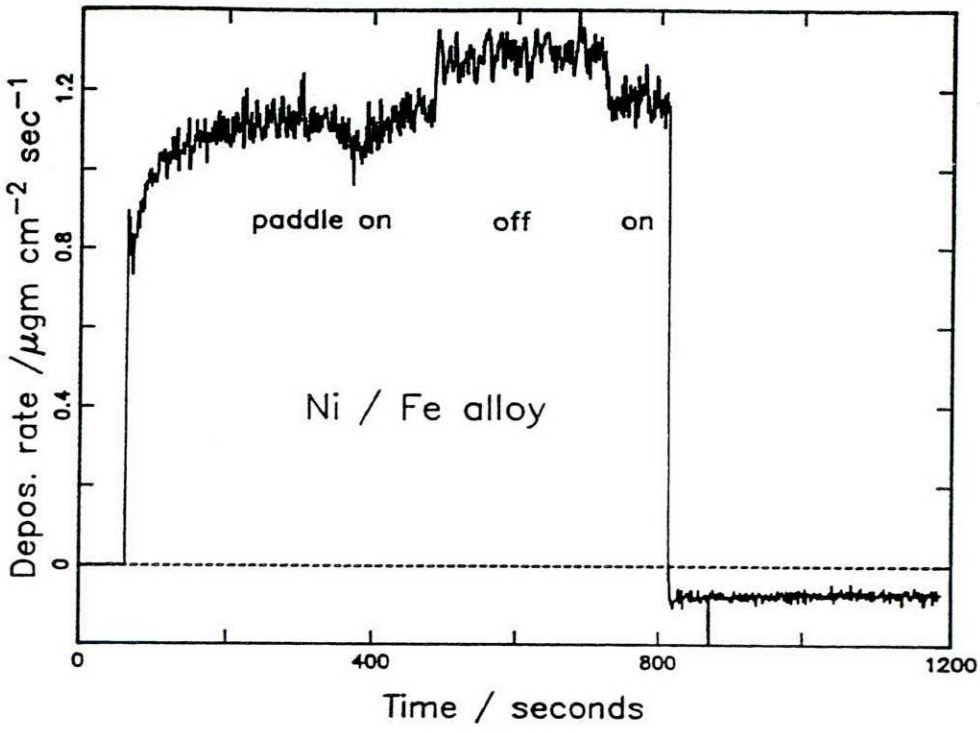


Figure 9. The rate of permalloy deposition as influenced by agitation. Also seen with zero current, is the stripping of the deposit (times > 800 sec).

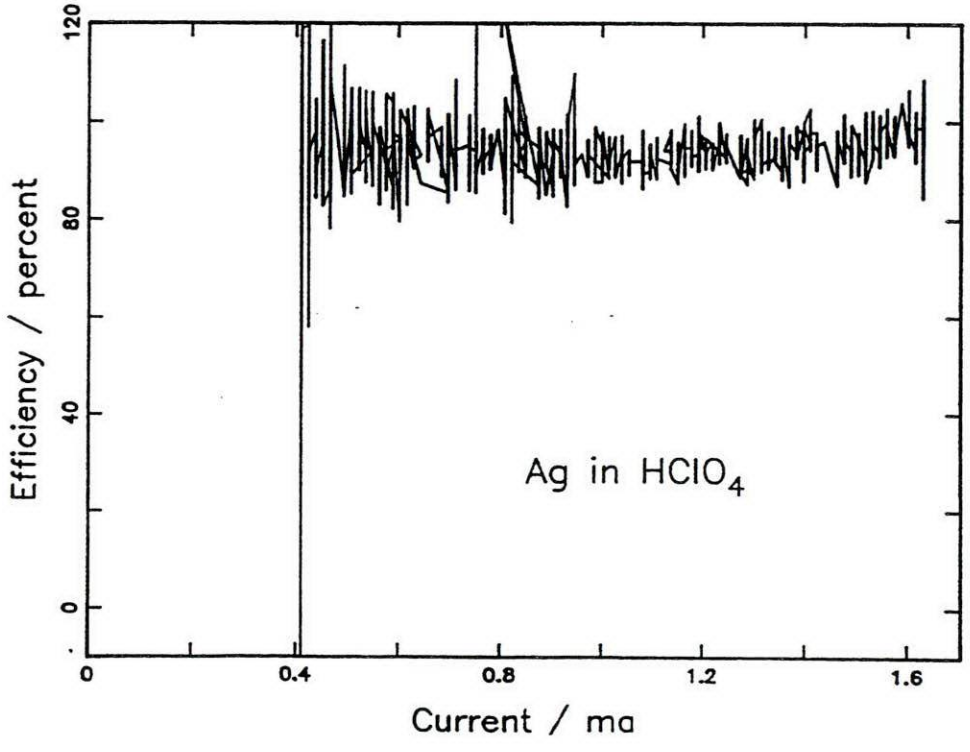


Figure 10. The Faradaic efficiency of silver deposition from perchloric acid onto an initially gold surface. High efficiency is indicated over the current range.

Use of a Spreadsheet-Based Computer Program to Calculate Chemical Additions and Implement a Feedback Control System

Michael R. Eckstein and Conrad P. Bowers

Industrial Plating, Inc., Lafayette, IN 47905

Abstract

The use of a spreadsheet-based computer program to assist with control of plating baths is described. This program saves time by automating record keeping, calculations, and graphing. The program calculates adds based on the chemical analyses, and provides adds for each shift until the next analysis is due. In addition to an immediate response to the analysis, the program examines the recent concentrations and compares them to the control limits. The estimated amount of chemical used per shift is adjusted in response, and this is used in future calculations, which helps prevent a reoccurrence of any excursion. The control of our tanks has improved as a result of the time saved and the consistency of the computer's response.

Introduction

Industrial Plating, Inc is a mid-sized metal finishing shop located in the Midwest. It operates on three shifts and electroplates tin, zinc, copper, nickel (several lines each), and silver. In addition to maintaining the quality of the finishes in general, much of the work must conform to thickness specifications. Some customers require statistical parameters such as Cpk (process capability) values. Increasingly tight control of the chemical composition of the plating baths has been required. The number of baths necessitates an efficient method of carrying out this control.

In its simplest form, control of a plating bath consists of the analysis of the components and the addition to the tank of the components in an amount proportional to the shortages. Complications arise during periods of production with no analyses; for example, if the plant runs three shifts but analyses are not performed on each shift. Moreover, after the addition made in response to an analysis, the consumption of the chemical may require further adds during the shift to maintain the concentration of the component.

The amount of chemical used during one shift (or per unit of production) is called the base add. If the

analysis is at nominal, the amount added over the course of the next shift would be the base add. However, if the chemical is above nominal, then the add must be less than the base add to allow the excess to deplete. Although a relatively simple calculation, this is time-consuming for every relevant tank in a mid-sized plant. Furthermore, many factors such as part type, efficiency of anode corrosion, etc. can change over time and require that the base add be changed. A method is needed to decide when to adjust the base add. A large change to the base add in response to every excursion in concentration could actually introduce more oscillation. Not changing the base add at all will usually cause the data to be biased towards one side of nominal.

A scheme has been suggested[1] in which the control chart is divided into two sets of three regions between the nominal target and each control limit (CL), plus two regions beyond the CLs (fig. 1). The further the region is from the nominal, the less points need be present in it to require a response. In our application, the response is to change the base add by 5%. This augments our immediate response to the analysis which is to restore the component to the desired level. The adjustment of the base add is permanent, and decreases the chances of another excursion. (This can be considered proportional and integral feedback, PIF.)

We have implemented the above scheme as well as the record keeping, graphing, and capability calculations on a commercially available spreadsheet. This saves a great deal of time, and provides consistent and timely adjustments to the base add. The PIF program consists of seventeen separate subroutines built around a main program in a spreadsheet environment. The use of a spreadsheet allows routine input of analysis data, and also any desired changes in tank parameters such as control limits.

Calculation of chemical additions. The approach of the program is to calculate an addition to restore the concentration to nominal and then to calculate several adds to be made during the day, to keep the concentration as close to the target as possible. The spreadsheet calculates the concentration from the beginning and ending volumes of a titration. Running the program results in a series of four chemical additions. The first addition (A_0, Eq. 1) is the amount of chemical needed at the moment of data entry to reach the nominal value. The second addition (A_1, Eq. 2) is the amount needed to maintain the component at nominal until the end of the shift. The third addition (A_2, Eq. 3) is the amount required for the shift following the analysis. The fourth addition (A_3, Eq. 4) maintains the component through the next shift until the tank is analyzed on the following day.

$$A_0 = \textit{current add} \quad (1)$$

$$A_1 = B\,t - E_0 \quad (2)$$

$$A_2 = B - E_1 \quad (3)$$

$$A_3 = B - E_2 \quad (4)$$

where E_0 is the amount in excess of nominal as indicated by the analysis. E_1 is the excess remaining at the end of the current shift, i.e., A_1 if it was negative. If A_2 is negative, that is E_2 in Eq. 4. The program determines t, (the fraction of the shift remaining) from the time of data entry. (This also permits identification of the adds on the output by shift number). If the analysis shows that the chemical is above nominal, the program adjusts the adds based on the

rate of usage of the component to allow the excess to deplete. The four chemical additions given by Eq. 1-4 are displayed on a easily read output screen. After a key is pressed the program saves the file and returns the user to the main spreadsheet menu.

Base add adjustment. The program uses the current analysis and data from the previous two days to determine if an adjustment to the base add is necessary. There are six zones placed between the nominal value and the control limits (CL), and one zone outside each CL (Fig. 1). The boundaries of the zones are located at an interval of one third the difference between nominal and the CL. (Unsymmetrical CLs are supported.)

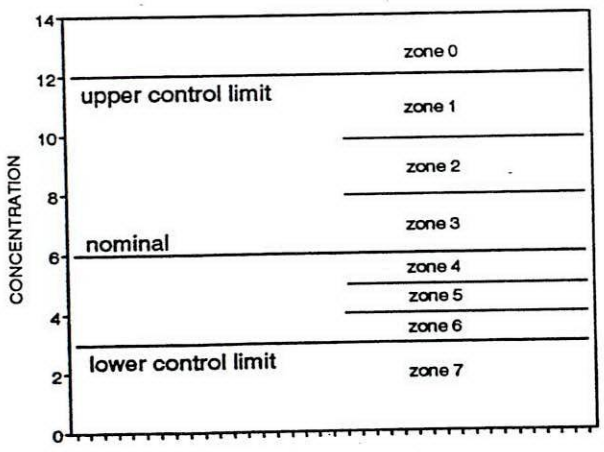


Fig. 1 Zones which the program uses to adjust the base add.

If the current analysis falls outside the CLs, the base add is modified by 5%. The analysis and base add are then used in Eq. 1-4. This will correct the immediate problem as well as institute a permanent change. If the datum is not outside the CLs, the program determines whether a significant trend has developed. If the current datum falls within zones 1 or 6, the program modifies the base add only if the datum for the previous day is in the same zone. The base add is adjusted when three points fall in the same zone for zones 2 and 5. Finally, if the current point is in zone 3 or 4 (close to the target), the base add remains unaltered. Thus the program is capable of adjusting to changing conditions. For new tanks, it will automatically optimize an initial estimate for the base add. The 5% change was selected to minimize oscillations, but could be easily changed to adapt to specific situations. The tradeoff is speed of response vs. immunity to oscillation. If more accuracy is desired, the CLs can be tightened by an easy entry in the spreadsheet. This would be appropriate if there was a series of data contained entirely in one zone, either 3 or 4.

Results

Figure 2 shows the zinc concentration (nominally 31.5 g/l) in one of our zinc chloride plating baths. The average prior to implementation of the PIF program was 33.5 g/l; the standard deviation of the concentration was 1.2 . After implementation, the average is 32.1; the std. dev. is 0.7 . The automated adds have decreased the offset (avg.-nominal) by two-thirds, from 6.3% to 2.1% over nominal. The average was at 53% of the range between nominal and UCL, now it is within 18%. There were a number of points close to or outside the UCL before, and now there are none.

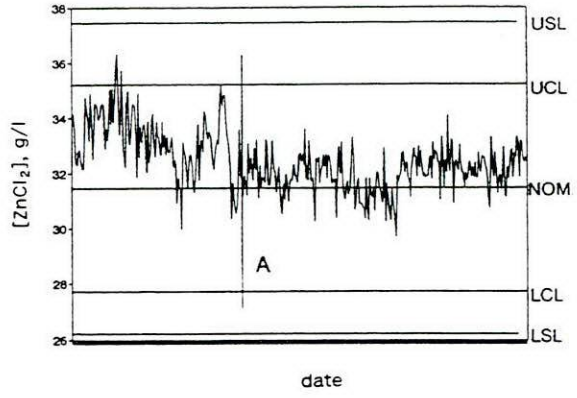


Fig. 2 Concentration before and after implementation of the PIF program for the last 18 months. USL, upper specification limit; UCL, upper control limit; NOM, nominal or target value; LCL, lower control limit; LSL, lower specification limit; A, implementation of PIF program.

The amount of $ZnCl_2$ added has been reduced by approximately half. Prior to PIF, the base add was 30 kg per shift. This amount was too large, but because of the greater oscillations in concentrations, we could not decrease the base add and be confident that the concentration would not become too low. As a result, excess $ZnCl_2$ was added, which resulted in a bias towards the UCL and in larger oscillations than presently observed. After the program was implemented, it optimized the base add to a current value of 18 kg.

Similar results have been obtained for two other zinc lines and a bright acid tin line.

Discussion

The lower variability and approach of the average to the nominal target should give more consistent plating results. This is particularly important in an automatic line such as the one illustrated, where it is not possible to vary the plating times as easily, or to check thicknesses and then continue plating. On a manual line a part which has a deposit under the thickness specification can be plated more. On an automatic such parts would be checked after they are completely out of the line, perhaps after postplate processes. An underspec part would be stripped and replated, because it would not be typically feasible to re-enter the plating tank directly. Significant costs are incurred for the labor, chemicals, and waste disposal related to strip-and-replate. If these costs can be reduced by better control of the tank, it is desirable. Depending on the process, better adherence to the tank content specifications can produce deposits with better thickness distributions, faster plating times, better appearance, etc.

Since the zinc from zinc chloride is approx. 2.5 times more expensive than from the anodes, the decrease in the zinc chloride addition is significant. The 4% decrease in concentration results in an equivalent decrease in dragout (solution adhering to barrels and parts). This results in waste minimization. Although a modest decrease, any savings on disposal costs are welcome.

Figure 2 shows a small bias in the concentration values above nominal in the most recent quarter. Because this offset is small, there are not typi-

cally three points in a row in zone 2 (Fig. 1). When this is true, and the standard deviation is also small, a tightening of the control limits can be considered. The computer could adjust these automatically or make such a suggestion to the user.

The precision in control (2.3%) is approaching the customary precision of the titration. If tighter control were necessary, increasing the sample size or number of replicates in the analysis, or an automated analysis/addition system would need to be considered.

Production. The amount of production may vary from shift to shift. This can be a significant factor in the amount of chemical that should be added. After the analysis and immediate adjustment (if needed), sufficient chemical is added for the remainder of the shift (Eq. 1-2). However, this assumes an average amount of production. The add during the subsequent shift can be adjusted when production of the previous shift deviates from the normal amount. To do this, Eq. 3 and 4 are modified to Eq. 5 and 6.

$$A_2 = B - E_1 - \frac{R_N - R_1}{R_N} Bt \qquad (5)$$

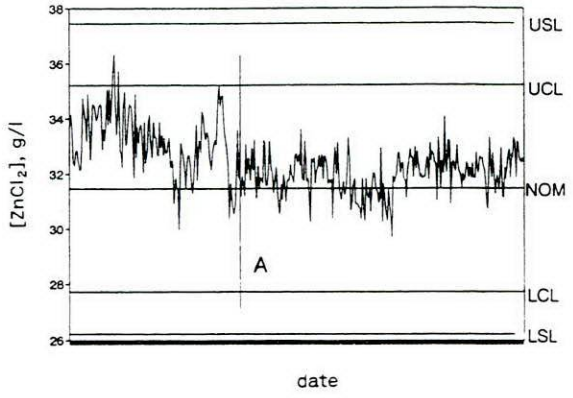
$$A_3 = B - E_2 - \frac{R_N - R_2}{R_N} B \qquad (6)$$

where R_N is the normal number of runs per shift, R_1 and R_2 are the number of runs of the shift on which the analysis was done and the subsequent shift, respectively. The necessary routines that accept input of production information have just been written and are in a testing stage.

Acknowledgement. A. Longworth, J. Tackett, & A. Niebling for chemical analyses; chemical maintenance staff (F. Clawson, D. Gaines, A. Belange, S. Smith, T. Saylor, K. Tyre, C. Landes, W. Rousch, J. Schick, D. Ward) for chemical additions. C.F. Williams, plant manager, for encouragement; Industrial Plating, for support and equipment.

Reference

1. Thomas, D.W.; Small, B.B.; et.al. Statistical Quality Control Handbook. 2nd ed. New York: Western Electric, 1958.



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ULTRASONIC AQUEOUS AND SEMI-AQUEOUS PRECISION CLEANING

Dr. Sami B. Awad
Crest Ultrasonics,
Trenton, New Jersey.

Abstract

Ultrasonic aqueous and semiaqueous precision cleaning or decontamination has recently found wide acceptance as effective and versatile alternative to replace the halogenated ozone depleting solvents (ODS's). This article presents the important aspects that must be considered in selecting an effective alternative process and discuss the role of ultrasonics in aqueous precision cleaning. It also discuss the new semiaqueous process and the roll of the solvent displacement solution (SDS)to yield higher quality decontaminated surfaces.

The current phaseout of the ozone depleting solvents (ODS's) as degreasing solvents highlighted two essential concerns. First, switching to a new cleaning process may affect the contaminant removal positively or negatively. Secondly, other related issues must be addressed, debated and resolved in advance, such as material and process compatibility, environmental issues, if any, new equipment performance and reliability, vendor technical service and support, space and facilities, operator training program etc. Particular areas of concern are in micro decontamination, defluxing and in critical surface preparation for coating or electroplating.

Also, many companies, for reasons other than eliminating CFC'c are considering other alternative processes. The use of volatile organic solvents (VOC's) and corrosive cleaners, without proper recycling, is being considered environmentally unacceptable and hazardous in the work place.

Surface preparation or surface decontamination is important in many applications and is so critical in others. For example, it would be unreasonable to setup new equipment and a process for deblocking lenses from waxes prior to polishing as one for surface preparation for vacuum deposition, coating, electroplating, or for cleaning delicate complicated precision components. The latter fall under precision or critical cleaning. Degree of cleanliness can be generally categorized at two levels : practical and atomic clean surfaces.

Precision cleaning by definition is the complete removal of undesirable contaminants to a preset measurable standard or better, and without introducing new contaminants. For example, precision cleaning of organic contaminants and particles can be achieved by an aqueous process, however, if rinsing is not adequate or water quality is not high enough, residual detergent or ionics will be the new contaminants. If drying is not effective, water residue can be the new contaminant. The preset measurable standard must be based on established proven level of decontamination.

A well defined process and proper equipment are needed to achieve consistently such levels of decontamination. Ultrasonics agitation offer several advantages over conventional immersion, pressurized air spray, tumbling or air bubbling agitation.

Ultrasonics generates cavitations in the cleaning media accompanied with acoustic streaming that effect the required scrubbing action. Uniformity, and consistency of the desired cleaning levels are two main characteristics of utilizing ultrasonics, particularly with the use of the appropriate frequency range, and the appropriate acoustic intensity. Other process parameters are also equally important such as compatible chemistries, operating temperature, rinse water quality, filtration of contaminants, and drying technique.

Ultrasonic Aqueous Cleaning

Aqueous cleaning is widely acceptable alternative for using solvents. Decontamination of surfaces with water is almost universal, except in rare cases where the substrate itself is a water sensitive or in the removal of certain high molecular weight hydrophobic coatings.

A typical ultrasonic aqueous batch cleaning equipment consists of four stations (fig. 1) :

ultrasonic cleaning, ultrasonic overflowing water rinsing (2 stations) and heated recirculated filtered air drying.

Ultrasonic cavitation energy provides the necessary scrubbing action through a continuous series of cavitation implosions. Energy released from each implosion results in two important actions: wave pressure and acoustic streaming of solution at high speeds. Cavitations can be optimized by operating the process at certain set of operating parameters. Maximum cavitation intensities can be generated at temperatures 130 - 160° F. Lowering the surface tension results in a faster degassing and better distribution of cavitation. The size of cavities is a function of the ultrasonic frequency. Larger size cavities and intense implosions occurs at frequencies in the range of 20 - 30 KHz while moderate sizes and implosions occur at frequencies of 40 - 70 KHz. Frequencies at the high end are utilized with thin films and micro components. A larger number of cavities with very fine implosions can be generated at frequencies in the range of 700 - 900 KHz. Most ultrasonic cleaning equipments operates in the range of 25 - 75 KHz.

Process And Chemical Selection

A well pre-defined process based on laboratory testings will save time and cost and will allow smooth switching. The new process design must take in consideration that the cleaning step is only one step in an integrated multistep operation. Throughput is a crucial factor in scaling up the required equipments.

The appropriate detergent chemistry for specific application resides largely in the ability of the detergent components microstructures to enable proper displacement and encapsulation of contaminants in the micro range. Another important characteristic is compatibility with the substrate. By using a well designed detergent system, various non-ferrous multimetal components can be decontaminated in the same cleaning batch. Also, we recently developed special short term and long term flash rust inhibitors technology for ferrous components. The new technology does not interfere negatively with the next treatment step(s) such as vapor deposition, coatings, painting, electroplating and heat treat.

Ultrasonic Semi-Aqueous Cleaning

Semi-Aqueous cleaning is an effective alternative process to clean wide spectrum of heavy organic contaminants including fluxes, greases & oils, waxes , buffing and lapping compounds, adhesives, coatings and other types of heavy soils. Semiaqueous cleaners are two types: water-immiscible and water-miscible. The nomenclature "Semiaqueous" originated from the two step cleaning method where the first step is always cleaning in an organic solvent concentrate followed by rinsing with water.

The water-immiscible semiaqueous solvents are generally include a base selected from refined mineral oil hydrocarbons or terpenes, a family of natural hydrocarbons, or it may be selected from other water-immiscible organic liquids such as synthetic or natural organic esters. The base material may be formulated to enhance properties such as solvency and rinsability with water. The other class of semiaqueous cleaners is water miscible and mainly formulated from certain types of linear or cyclic alcohols e.g. tetrahydrofurfuryl alcohol or cycloamides e.g. N-methylpyrolidinone. This class is characterized with flash points higher than 150° F, good solvency and good rinsability.

Water immiscible halogen-free semiaqueous cleaners are hydrophobic in nature and have low surface tensions, of about 30 $\pm$ 5 mN. Their main function is to solubilize the surface contaminants. Inducing cavitation in semiaqueous solvents is not simple It requires using a special power SA-generator, a properly designed circuitry for cavitating semiaqueous solvents, with matching PZT transducers to overcome the higher viscosities and larger molecular weights of such solvents.

Water miscible semiaqueous cleaners are easily to rinse with water. Ultrasonics assists in speeding both the cleaning and the rinse steps. It is known that hydrocarbon based semiaqueous solvent cleaners when rinsed with water never produced consistently surfaces free from the hydrocarbon residues i.e. water-brake free surface. Therefore, for water-immiscible semiaqueous process, the process must include an additional solvent

displacement step (SDS) prior to the water rinses. The new process involves the use of a formulated product(s) to be used in the SDS, prior to the water rinse step, in a station which include a circulating phase separation system (decanter). The SDS chemicals are formulated aqueous products designed to be compatible with any given cleaning application. For example, the SDS for cleaning fluxes from on circuit boards or other electronic components is designed so that it does not contribute any ionic contamination. Another SDS is designed for metal cleaning applications. It is designed to be compatible with multi metals and as well provides the necessary protection against corrosion. The SDS are Ozone-safe and environmentally benign. The SDS fully displaces the solvent film without emulsifying the semiaqueous cleaner. Because of its lower specific gravity, the semiaqueous phase will float and then continuously overflowed to a separating tank or decanter (Fig. 2). The bottom phase which contains the SDS is recirculated back to the SDS tank. The collected semiaqueous cleaner can be returned to the original first tank or discarded of as a waste. Replenishment of the SDS is roughly proportional to losses from the dragout.

The flash point of the semiaqueous solvent concentrate has to be seriously observed when deciding on water rinse temperature because of escaping vapors. Low flash semiaqueous cleaners in the range of 100 - 140° F, normally have higher vapor pressure values and potentially will be steam distilled at a higher rates with the water vapor particularly at higher rinsing temperatures and creating a potential emission or VOC problem.

Drying

The most common drying technique is the heated circulated air with an optional HEPA filter. Other drying techniques are also available including tunnel dryers, infra-red, water-dryers and vacuum dryers. The number and the size of stations are determined based on production throughput, the soil loading, and required drying time.

With respect to drying of surfaces which had never been treated with an SDS and carry residual hydrophobic spots, it was found that it tends to take longer time to dry.

Drying of hydrophilic surfaces takes less energy

and less time. An estimated 25% reduction in drying time is attainable. It is known that residual unremoved hydrophobic film or spots on the surface hinders water drainage and enhance the rinse water to coalesce forming droplets and therefore carry more rinse water to the drying step. Consequently, drying requires longer time and/or higher temperatures.

Numerous benefits are realized from using the SDS step. Complete removal of the hydrophobic solvent films and their contents from on cleaned surfaces. These films can negatively interfere with an important next step operation such as soldering, painting, electroplating, vacuum deposition coating, powder coating etc.

Drastic reduction in the semiaqueous solvents dragout into the rinse water and consequently to the dryer as well as to the water streams. Reduction of water consumption. Rinsing stations are successfully reduced to one or two station versus three or four in a typical batch cleaning system without the SDS. Also, the SDS helped in allowing the use of water preservation system, such as close looping of the water rinses with a system which include carbon filters and ion exchange resin beds.

Typical Examples

Examples (Table 1) of actual industrial contaminants and substrates, used to be cleaned with the ODS solvents, are now successfully cleaned and dried with ultrasonic aqueous or semiaqueous processes.

Table 1
Various materials and contaminants cleaned ultrasonically with aqueous and semiaqueous processes

bstrate	**Contaminants**	**Process****
uminum	Machining oils, coolants	1
ass	Buffing compounds, oils	1,2
ryllium-Copper	oils, lapping compounds	2
eel 400,1000&5000 series*	Cutting Oils, grinding swarf	1
ainless Steel	Machining oils	1
lybdenum , Turbin blades	Microcrystalline wax	2
tanium	Oils, waxes	1
licone wafers	Mineral oils, S powder	2
ass, Mirrors	Blocking wax, pitch, lacquer	1
D glass	Adhesives, fingerprints	1
sed silica	Beeswax, pitch, polishing	2
astics, Medical, Automotive	Silicone oil, Mold release	1
artz and Sapphire	Pitch, polishing compounds	2
B's, Semiconductors	RMA flux, conformer coatings	1,2
ramics, Semiconductor	Solder flux	1
tical polycarbonate lenses	Buffing, lapping ,fingerprints	1,2
ber glass	Grease, oils, particulates	1
n / lead plates	Stamping oils	2
tical Glass lenses	Polishing compounds, waxes,oils	1,2
nc die cast	Buffing compounds, oils	2

Processes to clean rustable steels included flash rust inhibitors

Process 1 : Aqueous , Process 2 : Semiaqueous

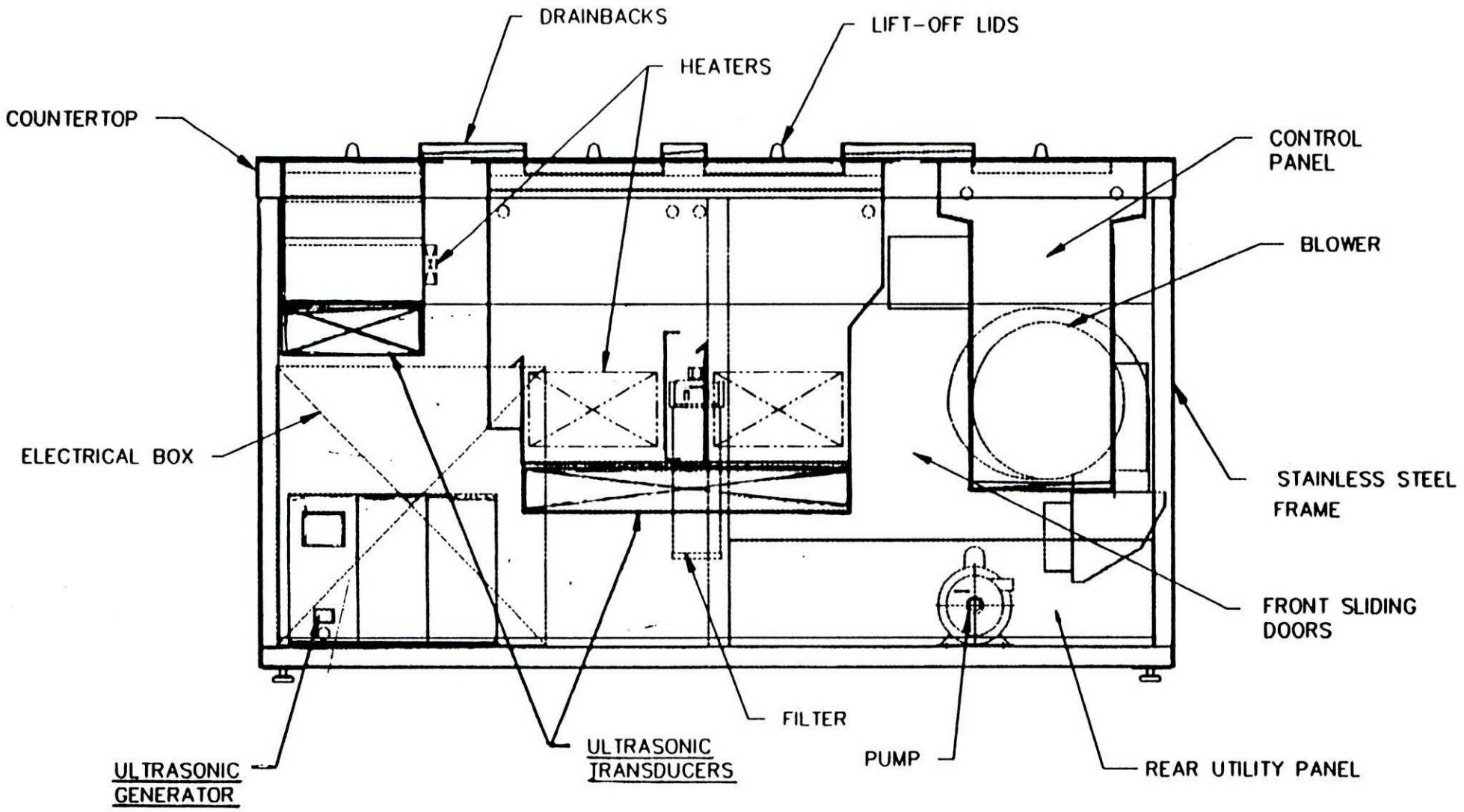


Fig. 1 Four-Station Ultrasonic Cleaning System

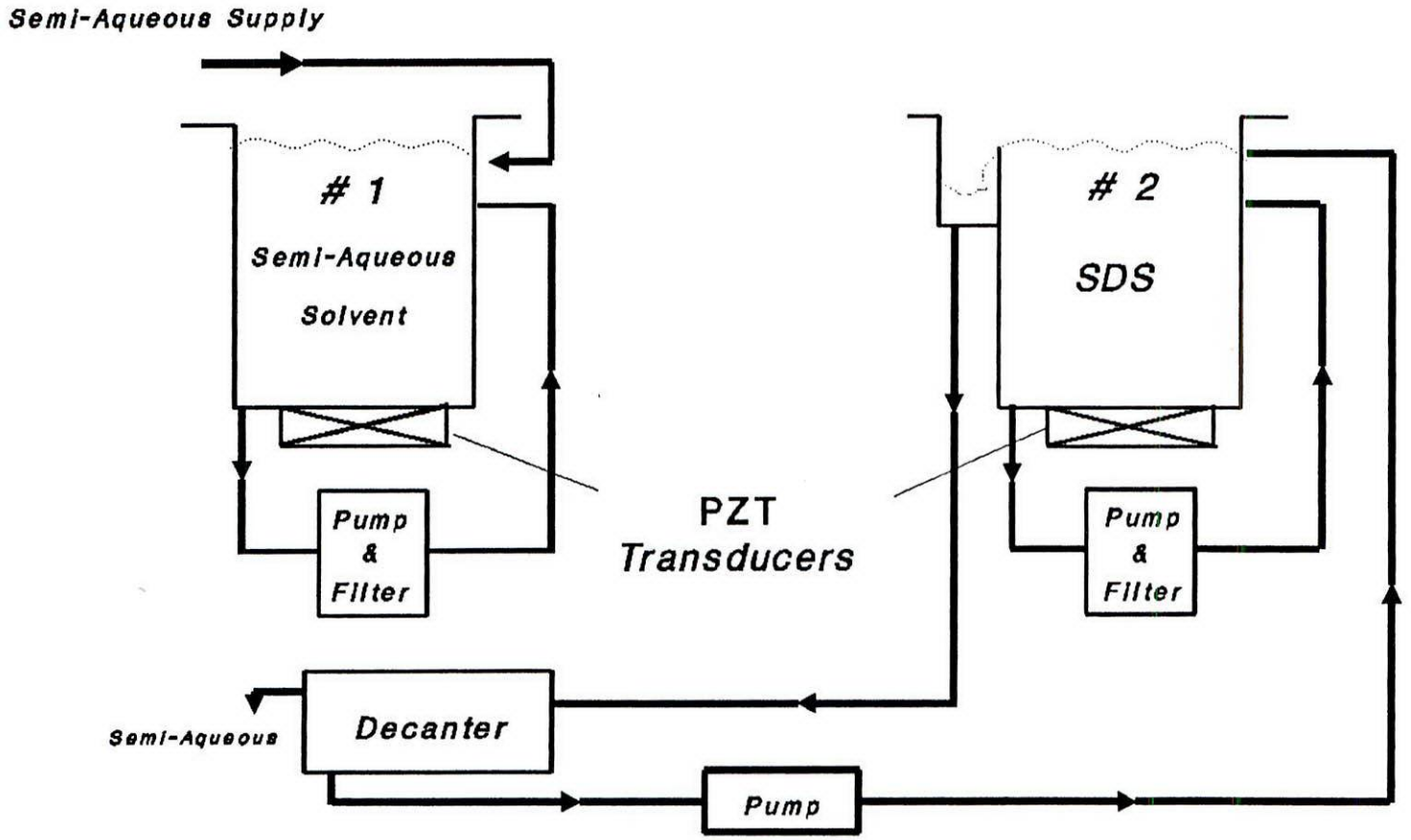


Fig. 2 ULTRASONIC SDS PROCESS STATIONS 1 & 2

EVALUATING YOUR ALTERNATIVES TO REPLACE AN OZONE DEPLETING CLEANING PROCESS

By Wayne L. Mouser
Director of Sales & Marketing
Detrex Corporation

By the time you read this paper you will have only two years left to fully convert to a non-ozone depleting cleaning process. The U.S. Environmental Protection Agency plans to implement a total ban on the production of trichlorotrifluoroethane (CFC-113) and 1,1,1-trichloroethane (methyl chloroform) in the United States by January 1, 1996. Further, participating countries of the Montreal Protocol plan to do the same. Solvent producers are warning that shortages may exist before the deadline since it may not be profitable to operate plants at reduced capacity. The time to act is now.

Conversion to Non-Ozone Depleting Solvents

The proposed SNAP (Significant New Alternatives Policy) as published May 12, 1993 in The Federal Register lists methylene chloride, perchloroethylene, and trichloroethylene as acceptable substitutes since they have no ozone depletion potential. That is the good news. The concerns with this group of solvents is their toxicity. It is necessary to control the loss of solvent to the atmosphere and minimize exposure to workers. It is anticipated new regulations will be in place requiring efficient equipment by early 1995. If you plan on converting your existing degreaser you should consider the following retrofits:

1. Extended Freeboard
2. Freeboard Chiller
3. Carbon Adsorption System

A new solvent saving device from the Detrex Corporation is the Enviro-Seal. This device covers an open top degreaser while still allowing product throughput. Solvent loss due to air currents is minimized and operators are isolated from solvent vapor contact. (See Figure I.)

Additionally, a number of new solvent systems are now available. These systems use vacuum technology or carbon adsorption to keep the vapors in the system.

Figure II. depicts a recently installed conveyorized system which meets the latest regulations by utilizing a built in carbon adsorption and distillation unit. This system utilizes trichloroethylene to degrease highly polished metal parts.

Conversion to Aqueous Cleaning

If your parts can tolerate contact with water and alkaline cleaning solutions, aqueous cleaning may be the most viable alternative. There are already many successful conversions. RCA Thomson Consumer Electronics, Marion, Indiana, a major manufacturer of televisions, converted from degreasing the picture tube masks, frames, and shields with chlorinated solvent by working with Industrial Chemical Specialties Division of Detrex to develop an aqueous chemistry to suit their specific needs. The parts required complete oil removal and drying before the next step, blackening in an inert atmosphere furnace. Cleaning is highly critical because any soil remaining on the surface of the parts will flake off after oxidation coating and cause a defective TV tube. Thomson Consumer contracted with the Detrex Equipment Division to modify three existing degreasers and to later build four new inline aqueous cleaning systems. The cleaning cycle consists of a spray in air wash using Detrex caustic liquid cleaner 75LC at 4% concentrate followed by three recirculating rinses, deionized rinse and turbo blower and infrared heated drying. Thomson states the current level of cleaning with the aqueous process exceeds 1,1,1 tri levels and the cost is less. (See Figure III.)

AVD - Advanced Vapor Degreasing

Not all cleaning requirements can be handled by water or other acceptable alternatives. Some parts may be damaged by water or their performance may be affected by the presence of water remaining from the cleaning operation. For these critical cleaning applications, a new process exists. AVD - Advanced Vapor Degreasing was invented by Petroferm, Fernandina Beach, Florida. The process uses a Petroferm solvating agent which is non-ozone depleting, non-flammable and highly compatible with a wide range of parts. The parts are rinsed and dried with 3M's Rinsing Agent 6000. Perfluorohexane (PFC) produces a spot free, dry surface required on some critical parts. The equipment produced by Detrex looks very much like a typical vapor degreaser. The main difference is the tight controls to keep the vapor from escaping the machine. PFC is very stable, non-toxic and not an ozone depleter or VOC. However, like methyl chloroform and CFC's, PFC's have the potential to contribute to global warming. The U.S. EPA has determined that PFC should be used only in critical cleaning applications that cannot be handled by other viable alternatives such as aqueous or semi-aqueous. The next generation of AVD rinsing agents will eliminate this disadvantage. These new materials are expected to become commercially available in two to three years, and will be usable in current AVD equipment.

Since its introduction at last year's CFC Conference, AVD has been successfully implemented at selective critical

cleaning sites. Process performance has been excellent and low chemical use rates have resulted in low operational costs. One of the big three automotive OEM's chose AVD to replace CFC 113 cleaning of delicate screw machine parts. The parts could not tolerate tumbling which would have been necessary for adequate cleaning and drying with aqueous or semi-aqueous processes. The AVD process, utilizing an inert vapor blanket, thoroughly dries the parts without part rotation. By replacing the CFC process with the AVD process, ozone depletion was completely eliminated and global warming potential was reduced by more than 50% in this application.

Conversion to Semi-Aqueous Cleaning

Some parts are highly sensitive to ionic contamination and corrosion from alkali saponifiers. For this reason, CFC 113 has been very popular in the precision and electronic cleaning arena. Semi-aqueous cleaning utilizes a pH neutral aliphatic hydrocarbon or terpene to wash organic residue. Water is then used to rinse away the wash solution. Deionized water is normally used as a final rinse followed by mechanical drying. Convex Computer, Richardson, Texas, a highly regarded super computer manufacturer, recently implemented a semi-aqueous cleaning system for their sophisticated printed wiring assemblies. They chose DuPont AXAREL as the defluxing agent and a model LE 20 Inline Defluxing System by Detrex. Convex reports superior ionic cleaning with the new system. (See Figure V.)

Conversion for the Small to Medium Cleaning Requirements

Many small companies cannot afford high priced new equipment. Even for large companies, replacing a vapor degreaser that costs less than $10,000 with a far more expensive aqueous system is a bitter pill to swallow. For these companies, an inexpensive alternative is now available. PPG has implemented Micro Phase III at KSG Industries Manley Valve Division, York, Pennsylvania. This new micro emulsion is used in a single tank Detrex model MLW-1D to remove oil from valve bodies. Oil can be automatically separated from the wash bath at a 97% rate of efficiency. Manley Valve has experienced a bath life of over five months. Since no effluent is going to drain, this is a very inexpensive cleaning operation. Manley Valve reports the new process actually costs less to operate than their old 1,1,1 tri process. (See Figure VI.)

Guidelines for Conversion

The above examples are some, but not all of the alternatives available to you. The following guidelines are offered to help you through the conversion:

1. Determine your cleaning needs. How clean does the part

have to be? Can you consolidate two or more cleaning operations? Carefully define the contaminant to be removed.

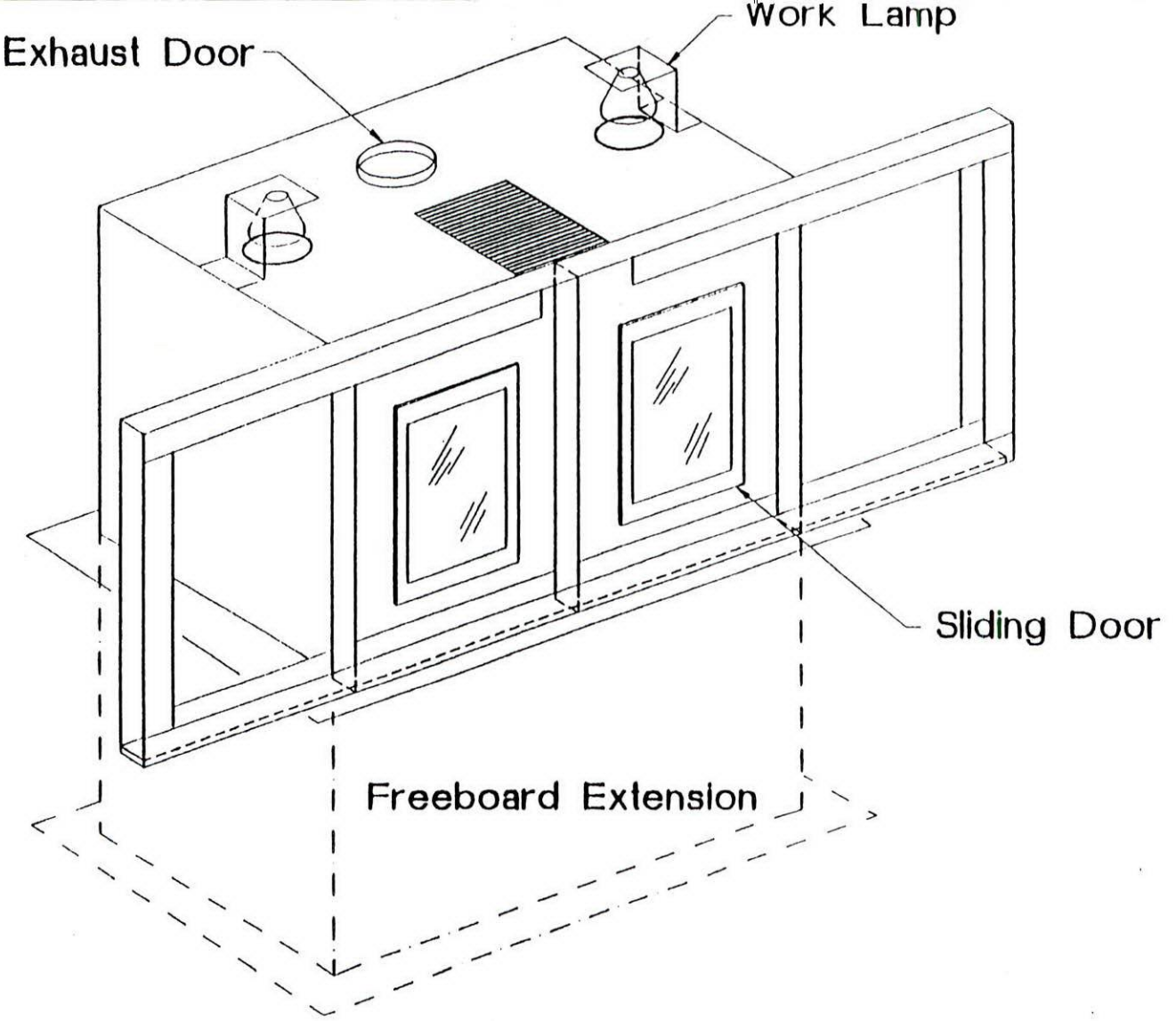
2. Select two or more prospective vendors carefully. A qualified vendor should offer a number of alternatives for your consideration, not just one or two.

3. Test your parts. Don't rely on a "try it, you'll like it" sales pitch. A qualified vendor can arrange a well defined cleaning test and should be willing to guarantee the new process. You should supply fresh parts in sufficient quantity to represent a typical cleaning requirement.

4. You should travel to the vendor's test site and personally witness the test. A little money spent up front could save a bundle. Considering the time constraints, choosing the wrong cleaning system could be a real problem, not to mention the cost.

5. Plan for waste treatment. All cleaning systems have a waste stream of some type. Learn what these requirements are and plan for implementation.

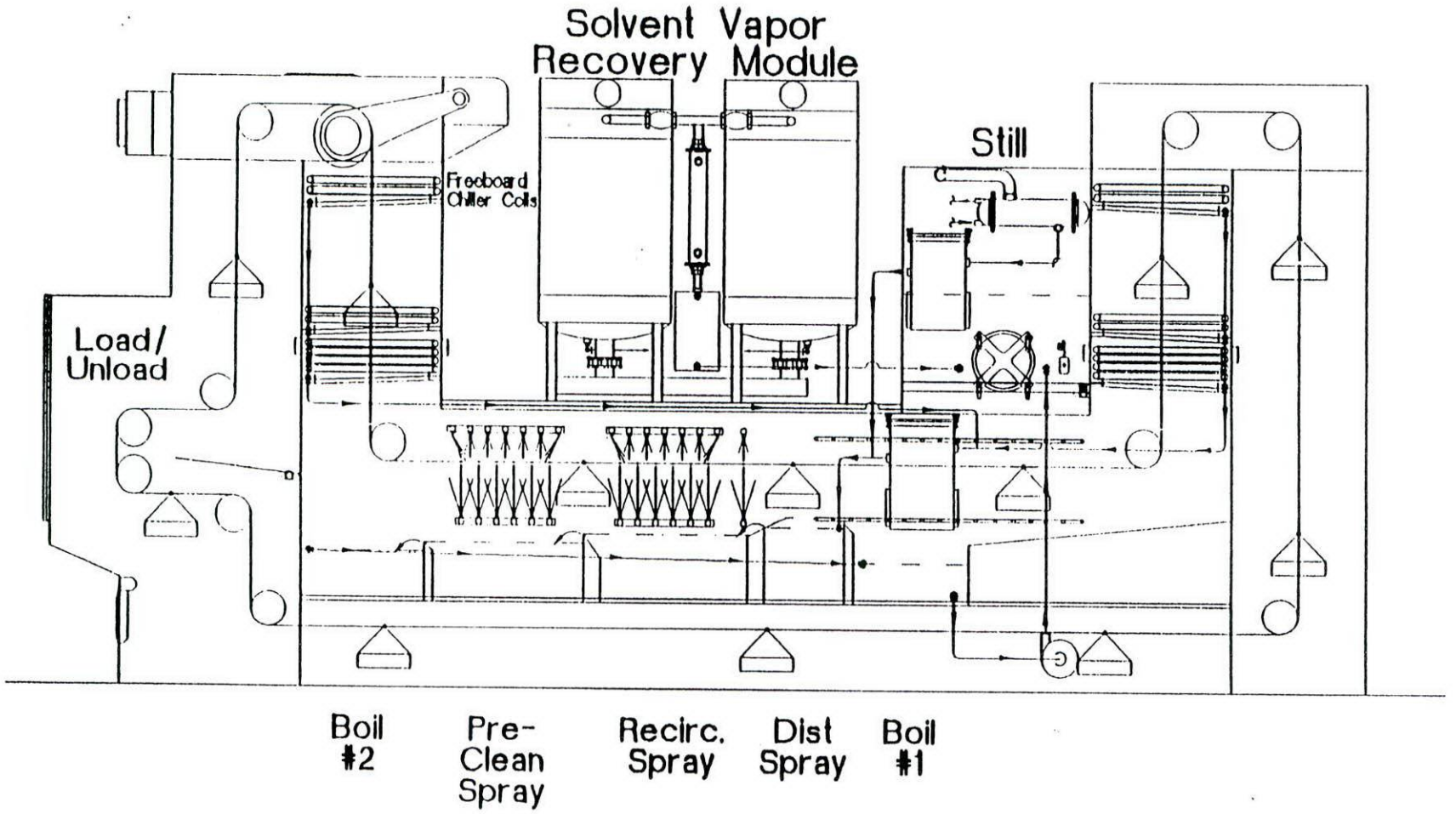
6. Don't wait until the last minute. Get started now so that you can choose the best, most cost efficient alternative to suit your needs.



Enviro-Seal

Exhaust Hood Assembly

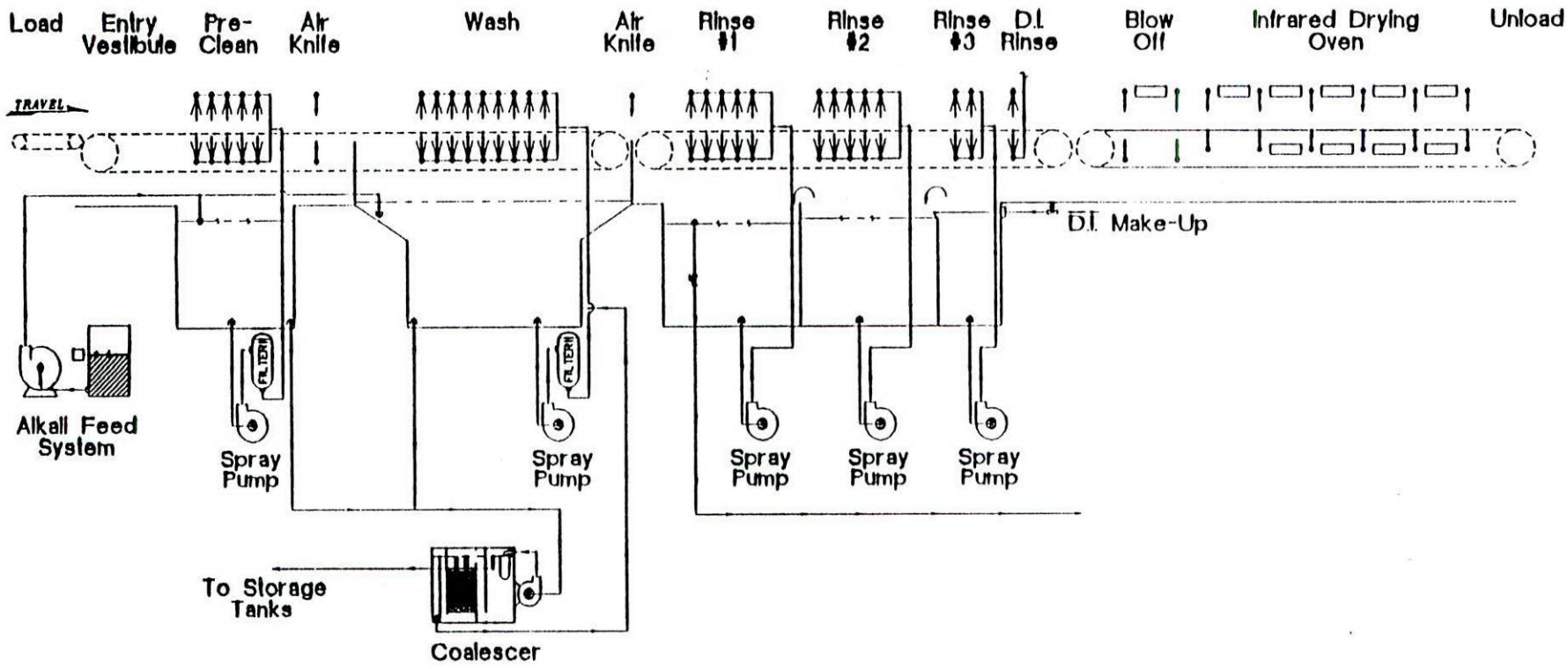
Figure I



Detrex

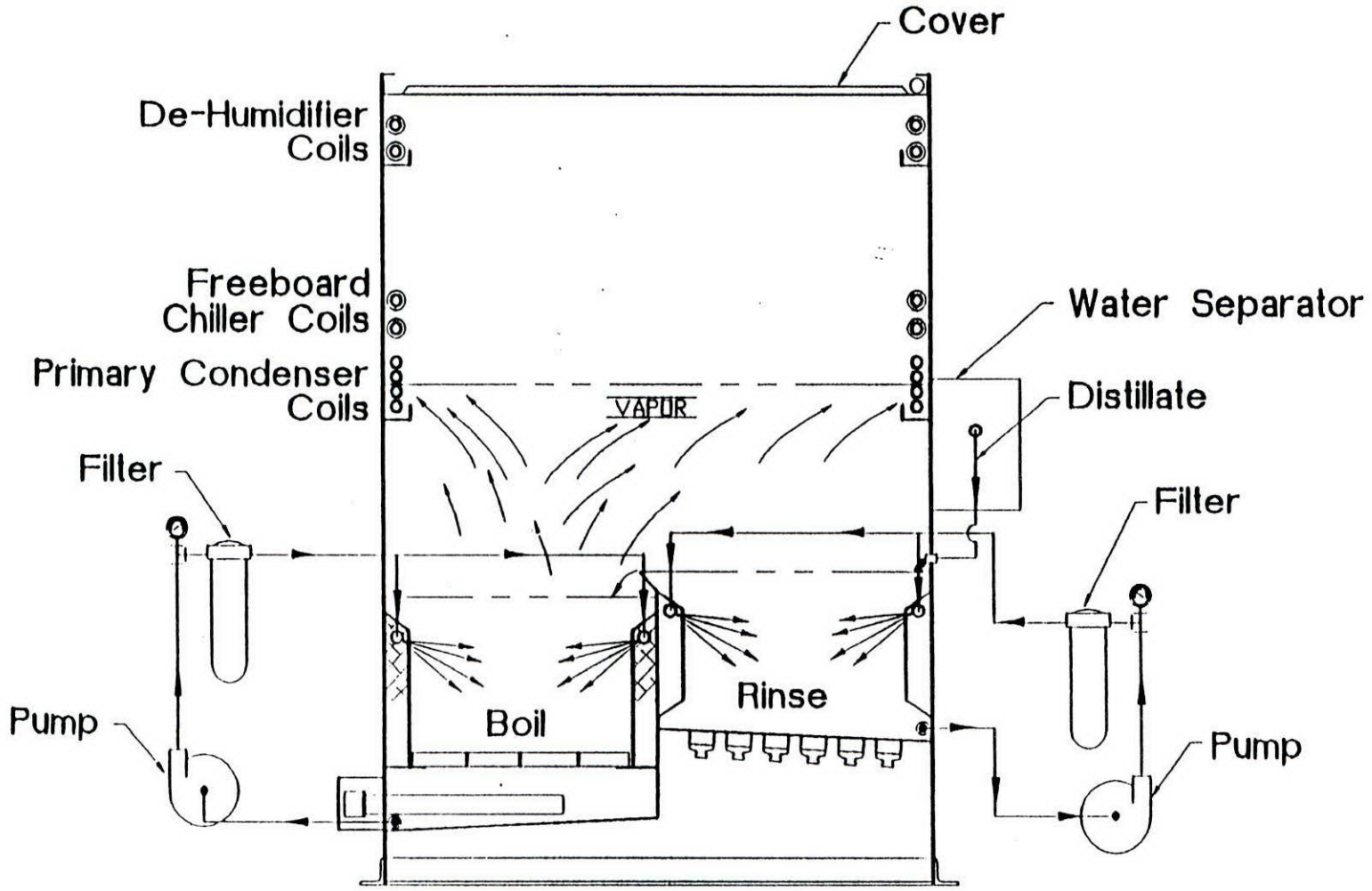
Conveyorized Degreaser

Figure II



Detrex
Industrial Washer

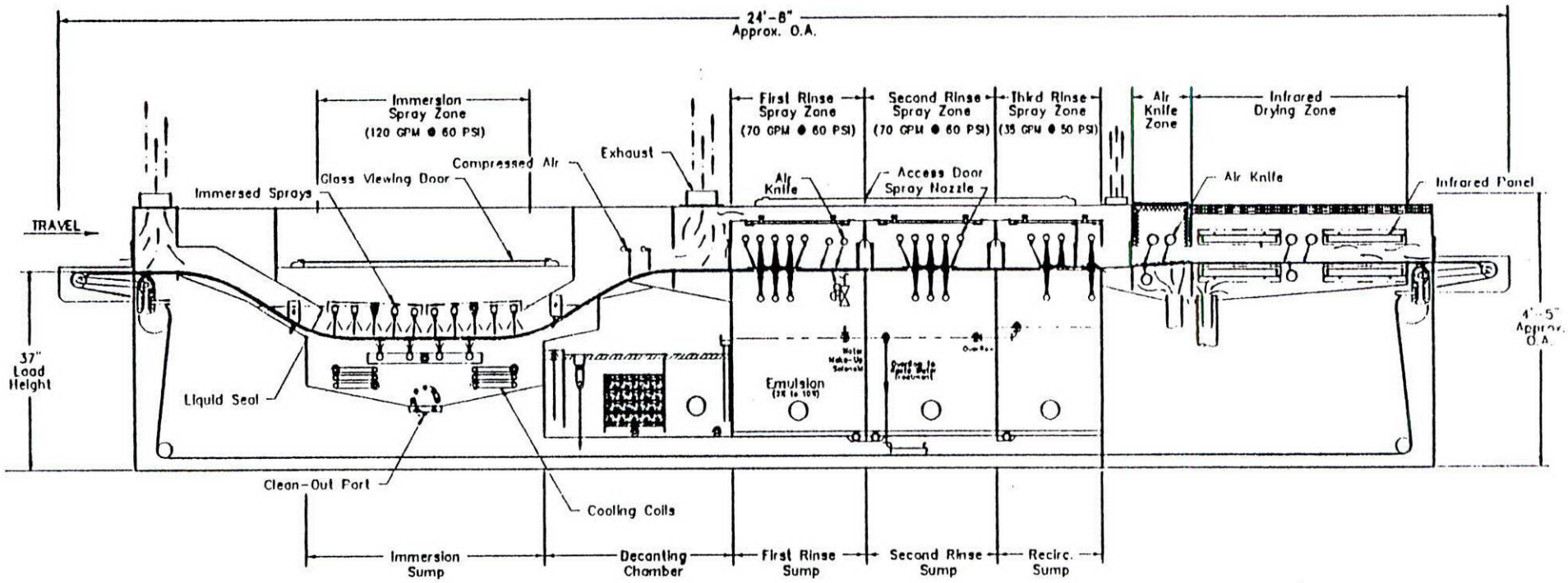
Figure III



Detrex

Advanced Vapor Degreasing

Figure IV



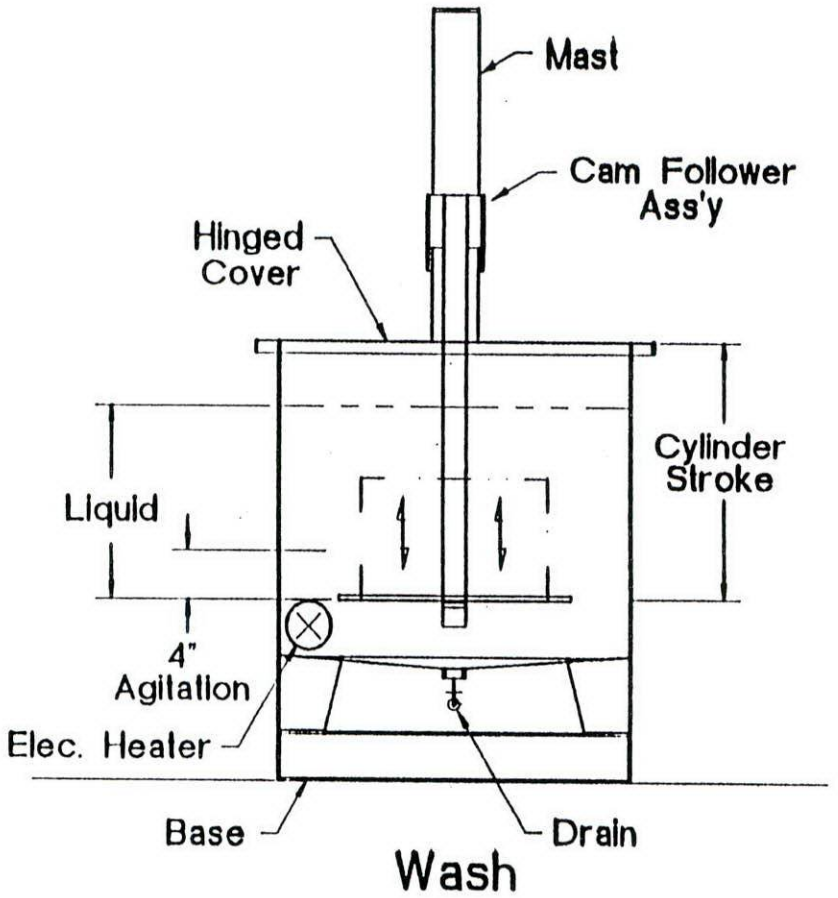
Detrex

LE-20A Defluxing System

Figure V

Modular Lift Washer

Detrex MLW-1D



Single Stage System

* Emulsions
* Hydrocarbons

Figure VI

The corrosion resistance of tin/zinc alloys.

Jean Rasmussen[1]
The Centre of Advanced Electroplating
The Technical University of Denmark
DK-2800 Lyngby, Denmark

Abstract.
The corrosion resistance of tin/zinc alloys, electrodeposited from a modified DIPSOL SZ-240® electrolyte is investigated in neutral salt spray (ASTM B117) and Prohesion® tests. Electrochemical (EC) and CMT (Corrosion Measurements by Titration) measurements of the corrosion current, is used to identify the optimal alloy composition and the process conditions under which a porefree coating is obtained.

The corrosion tests include unpassivated and yellow chromated alloys. A chromate free posttreatment, based on molybdenum and phosphate (Molyphos®) is also investigated.

The best results in the corrosion test, are achieved when the zinc content in the alloy is kept between 20 and 25 wgt-%. Higher and lower values reduce the corrosion performance. The alloy is porefree, when the cathodic current is increased. This is done in order to lower the potential below a value necessary for degradation of additives in the electrolyte. The breakdown products are believed to act as grain refiners.

In the Prohesion® tests, the corrosion resistance of unpassivated tin/zinc alloys is comparable to yellow chromated acid zinc. A posttreatment with Cr(VI) or Molyphos® increases the corrosion protection of tin/zinc plated steel. The alloy then becomes superior to the zinc.

The new chromate free passivation system raises the corrosion resistance of the alloy to a level comparable to that of a chromate treatment. The performance of chromated tin/zinc alloys depends on the formulation of the chromate solution.

Introduction.

Both tin and zinc are widely used for the protection of steel against corrosion. Each has it's own area of application and they protect steel by different mechanisms.

Tin is more noble than steel, and under ordinary atmospheric exposure it forms a corrosion protective envelope around the steel substrate. However, rusting does occur through pinholes and imperfections in the tin coating.

Zinc, on the other hand, is less noble than steel and offers protection by a sacrificial action. The steel underneath the imperfections in the coating is galvanically protected by the zinc, which forms the anode. The steel substrate forms the cathode.

The corrosion protective ability of both metals are combined in tin/zinc alloys containing 80 per cent tin. Like zinc, the coating protects steel sacrificially. Consequently steel does not rust through pinholes, as it does when protected with tin coatings; and yet the coating does not form such voluminous white corrosion products as zinc coatings.

In the past years, new non-cyanide processes for electrodepositing tin/zinc alloys have been developed. Compared to the cyanide process from the fifties, these new electrolytes are more stable and easier to handle. Furthermore, the alloys are deposited as porefree coatings.

The purpose of this investigation, is to determine the corrosion resistance of tin/zinc coatings in relation to the alloy composition and other process conditions. Both unpassivated and passivated coatings are tested. A new chromatefree posttreatment is also investigated.

[1] Danfoss A/S, L3-V127, DK-6430 Nordborg, Denmark. Direct dialing: + 45 74884432, Fax: + 45 74490949.

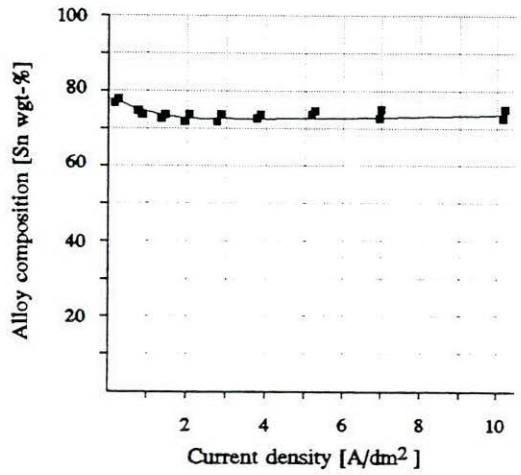


Figure 1. The alloy composition in relation to the current density for the modified electrolyte.

Experimental conditions.

The DIPSOL SZ-240® for rack plating is a slightly acid process for the electrodeposition of tin/zinc alloys /1/. A tin/zinc coating offers optimal corrosion protection, when the zinc content is between 20 and 25 per cent (w/w) /1/. Concentrations outside this narrow range, result in a decreased protection of steel. In the experiments, the recommended electrolyte is modified in order to improve the relation between alloy composition and the cathodic current density (figure 1).

The corrosion resistance of electrodeposited tin/zinc alloys is determined in accelerated laboratory tests. The investigation comprises neutral salt spray (ASTM B117) and Prohesion® tests /2/. The amount of rust is assessed according to ISO 4540.

The Prohesion® test is a cyclic, accelerated corrosion test. It relates more closely to longterm natural exposures, than conventional salt spray tests /2/. The test uses an electrolyte of 0.4% ammonium sulphate and 0.05% sodium chloride. A cycle consists of one hour spray at ambient temperature and one hour drying at 35°C (95°F).

The corrosion current is measured electrochemically (EC) and by the CMT (Corrosion Measurements by Titration) method /3/. The general condition for applying the CMT method is that the anodic metal dissolution reaction:

$$(1) \qquad Me \rightarrow Me^{n+} + n \cdot e^{-}$$

combines with one of the following cathodic reactions:

$$(2) \qquad n \cdot H^{+} + n \cdot e^{-} \rightarrow \frac{n}{2} \cdot H_2$$

or

$$(3) \qquad \frac{n}{4} \cdot O_2 + n \cdot H^{+} + n \cdot e^{-} \rightarrow \frac{n}{2} \cdot H_2O$$

so that a net consumption of acid takes place, equivalent to the number of electric charges, (flowing as the corrosion current) and to the number of metal atoms dissolving.

A chromatefree posttreatment for zinc and zinc alloys is also investigated. It is based on molybdenum and phosphate (MolyPhos®; in this context referred to as MoP) /4/. Various versions are tested against passivation with chromium(VI).

Results.

The CMT and EC measurements show that the corrosion current for unpassivated alloys in a 3% sodium chloride solution at pH=6.500, has a minium, when the alloy contains from 20 to 25 wgt-% of zinc (figure 2). The CMT determination of the optimal alloy-composition is supported by Prohesion® and neutral salt spray tests (table 2 and 4). Under the same experimental conditions, an unpassivated zinc coating corrodes with approximately 120 $\mu A/cm^2$ /3/. A passivation with Cr(VI) results in values from 4 to 5 $\mu A/cm^2$.

An increase in the plating current, keeping the current density constant, results in an improved corrosion current in the CMT measurements (table 1). A reduced number of pores in the coatings are responsible for the lowering of the corrosion rate. The CMT observations are sup

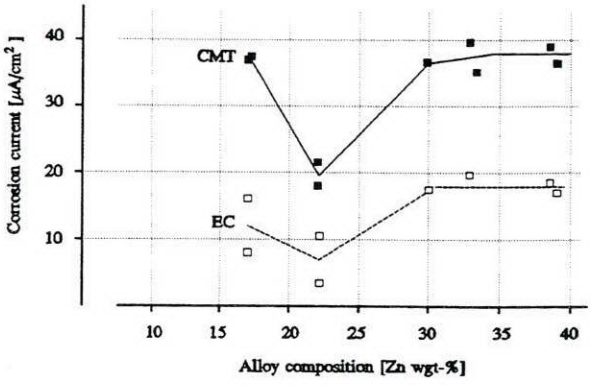


Figure 2. The corrosion current with varying alloy composition. Measured by the CMT-method and EC.

Table 1. The corrosion current of tin/zinc alloys.*

Composition (wgt-% zinc)	Current density (A/dm^2)	Plating current (A)	CMT ($\mu A/cm^2$)
34	2.0	0.5	35
34	2.0	0.5	32
33	2.0	0.5	38
38	2.0	3.4	18
39	2.0	3.4	17

* unpassivated coatings

ported by the results from Prohesion® (figure 4) and neutral salt spray tests (table 2).

The E-I curve for the electrodeposition of tin and zinc, shows that tin is deposited at a potential around -850 mV (vs. SCE) and zinc at -1100 mV (vs. SCE.) (figure 3). At lower values, the cathodic current decreases, because of an anodic reaction. A degradation of additives is believed to take place, and the breakdown products are assumed to act as grain refiners, making the coating porefree.

The hydrogen evolution causes a pronounced increase in the cathodic current at a potential close to -1500 mV (vs SCE). SEM-images shows that the coating becomes more fine grained, when the plating current is increased without changing the cathodic current density.

In the neutral salt spray test, the resistance of the alloy is improved significantly, when post-

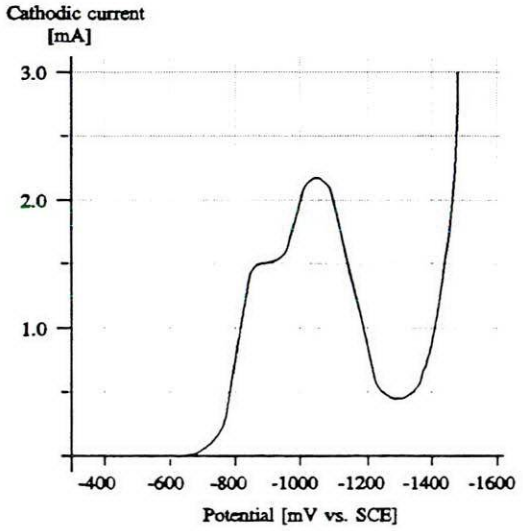


Figure 3. The E-I curve for tin/zinc alloy plating.

treated with Chromium(VI) (table 2). The time for the appearence of red rust depends on the plating conditions. Keeping the cathodic current density at 2 A/dm^2, but increasing the plating current improves the performance of unpassivated and chromated tin/zinc alloys. The time for a 1 per cent coverage of red rust is not influenced, indicating that the porosity of the coating is decreased.

Compared to unpassivated tin/zinc alloys containing 20 to 22 wgt-% of zinc, the time taken for 1 per cent coverage with red rust is doubled when

Table 2. The results of the neutral salt spray test (ASTM B117) on tin/zinc coatings on steel. The current density is 2 A/dm^2.

Passivation	Thickness (μm)	Zn (wgt%)	Plating current (A)	Time to red rust (hours) first appearence	Time to red rust (hours) 1% coverage
Cr(VI)	10-11	20-22	12.8	>960	1512
		20-22	12.8	>960	1536
		20-22	3.2	480	1536
		20-22	3.2	480	1440
None	10-11	16-18	12.8	288	528
		20-22	12.8	288	816
		20-22	3.2	240	816
		20-22	3.2	216	792

Table 3. Prohesion® test of 10 µm thick tin/zinc coatings containing 28-30 wgt-% of zinc: corrosion vs. time.

Rating according to ISO 4540	Passivation	Prohesion®: Exposure time (hours)						
		2	8	14	24	48	168	984
White rust	Cr(VI)	10	10	10	10	7	1	0
	MoP66	10	10	10	10	4	4	0
	None	4	2	1	1	1	1	0
Red rust	Cr(VI)	10	10	10	10	10	8	2
	MoP66	10	10	10	10	10	10	0
	None	10	10	10	10	10	5	1

posttreated with Cr(VI) (table 2). On the other hand, the corrosion resistance is reduced if the content of zinc is in the range of 16 to 18 wgt-%.

The results of Prohesion® tests also show, that the plating current, at a constant current density, influences the corrosion resistance of the alloy (figure 4). For unpassivated and yellow chromated alloys, the corrosive protection of tin/zinc on steel improves significantly, when plating current is increased from 3.2 to 12.8 A. The time for the first appearence of red rust is improved slightly, when the alloy is chromated.

The finer grain size of the alloy, increases the time before 1 per cent of the surface is covered with white rust (rating 6 in figure 4); from 7 days (168 hours) to 20 days (480 hours). The number of days before red rust covers the surface is increased from 13 days (312 hours) to 26 days (624 hours).

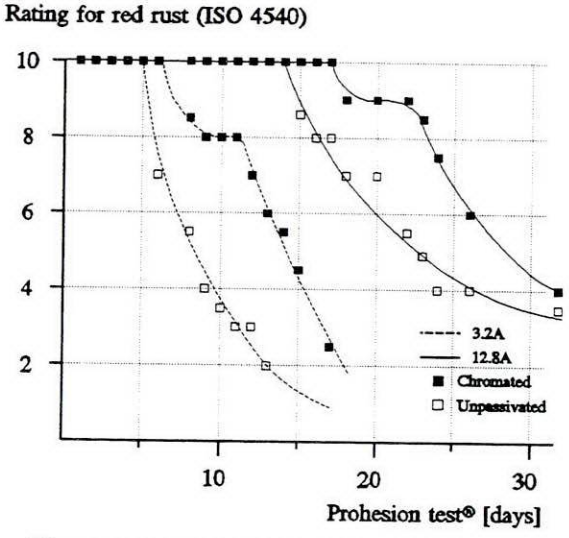


Figure 4. The results of Prohesion® test for 10 µm thick Sn/Zn coatings containing 20-22 wgt-%.

The amount of white rust for unpassivated alloys is very pronounced after a couple of testing hours. The corrosion products on the tin/zinc coatings are not as voluminous as for zinc coatings. The amount of white rust is reduced significantly (in the Prohesion® test) if the alloys are posttreated with Cr(VI) (table 3).

There seems to be no difference between chromated and unpassivated tin/zinc alloys, when red rust vs. time is concerned. The chromate referred to in table 3, is normally used for passivating acid zinc. In the salt spray test (table 2) and in all other corrosion tests in this investigation, the chromate used is formulated with reference to the tin/zinc alloys /1/.

The first experiments with passivation using a combination of molybdenum and phosphate show, that the amount of white and red rust is significantly less when compared to unpassivated alloys (table 3). The results of this accelerated laboratory test is supported by CMT measurements /5/.

The formulation of the MoP-solution with ammonium salts has been shown to improve the corrosion resistance of the passivation system. CMT measurements on porefree alloy coatings containing 22 wgt-% of zinc shows a corrosion current of 4μA/cm^2 at pH 6.500. It is comparable to the values obtained for yellow chromated zinc coatings.

The results of Prohesion® tests on alloys containing 18 wgt-% of zinc, show that the amount of red rust, when version MoP#3 is used in the posttreatment process (figure 4), is no better than an unpassivated coating. On the other

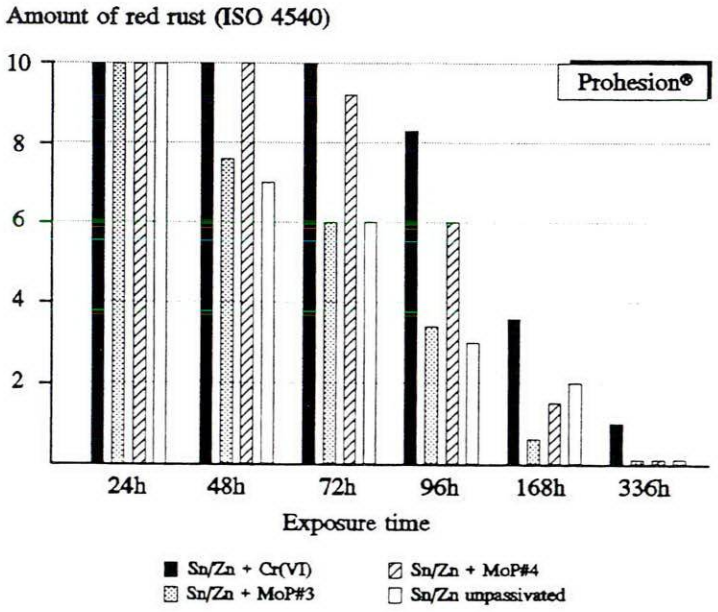


Figure 5. The results of Prohesion® tests for 4μm thick Sn/Zn coatings containing 18 wgt-% zinc.

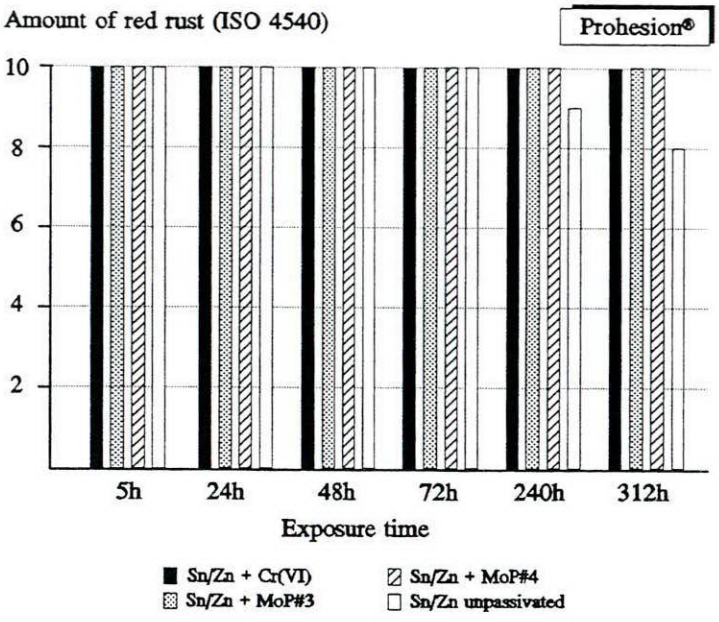


Figure 6. The results of Prohesion® tests for 5μm thick Sn/Zn coatings containing 22 wgt-% zinc.

hand, the performance of MoP#4 is only slightly reduced compared to yellow chromated alloys.

Increasing the content of zinc in the alloy to 22 wgt-% improves the performance of MoP#3 and MoP#4 (figure 6). The difference in thickness (4μm vs. 5 μm) is assumed to cause a slight change in resistance. The corrosion resistance of unpassivated alloys is also improved compared to coatings containing 18 wgt.% of zinc. The performance of both versions of MoP is believed to be correlated with the content of zinc in the alloy.

In the neutral salt spray test (ASTM B117), the corrosion resistance of MoP-passivated alloys containing 18 wgt-% of zinc, is lower than chro-

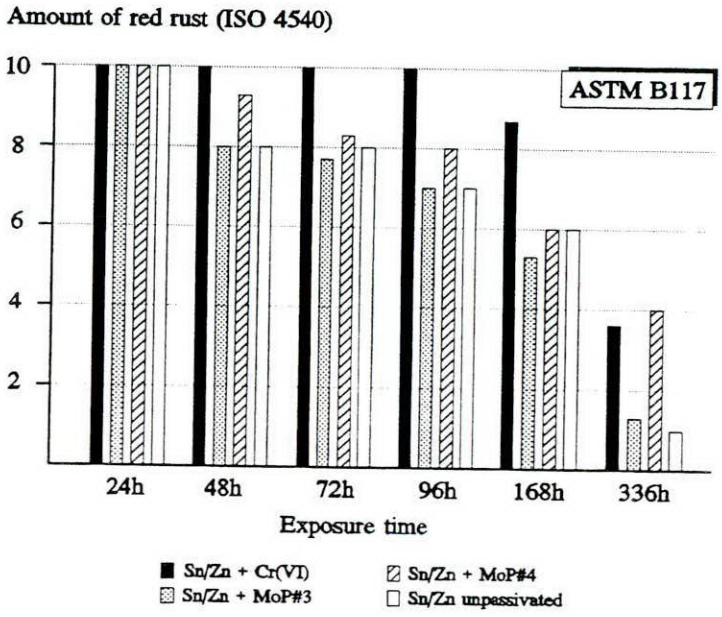


Figure 7. The results of neutral salt spray tests (ASTM B117) for 4μm thick Sn/Zn coatings containing 18 wgt-% zinc.

mated alloys, and no better than an unpassivated alloy (figure 7).

The corrosion resistance of tin/zinc alloys post-treated with molybdenum and phosphate is related to the content of zinc in the alloy. The new passivation system was optimized in relation to zinc coatings /4/. It is therefore likely that the amount of alloy zinc is important for the corrosion resistance, when passivation in a MoP solution takes place by a simple immersion.

The amount of red rust for tin/zinc alloys in the Prohesion® test is compared to chromated acid zinc in table 4. Both chromated and MoP#3 treated tin/zinc alloys are superior to the zinc coatings, when the alloy composition is optimal. If so, then an unpassivated alloy performs as well as chromated acid zinc. No difference was seen in performance between the two posttreatments after 316 hours of exposure.

Conclusion.

The corrosion resistance of tin/zinc alloys electrodeposited from the DIPSOL SZ-240® electrolyte has been investigated in neutral salt spray (ASTM B117) and Prohesion® tests.

The corrosion resistance depends on the alloy composition. The best results are obtained, when the concentration of zinc in the alloy is between

Table 4. The results of Prohesion® tests: corrosion values (ISO 4540) vs. time.

Coating	Zn	Passivation	Thickness	Prohesion®: Exposure time (hours)						
	(wgt-%)		(μm)	24	48	72	96	168	240	312
Acid zinc	100	Cr(VI)	5	10	10	10	-	-	8	8
Sn/Zn	22	Cr(VI)	5	10	10	10	-	-	10	10
	18	Cr(VI)	4	10	10	10	8	4	-	1
	22	MoP#3	5	10	10	10	-	-	10	10
	18	MoP#3	4	10	8	6	3	1	-	0
	22	None	5	10	10	10	-	-	9	8
	18	None	4	10	7	6	3	2	-	0

20 and 25 wgt-%. Higher and lower values result in a very pronounced lowering of the resistance.

The tin/zinc coatings are porefree, when the cathodic current is increased in order to lower the potential to the values necessary for an anodic degradation of additives in the electrolyte. The breakdown products probably act as grain refiners.

A post-treatment with Cr(VI) improves the corrosion resistance of the alloy in the two accelerated tests. Passivation in a solution containing molybdenum and phosphate (MoP), increases the resistance to a level comparable to a yellow chromate treatment.

In the Prohesion® test, the corrosion resistance of unpassivated tin/zinc alloys containing 22 wgt-% of zinc, is comparable to chromated acid zinc. Post-treatment with chromate or MoP results in a coating system which is superior to chromated acid zinc.

Acknowledgements.

The author is indebted to Hans Jørgen Gabel, Danfoss A/S for commenting the manuscript. Dipsol Gumm Ventures has kindly supported the experiments with chemicals.

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NEW NON-FORMALDEHYDE, NON-COUMARIN, NON-SULFUR, ELECTROLYTIC BRIGHT NICKEL PLATING PROCESS

Steven W. Erwin and Richard O. Watson, CEF

Historically, electroplaters of duplex nickel had to use formaldehyde and coumarin-bearing nickel plating solutions to obtain a non-sulfur nickel deposit, which is essential to the duplex nickel process, for maximum corrosion protection of external automotive trim and bumpers. Mounting regulatory pressures to reduce formaldehyde and coumarin in the workplace necessitate that an alternative nickel bath be found and implemented. Described will be a new bath that deposits non-sulfur bright nickel which meet automotive specifications for STEP testing, corrosion protection and appearance.

HISTORY OF DUPLEX NICKEL AND NEED FOR FORMALDEHYDE AND COUMARIN

Before discussing developments to preserve our environment, let us recollect the days when many chemicals were utilized because of their effectiveness, without knowledge of their long term effect on people or nature.

According to one historian[1], usable nickel plating has been around since the mid-eighteen hundreds. However, the first applicable nickel plating didn't exist until O. P. Watts introduced his nickel bath in 1916. The Watts' bath made it possible to increase the speed of deposit a factor of ten by increasing the current density from approximately 4 amp/ft^2 to 50 amp/ft^2. This development led to the modern bright nickel plating baths we know today, using organic and inorganic additives.

In 1927, M. Schlotter was responsible for adding an organic aromatic sulphonic acid to the Watts bath to achieve the first practical bright nickel plating solution. Weisberg and Stoddard introduced formaldehyde in 1936. Many new additives followed in rapid succession, particularly in the 1945-1960 period. Coumarin was one of the multitude of brighteners that acted as levelling agents on its own, and with formaldehyde, became the important ingredients in a variety of nickel plating baths referred to as "semi-bright". Today, semi-bright nickel plating occupies an important position in plating. However, the term "semi-bright" nickel does not necessarily express the application. Except for a few instances, the main utilization of semi-bright nickel deposit is for better corrosion resistance.

The original application of semi-bright nickel coatings was to replace dull nickel coatings deposited from the Watts nickel bath because it had better polishing characteristics. The first use of semi-bright nickel solutions, which were based on the use of coumarin as an addition agent, dates back to October 1945. This application was for nickel plating of motor car bumpers. The purpose was to reduce the polishing effort. Today, the importance of duplex nickel plating is the electrochemical potential difference between the semi-bright nickel deposit and the bright nickel deposit. As the multiple nickel layer coatings were developed for better corrosion resistance, the semi-bright nickel deposit served as the initial coating. Unfortunately, formaldehyde and coumarin have been key chemical additives in the semi-bright bath.

OSHA REGULATION OF FORMALDEHYDE

Beginning in the sixties, industry experienced an unparalleled demand for safety. During that time Congress passed many laws which reinforced or newly established the federal safety presence in areas that concerned the public. One of the most significant is the Federal Occupational Safety and Health Act of 1970 (OSHA).

Formaldehyde, one of the two chemicals used to produce the desired levelling, corrosion resistance and semi-bright nickel appearance, was a suspected carcinogen. Under the direction of the National Institute for Occupational Safety and Health, formaldehyde was listed as a toxic and hazardous substance, requiring adequate ventilation and frequent employee airborne exposure evaluations. The permissible exposure limit[2] (PEL), based on a time-weighted average (TWA), is three-quarter parts of

airborne formaldehyde per million parts of air (0.75 ppm) as an 8-hour TWA. The short term exposure limit (STEL) is two parts of formaldehyde per million parts of air (2 ppm) for any 15 minute period of exposure. This standard applies to all occupational exposures to formaldehyde, *i.e.* from formaldehyde gas, its solutions, and materials that release formaldehyde. A working bath of a traditional semi-bright electrolytic nickel plating bath produces airborne formaldehyde mist and vapors.

THE DILEMMA OF COUMARIN

The safety profile on coumarin indicates it is a possible carcinogen but it is not on the toxic and hazardous substances list. It has been our experience that the main reasons platers want to eliminate coumarin in their semi-bright electrolytic nickel baths are the obnoxious odor and the required frequency of carbon treating.

The chemical dictionaries describe coumarin as having a pleasant odor similar to vanilla, one can only suppose that too much vanilla odor can be obnoxious, because the smell of coumarin is becoming unacceptable and there is a desire to eliminate it. One company we know of has received complaints of the odor from neighboring residences.

Another disadvantage of coumarin is the carbon treatments required to remove breakdown compounds formed during plating. If these breakdown compounds are not maintained at a RP value of 5 to 6 or below, problems, *e.g.*, increase in stress, loss of levelling and a slate gray color in the low current density areas, will occur.

CHLORAL HYDRATE'S ROLL IN SEMI-BRIGHT NICKEL

A low sulfur content (0.005%) in the semi-bright nickel deposit is essential for satisfactory simultaneous thickness and electrode potential (STEP)[3] values and improved corrosion resistance. An excellent scavenger for sulfur in the semi-bright electrolytic nickel plating bath is chloral hydrate. The disadvantage to the presence of chloral hydrate is that it can eventually work its way into the waste water and be detected as chloroform.

NEW ELECTROLYTIC SEMI-BRIGHT NICKEL BATHS

New processes have been developed to improve the performance of electroplating while significantly reducing the environmental impact of the chemicals. The new semi-bright electrolytic nickel processes are free of coumarin, aldehydes, and chloral hydrates, and maintain the properties of the traditional coumarin/formaldehyde formulations. There are now many installations producing parts and meeting the decorative and quality requirements of the automotive industry. Usually, these installations are made as a running conversion of an existing traditional coumarin semi-bright nickel bath. Surprisingly, the conversions are simple and require no capital investment. In fact, many of the conversions are executed to avoid capital expenditure for additional ventilation equipment to meet regulations. Other reasons for converting have been the elimination of the odor from coumarin, the reduction in carbon treatment, and traces of chloroform in waste sludge.

EVALUATING THE NEW PROCESS

The evaluation of these new semi-bright nickel processes can be readily accomplished by comparing tensile stress, STEP and levelling properties. Tensile stress is easily determined with a deposit stress analyzer using one gallon of nickel stock solution made up with addition agents according to the supplier's recommendations. With running conversion, mixtures of the old and new solutions in various proportions can be checked for the degree of stress. The desired tensile stress of this particular process is approximately 6000 PSI. The average range of tensile stress of solutions converted is 10,000-12,000 PSI.

The STEP test provides a means of quickly assessing one of the important elements contributing to the overall corrosion protection of the total deposit. Parts that fail the STEP test are likely to fail accelerated corrosion tests (Cass test, salt spray, etc.) or corrode prematurely in service.

Prior to installing in production, STEP values of a different semi-bright nickel solution can be easily determined using 267 mls Hull Cells, in the lab. Steel panels are plated with the semi-bright nickel

bath followed by the production bright nickel solution. Panels are plated at 2 amps for a total time of 20-30 minutes in the same ratio as production parts. If your duplex nickel is plated at a 70:30 ratio, panels are plated 70% of the total time in the semi-bright nickel solution and 30% of the total time in the bright nickel solution. Temperature and agitation are the same as production. Using the STEP instrumentation, values are determined on the Hull Cell panels, at 2 cm (1 inch) from the bottom edge in the 40-50 amp/sf^2 and 60-80 amp/ft^2 current density range on the panel as in Fig. 1. Most automotive specifications require an average STEP value of 100-130 mV or 130-150 mV.

The comparative levelling properties of new semi-bright processes can be easily determined using scratched brass panels and a Hull Cell. With 600 grit paper, scratch a streak the entire length of the panel, approximately 1 cm (0.5 inches) wide, 2 cms (1 inch) from the bottom edge of the panel as in Fig. 2. The scratched brass panels should be plated in both the semi-bright and bright nickel, for the same length of time as the steel panel for STEP testing. To be less subjective, levelling may be graded using a surface analyzer instrument.

CONCLUSION

As the saying goes, "necessity is the mother of invention". If there was no need to eliminate formaldehyde, coumarin or chloral hydrate, the time probably would not have been spent looking for alternatives. Fortunately, their elimination in semi-bright nickel plating baths is easy. The new process eliminates the necessity to manage the formaldehyde fumes, drastically reduces costly carbon treatments and frees the waste sludge of chloroform. The quality of levelling, appearance and corrosion resistance of the new process are equal to the old.

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267 ml Steel Hull Cell Panel

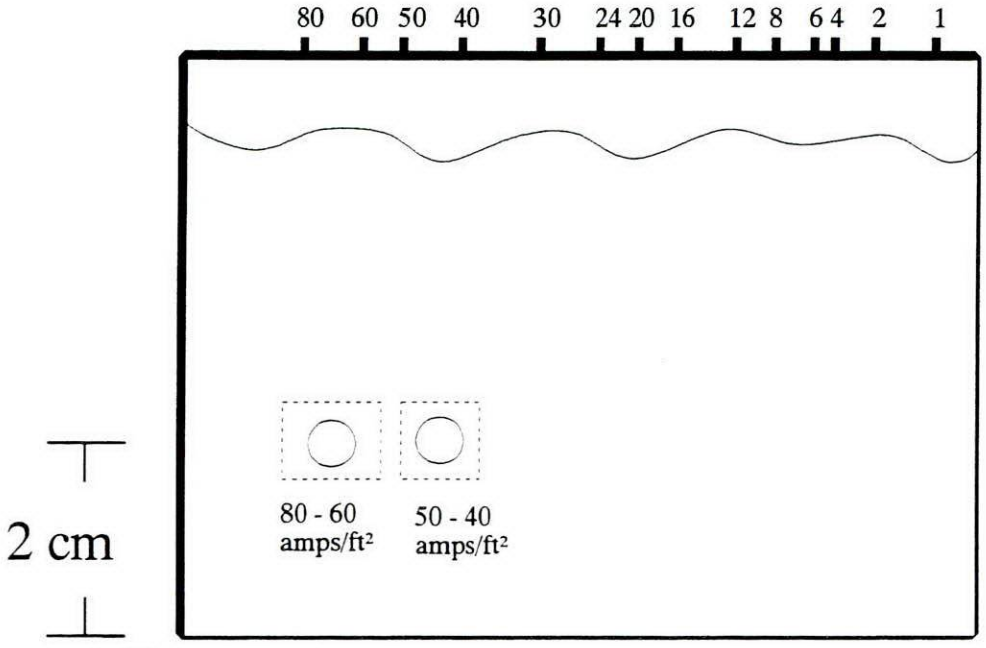

Figure 1 - Area For Reading STEP Values

267 ml Brass Hull Cell Panel

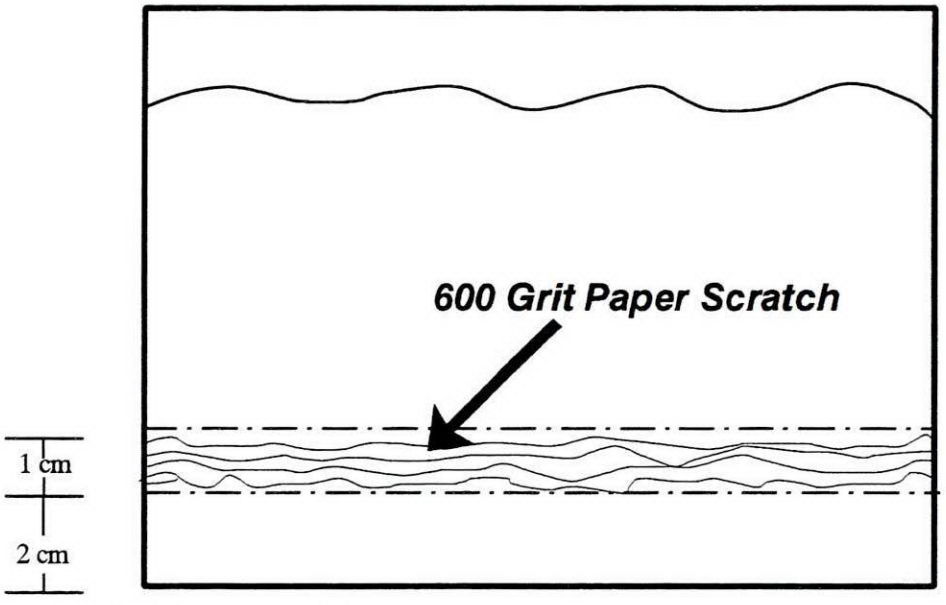

Figure 2 - Areas For Scratching And Evaluating Levelling

Stress, Additives and Adhesion in Electroplated Zinc Deposits

D. Crotty, Ph.D.
J. Greene
Allied Kelite
A Witco Company
29111 Milford Rd.
New Hudson, MI 49069

Introduction

One of the important mechanical properties of plated deposits is the internal stress. Discussions on the effects of internal stress can be found in many of the standard references [1,2]. Internal stress can be especially important in determining the suitability of some deposits for an application, and sulfamate nickel [3,4] and electroless nickel [5] are excellent examples of such deposits.

The internal stress of modern zinc electrodeposits has not been studied extensively, but a preliminary study was conducted by Kansupada [6]. This study presented the as plated internal stress of cyanide, alkaline non cyanide, acid chloride and acid ammonium chloride deposits over a normal range of current density.

The question of adhesion loss for zinc deposits has been a subject of concern, especially for alkaline non cyanide zinc [7], but has been a problem for the other types of zinc as well. Generally it is recognized that the cyanide processes are much less susceptible to adhesion loss since the cyanide bath itself acts somewhat as a cleaner. The acid and alkaline non cyanide processes require more careful cleaning to achieve good adhesion, even though the acid processes are able to cover some difficult to plate castings as well as heat treated and leaded steels. However, the early additives for the non cyanide processes were largely to blame for adhesion problems and this has improved significantly in recent years.

A very recent unpublished report [8] suggests that part of the "delayed blistering" phenomenon can be explained by generation of hydrogen by codeposited additives during the days following the deposition of the zinc deposit. This can be taken with the analysis of stress provided in the literature [9] for nickel deposits. A compressive stress builds up as hydrogen is formed by the plating

additives and the deposit expands. The deposit shrinks as hydrogen is expelled causing tensile stress.

Our preliminary investigation into the stress of zinc deposits suggested that the subject was somewhat complex, and a relationship between stress and adhesion was not clear. A comparison of the stress behavior of cyanide, acid chloride and alkaline processes reveals similarities and differences in these processes. The emphasis of this study is the stress behavior of alkaline non cyanide zinc deposits and the effects that additives have on stress and adhesion.

Measurements

The internal stress of zinc deposits was measured using the spiral contractometer as described by ASTM B 636. Mild steel helixes used by Kansupada [6] are not readily available and the difficulty in making them causes the helix manufacturers to be very reluctant to supply them. Thus the zinc deposits were plated on stainless steel helixes with Teflon backing that had been given a fresh sulfamate nickel strike. To avoid adhesion loss on this substrate the helix must be placed into the plating bath with the current on. For comparison, some deposits were plated on a copper helix as well. Results are reported in pounds/square inch with positive values being tensile and negative values being compressive stressed.

The internal stress of plated deposits has also been measured by plating steel strips. One method measures the bow of the metal strip at the center [10,11,12]. Two equations were provided by Soderberg and Phillips independently in 1947 and both equations have suffered printing errors over the years, even in the original papers. A few tests were conducted using this method since the zinc deposits are more easily plated onto mild steel.

The plated helixes and strips were usually plated at 10, 25 and 50 ASF to 0.5-0.6 mil thickness. The plating baths and additive systems used are noted in the discussions.

Brass tabs are available from several suppliers for use in estimating the stress of plated deposits. The stop off used on these products is attacked by the high alkalinity of the alkaline zinc plating processes. At this writing we have not found a suitable stop off material. The use of these types of products would greatly simplify the estimation of the stress of zinc deposits.

Panel Tests

An informal method was devised to test the tendency of a deposit to suffer delayed adhesion loss. A two amp Hull cell panel was plated in the test solution for about 20 minutes so that the deposit was at least 0.3 mil in the 25-30 ASF range. A 500 mL Hull cell was used as a means of avoiding an increase in temperature as well as a depletion of the bath chemistry. The panels were stored individually in the open and were observed over a period of time. Usually, blisters appeared in 5-10 days if they were to blister at all.

It was found that if panels are stacked tightly together the panel that was due to blister might not show blisters where it touched the stack of panels but would only blister where the panel protruded from the stack. Thus, all panels were stored separately, often taped to a wall.

Cleaning of the panels was found to be especially important. Zinc plated Hull cell panels were used exclusively since it is very difficult to adequately clean the plastic coated panels. After the zinc was stripped in hydrochloric acid the smut was wiped from the surface with a paper towel under running water. The panels were placed in a hot commercial soak cleaner for 5-10 minutes, rinsed, dipped in 30% hydrochloric acid and rinsed again. The use of an electrocleaner was found to be unnecessary but not harmful to results of the test.

Repeatability and Comparison of Methods

Several helixes were plated from similar alkaline non cyanide zinc baths to check repeatability of the methods. Copper helixes were used for some tests as well. In addition, metal strips were plated on both sides and the deposit was dissolved from one side in hydrochloric acid. The bow of the strip was measured as an indication of the internal stress. Table 1 lists the results of this test series.

A pilot plant alkaline non cyanide zinc bath was run three times using the stainless steel/nickel strike helixes for the same thickness and current density, which resulted in initial stress values of about 9-11K psi compressive. The measured stress changed with time for all of these tests, stabilizing in about 5 days. The final stress values are about 29-35K psi compressive.

Fresh plating baths were used to compare the stress obtained with stainless steel/nickel helixes, copper helixes, and steel strips. The use of the copper helix resulted in slightly lower initial an final stress values compared with values

obtained with the stainless steel/nickel helixes. The use of copper had a disadvantage in that the copper and zinc formed an alloy with repeated use that changed the helix constant significantly with each use.

Table 1
Repeatability and Comparison Study
Non Cyanide Zinc
0.5-0.6 mil Thickness

Helix	ASF	Initial Stress PSI	Final Stress PSI
Pilot Plant Bath			
SS/Ni	25	-11K	-33K
SS/Ni	25	-9K	-29K
SS/Ni	25	-9K	-35K
Fresh Lab Bath			
SS/Ni	10	-16K	-28K
SS/Ni	25	-18K	-33K
SS/Ni	50	-12K	-34K
Copper	10	-11K	-18K
Copper	25	-9K	-24K
Copper	50	-9K	-25K
Steel Strip	10	-3K	-6K
Steel Strip	25	-5K	-5K
Steel Strip	50	-6K	-12K

The use of mild steel strips results in much lower stress values and the change with time is much less. The regular use of steel strips is difficult since it is difficult to prepare flat strips and the measurement methods described in the literature are not very accurate. The differences in the results between the steel strips and nickel plated helixes appears to be quite significant. This effect will be studied further if a source of flat steel strips can be found.

Acid Chloride Zinc

An acid chloride zinc solution was prepared with 37 gm/L zinc metal ions as zinc chloride, 205 gm/L potassium chloride, 25 gm/L boric acid and adjusted to pH 5.5. Deposits were plated from this electrolyte at 25 ASF both with and without additives and the results plotted in Figure 1. The deposit without additives is low compressive stressed, and remains unchanged with time.

The addition of a commercial carrier (wetter) component to the electrolyte raises the compressive stress to about 10,000 psi, but this drops quickly over the next few hours to near zero. Over the next few days the stress slowly returns to close to the original stress value. Addition of the commercial brightener component has a similar effect. The initial stress is about 15,000 psi compressive. This drops quickly to about 8000 psi, but over the next few days the stress returns almost to the original value.

The addition of excess brightener, however, has a very powerful effect. The initial stress is in the same range as is measured for normal concentrations of additives, but the stress quickly becomes much more compressive.

A change in stress in acid zinc deposits with time has been noted in the past [1] for sulfate and chloride electrolytes but the additives used in the early studies were quite different from those used in modern commercial additives. The stress shift noted was usually toward compressive.

Alkaline Cyanide Zinc

A similar study was conducted using a mid cyanide zinc electrolyte prepared with 20 gm/L zinc metal, 75 gm/L sodium hydroxide, 45 gm/L sodium cyanide and 30 gm/L sodium carbonate. Figure 2 shows the results of plating at 25 ASF from the electrolyte with and without additives.

The deposit plated without additives is low compressive, like the acid chloride deposit, and the stress value remains relatively unchanged with time.

The addition of 0.3-0.6 % of a commercial additive system increases the initial stress to about 15,000-20,000 psi compressive. Over time the stress becomes more compressive and stabilizes in the 30,000-40,000 psi compressive range.

Finally, an addition of 2% of the commercial brightener mixture was added to the electrolyte. This represents a great excess of additives, however, there was little effect on the stress of the deposit.

A mid cyanide zinc bath from a commercial plating shop was tested in the same way, Figure 3, at 25 ASF. The initial and final stress values fall in the same ranges, and excess brightener additions had little effect on this stress behavior.

The zinc deposits from a mid cyanide bath have initial internal stress in the range of 10,000-20,000 psi compressive. As the deposit ages the stress becomes more compressive and stabilizes in the range of 30,000-40,000 psi. Addition of excess brightener seems to have little effect on the stress, as opposed to the acid chloride zinc baths which become considerably more compressive when excess brightener is added.

Alkaline Non Cyanide

With the results of stress tests on acid chloride and mid cyanide zinc processes as a background, a survey of alkaline non cyanide laboratory prepared and commercial plating shop baths were studied.

A laboratory prepared bath was used to plate helixes at 10, 25, and 50 ASF. The bath composition was 12 gm/L zinc metal, 120 gm/L sodium hydroxide, and 30 gm/L sodium carbonate along with the normal 2% of a commercial additive. It is not possible to plate an additive free deposit for alkaline non cyanide zinc as with the acid and cyanide since the resulting deposit is black and powdery. Figure 4 shows the resulting stress measurements. The graph looks very much like that of the cyanide bath. The initial stress is about 10,000-20,000 psi compressive, but with time the stress becomes more compressive, and stabilizes between 25,000-35,000 psi.

The addition of excess brightener to the bath has an unexpected effect, Figure 5, in that the stress becomes more tensile. Several sets of steel strips were also plated using a plating bath containing excess brightener component. The stress values obtained followed the same trend, excess brightener causes the stress to move toward tensile. Hull cell panels were plated from fresh solutions that had excess brightener and these panels almost always blistered if a significant excess of brightener additive was used. Thus, there is a relationship between delayed blistering and tensile stress in non cyanide zinc deposits at least in fresh plating solutions.

For comparison, excess carrier was added to a commercial plating bath with little effect on the internal stress, Figure 6.

This effect was further studied with baths from commercial plating shops. Table 2 lists the results of stress tests on a number of commercial baths using the same commercial brightener system. Most of these baths exhibit stress behavior similar to that shown in Figure 4. Two baths, from shops E and F, show the tensile behavior seen with excess brightener, Figure 7. The deposits are low compressive stressed or tensile. On further examination, it was found that these two shops were adding considerably more additives than might be considered normal. In both cases the plater found that the higher addition rate was required to provide the desired brightness. In both cases a metallic contamination was found in the baths, and when this was treated properly with purifier the need for extra additives was eliminated. Hull cell panels were plated from the solutions from shops E and F and none of the panels blistered despite the tensile stress. Neither of these shops reported blistering problems on their work, but the work from shop F is sometimes stamped with an identification number resulting in chipping if the deposit is thicker than 0.5 mil.

Table 2
Stress Measurements
Commercial Plating Baths
Alkaline Non Cyanide Zinc

Shop	Type	Initial Stress			Final Stress		
		10ASF	25ASF	50ASF	10ASF	25ASF	50ASF
A	Barrel	-13K	-15K	-16K	-26K	-35K	-36K
B	Barrel	-15K	-17K	-13K	-31K	-33K	-18K
C	Rack	-10K	-9K	-11K	-31K	-36K	-41K
D	Rack	-10K	-7K	-10K	-37K	-37K	-48K
E	Rack	-5K	-1K	-3K	-8K	5K	12K
F	Barrel	-0.3K	-1K		18K	17K	--
G	Barrel	-3K	-9K	-7K	-16K	-28K	-29K

A single bath from shop C was studied over a four month period during a test of the effectiveness of an experimental purifier to improve brightness. The stress results from this series is given in Table 3.

Table 3
Stress Measurements
Time Study Shop C

Date	Initial Stress			Final Stress		
	10ASF	25ASF	50ASF	10ASF	25ASF	50ASF
November	-10K	-9K	-11K	-31K	-36K	-41K
December	-17K	-12K	-17K	-35K	-35K	-42K
January	-17K	-16K	-20K	-35K	-33K	-39K
February	-18K	-15K	-19K	-36K	-31K	-43K

The study with shop C shows that the initial stress increased slightly after the first month, but the final stress did not change significantly. This particular shop was using slightly more of the additive system than the average but brightness was not optimum. During this purifier test brightness increased and the shop began to use less additives accompanied with a slight increase in compressive stress in as plated deposits.

Carrier and Brightener and Competitive Systems

Shop G is a barrel operation. An important requirement for this shop is that the zinc plate be about 0.5-0.8 mil and must not chip from the part on impact. For this requirement it was found that an additive containing very little brightener, but the usual amount of the carrier component was required. If the normal amount of brightener is used the deposit sometimes chips. As mentioned above, shop F had experienced chipping of the deposit and once brightener additions were reduced to normal levels this problem was alleviated.

Table 4 shows the effect on stress of adding extra carrier material or extra brightener material to a non cyanide plating bath. A normally operating bath sample from shop B was spiked with either excess carrier or excess brightener for an additive system we will call Type A. Excess carrier had relatively little effect on the internal stress. However, a large excess brightener caused the stress to tend strongly toward tensile. Hull cell panels plated from the shop B sample spiked with 1% excess Type A brightener did not blister.

Shop H had reported unpredictable delayed blistering on work when using additive system Type B (a competitive system). Table 4 shows that the deposit from the bath was tensile as plated but moved to compressive on aging.

However, a small addition of the Type B additive drove the stress strongly tensile. Hull cell panels from this bath sample, both as received and spiked with additive, did not blister on aging. However, a few of the panels plated from fresh plating baths using the Type B additive did blister.

Table 4
Stress Measurements
Carrier and Brightener Study
25 ASF

Materials	Initial Stress 25 ASF	Final Stress 25ASF
Type A Additive (Shop B)		
As Received	-17K	-33K
1% extra carrier	-18K	-33K
2% extra carrier	-17K	-25K
0.5% extra brightener	-15K	-22K
1.0% extra brightener	-5K	-1K
Type B Competitive Additive (Shop H)		
As Received	10K	-18K
0.2% extra additive	8K	32K
0.5% extra additive	8K	4K
Type C Competitive Additive (Shop I)		
As Received	20K	-15K
Type D Competitive Additive (Shop J)		
As Received	9K	-8K

These results show that the addition of excess brightener has the effect of driving the stress toward tensile. Kansupada [6] alluded to a similar effect. The use of excess brightener and related tensile stress shows a tendency to result in blistering on Hull cell panels if plated from fresh plating baths, but this effect is not so evident when the excesses are added to well used commercial plating baths. Finally, the Type A and Type B additive systems differ markedly in their ability to drive the stress toward tensile.

The competitive systems (Types B, C, and D) show the characteristic tensile stress when excess brightener is used and occasional delayed blistering was experienced is each plating bath that exhibited this behavior. This shows clearly that the effect of brightener to cause tensile stress is independent of the type of brightener used. Each brightener, if used in excess, will cause a tensile stress to develop in the zinc deposit.

Anatomy of a Blister

Blisters found on commercially plated parts can be caused by one of at least two problems: high brightener and or poor pre-treatment. The blisters that are produced by these two problems are often different in appearance.

The blisters caused by poor pre-treatment generally are compressive in appearance, in that the zinc deposit rises from the surface in a dome before the zinc cracks. Figure 8 is an SEM (Scanning Electron Microscope) photomicrograph showing the typical appearance of this type of adhesion loss. The zinc deposit that rises from the surface is larger than the hole it came from. This illustrated problem was traced to a stamping oil that was baked onto the surface during the manufacture of the part. The evidence for this conclusion comes from the appearance of dark spots under the zinc deposit. Figure 9 is an EDX (Energy Dispersive X-Ray) scan of these spots showing the carbon residue. The explanation for this type of adhesion loss is that the residue made it impossible for the zinc to bond with the steel and compressive forces caused the deposit to lift from the surface and to eventually crack.

A second cause for adhesion failure is the excessive use of brightener. Figure 10 is an SEM photomicrograph of a field of blisters that did not rise from the surface as domes before they cracked. The individual pieces of zinc deposit are just the size of the hole in the zinc deposit or perhaps slightly smaller. This type of adhesion loss is caused when the hydrogen formed from the excess brightener is released from the deposit. The deposit shrinks causing tensile stresses which crack the surface. Indeed, this sample came from a plating shop that had been feeding the additives at 3-4 times the recommended rate for about 4 months.

The explanation provided in the literature [8,9] can be applied here. Brightened zinc demonstrates a natural tendency to expand during the time after plating, partially from the additives and partially from hydrogen diffusing from the steel substrate. If the hydrogen content is so high that the deposit cannot absorb it, the hydrogen is expelled from the deposit and the deposit shrinks building tensile

stress. Nickel, being considerably more ductile than zinc, accepts the tensile stress if hydrogen is released. The more brittle zinc, however, sometimes cracks and exfoliates if excess hydrogen is released and the deposit shrinks.

Other Factors that Affect Internal Stress

A number of other factors have been investigated. The stress does change with the thickness of the deposit. For a bath containing "normal" amounts of additives the stress will continue to become more compressive with increasing thickness. Thus, it is important to use the same deposit thickness when comparing the stress of various deposits.

The temperature of the plating bath, within normal ranges, does not appear to affect the internal stress. Despite this observation we have noticed an increased tendency for delayed adhesion failure on some types of steel to occur if the temperature of the plating bath is below 70°F. The plating bath is less efficient at lower temperatures and the excess hydrogen formed may be partially responsible for this effect.

The stress vs. time plots presented here show that the internal stress changes rather rapidly during the first day after plating, and then the changes are more gradual. If the deposit is placed in very hot water (near boiling) for a few minutes soon after plating the stress does not change quickly the first day, but changes slowly over a 5-10 day period, reaching a final value similar to that of a deposit that is treated normally.

A deposit that is expected to blister, due to a excess of brightener for example, will usually blister quickly if heated in boiling water. However, sometimes the deposit does not blister in the water but blisters later anyway. Thus, treatment with boiling water does not always insure blister free deposits. Some platers routinely bake parts to avoid delayed adhesion failure but occasionally experience this problem anyway. In these cases the shop either uses larger that "normal" amounts of additives in an effort to obtain especially bright work, or the work is especially difficult to clean.

Discussion

The results of this study suggest that the internal stress of commercial acid, cyanide, and non cyanide zinc electrodeposits have certain features in common when the additives are present in the plating bath in "normal" concentration

ranges. However, if certain additives are used in excess the deposit reacts differently depending on the nature of the plating process. This difference can provide an insight into the cause of adhesion loss where it can be related to additives.

The acid chloride and cyanide processes provide a deposit without additives that is low compressive and the stress remains somewhat stable as the deposit ages. The powdery nature of the alkaline non cyanide deposit without additives prevents this deposit from being used in this comparison.

When "normal" concentrations of additives are used in each of the three electrolyte systems studied here, the deposit is low compressive stressed when measured using the stainless steel/sulfamate nickel helix. As each deposit ages, the stress becomes more compressive. The stress usually stabilizes in about 5 days. The two alkaline bath deposits become considerably more compressively stressed than does the acid chloride bath deposit.

The addition of excess additive materials to a cyanide plating bath seems to have little effect on the internal stress of the deposit, while the addition of excess brightener component to an acid chloride bath causes the stress to become more compressive on aging. These observations were made using commercial plating baths that had been maintained normally. There are instances known where delayed blistering occurs with cyanide baths but such baths were not available for study. Shops where this has occurred have been known to use larger than optimum addition rates of additives and it is possible that the mechanism described here applies.

The deposits from the alkaline non cyanide zinc electrolyte react somewhat differently to excess materials. While excess carrier seems to have little effect on the internal stress when added to a well used solution, the addition of the brightener component has a powerful effect. When excess brightener component is added to the plating bath the internal stress becomes more tensile. There is some tendency for the deposit to blister when the deposit stress is very low compressive or tensile and this effect is unpredictable both on work and on Hull cell panels. There is also some evidence to show that chipping of the deposit on impact is related to this same effect.

The explanation for the increased compressive stress could lie in expansion as hydrogen is absorbed by the deposit. If the hydrogen can be absorbed by the deposit no ill effects result unless the adhesion is poor due to substrate problems.

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If, however, the amount of hydrogen is so great that it cannot be absorbed by the deposit, then the hydrogen is expelled from the deposit and the deposit shrinks. This results in a more tensile stress and the zinc deposit may crack and exfoliate.

Blisters can occur despite proper maintenance of the plating bath if the substrate is not prepared properly. A zinc deposit that has been plated on a soiled substrate cannot bond properly. As the deposit expands compressively upon itself the deposit will rise from the soiled surface forming a dome or blister that will certainly crack and exfoliate.

Perhaps the most important conclusion of this work is simply that the use of excess additives can cause adhesion loss, and this follows closely with observations of platers over the years. Certainly some of the additive systems in use today are much more tolerant to over use than was true even 5 years ago. But some care must be taken. If a large addition rate is required to maintain adequate brightness then there is likely some other problem. Usually metallic impurities are to blame and the proper use of purifiers should improve the brightness of the work without excessive brightener additions.

The use of internal stress measurement is one method that can warn of the danger of adhesion loss related to excessive additive use. This method is tedious and requires about 5 days for the stress to stabilize. The method may be used with acid chloride and alkaline non cyanide processes but may not warn of danger with cyanide processes. Most importantly, the method does not address the problem of improper cleaning of work, which is the most common cause of adhesion loss.

Summary

Cyanide, acid chloride, and alkaline non cyanide processes provide deposits that are compressive. Deposits become more highly compressive on aging, and the stress stabilizes in about five days.

The internal stress of cyanide zinc deposits does is not strongly affected by the use of excess additives, within the range of concentration studied.

The internal stress of acid chloride deposits becomes more compressive when excess brightener component is used.

The internal stress of alkaline non cyanide deposits is not strongly affected by carrier additions but is strongly affected when excess brightener is used, and the stress tends toward tensile.

Hull cell panel tests reported here indicate a tendency toward delayed blistering when excessive brightener is used and the stress is low compressive or tensile, but only on fresh baths. Well used commercial plating baths are less consistent in this regard.

Commercial alkaline non cyanide plating baths that experience high additive use provide deposits that are more tensile, sometimes very tensile. Work from these baths sometimes exhibits problems with impact chipping or delayed adhesion loss.

The ability of an additive system to drive the internal stress toward tensile varies with the type of additive system. Some additive types are more gentle than other types.

The effect of excess brightener causing tensile stress is independent of the source of the brightener.

Commercial shops that tend to use more than "normal" amounts of additives to achieve desired brightness are usually trying to overcome an impurity. The proper use of purifiers or methods to avoid the impurities can usually improve brightness without the use of excess brightener additives.

The use of internal stress measurement of zinc deposits can warn of the danger of delayed adhesion loss for alkaline non cyanide processes due to over use of additives. This method cannot address the most common cause of blistering, which is poor cleaning.

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Figure 1
Acid Chloride Zinc
25 ASF

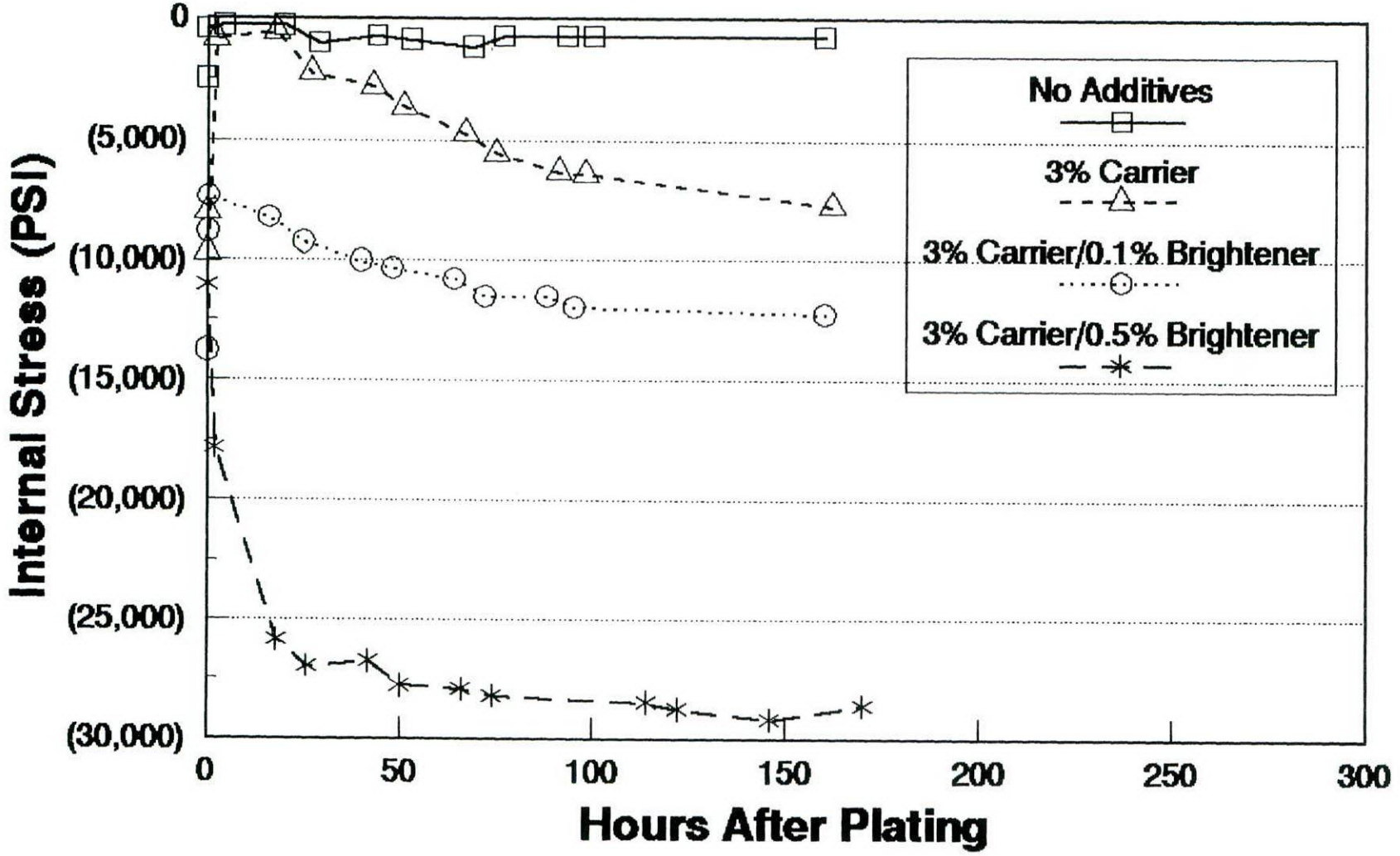


Figure 2
Mid Cyanide Zinc
25 ASF

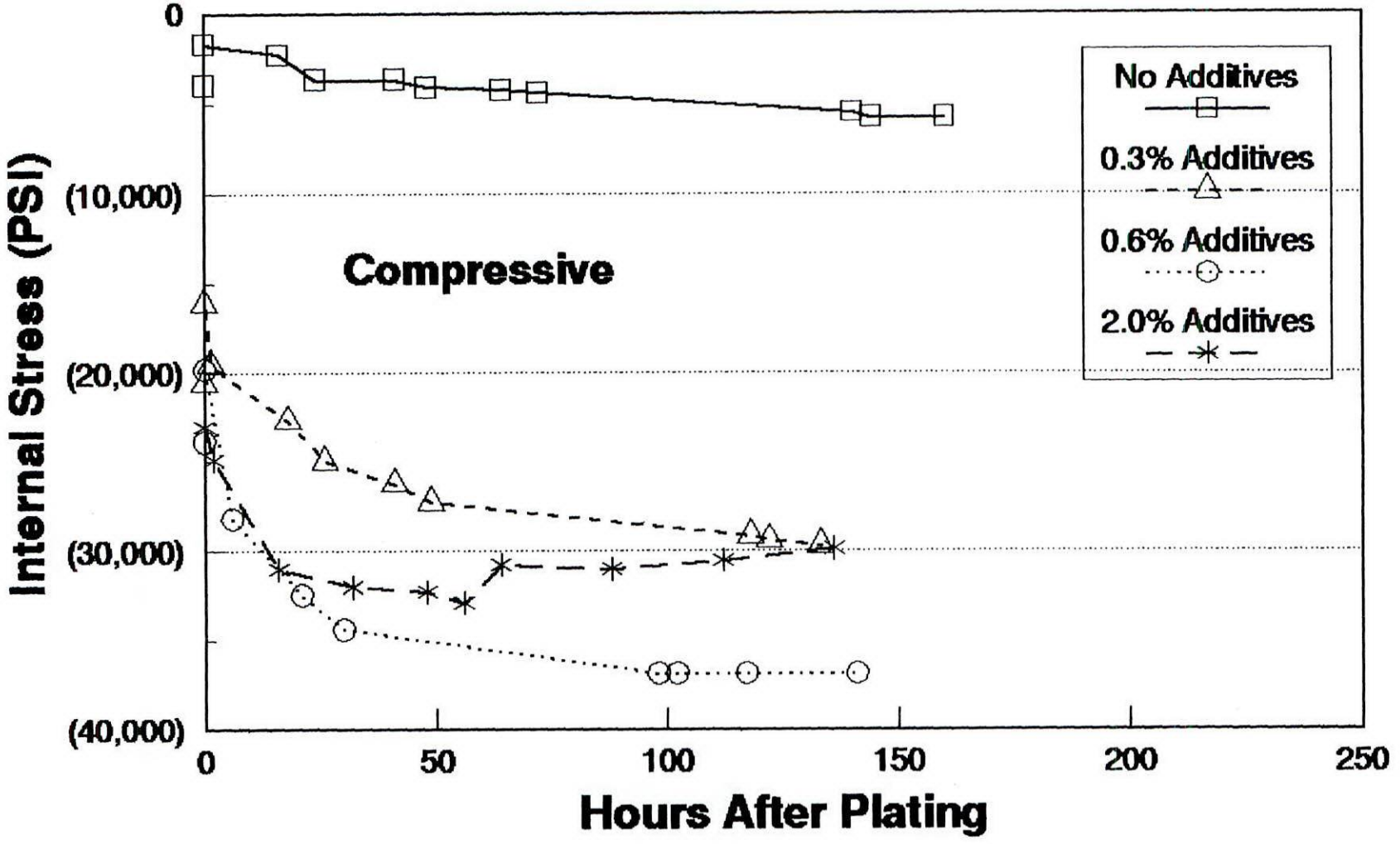


Figure 3
Commercial Mid Cyanide Zinc
25 ASF

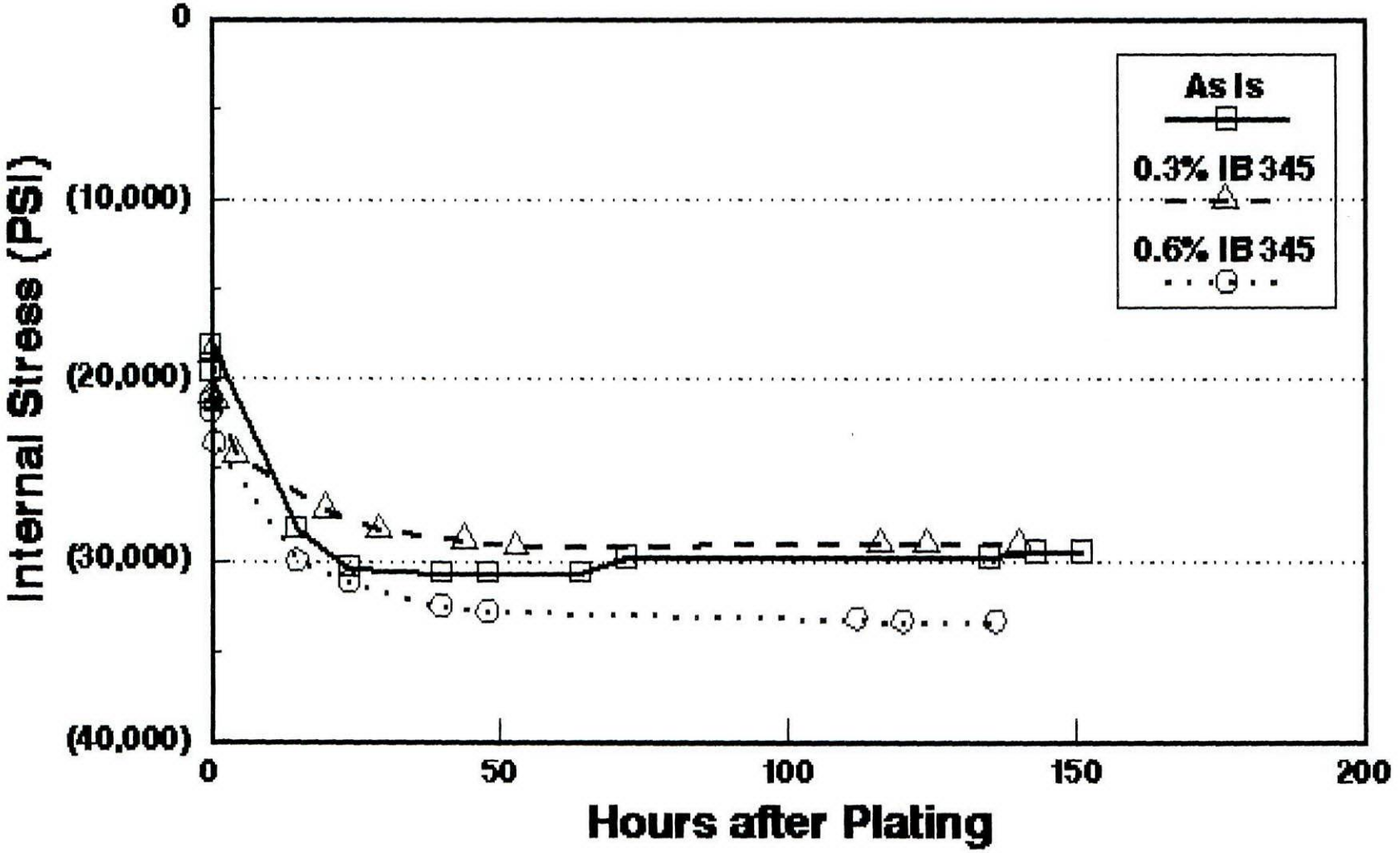


Figure 4
Alkaline Non Cyanide Zinc
2% Additives

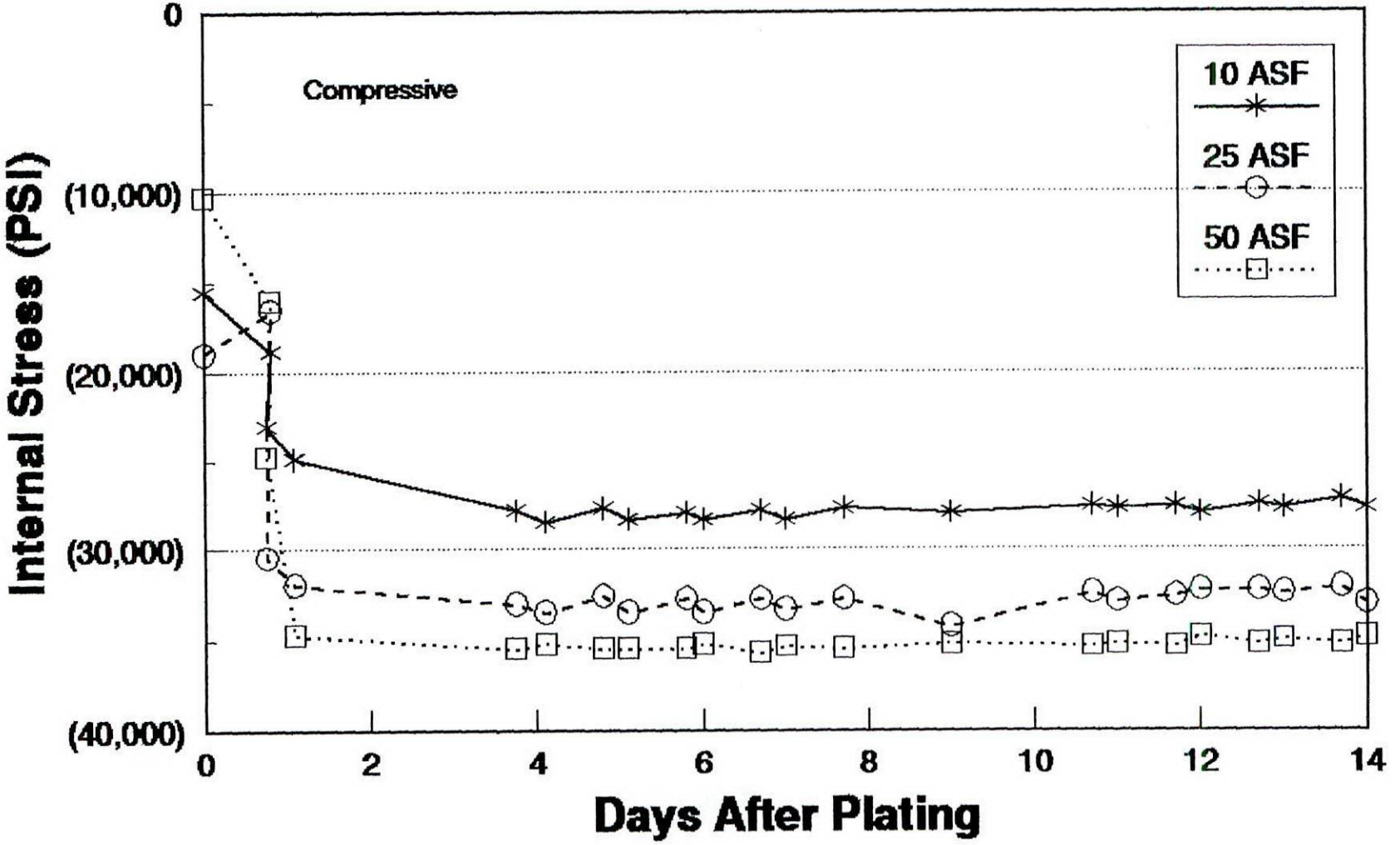


Figure 5

Alkaline Non Cyanide Zinc

Excess Brighterner Component

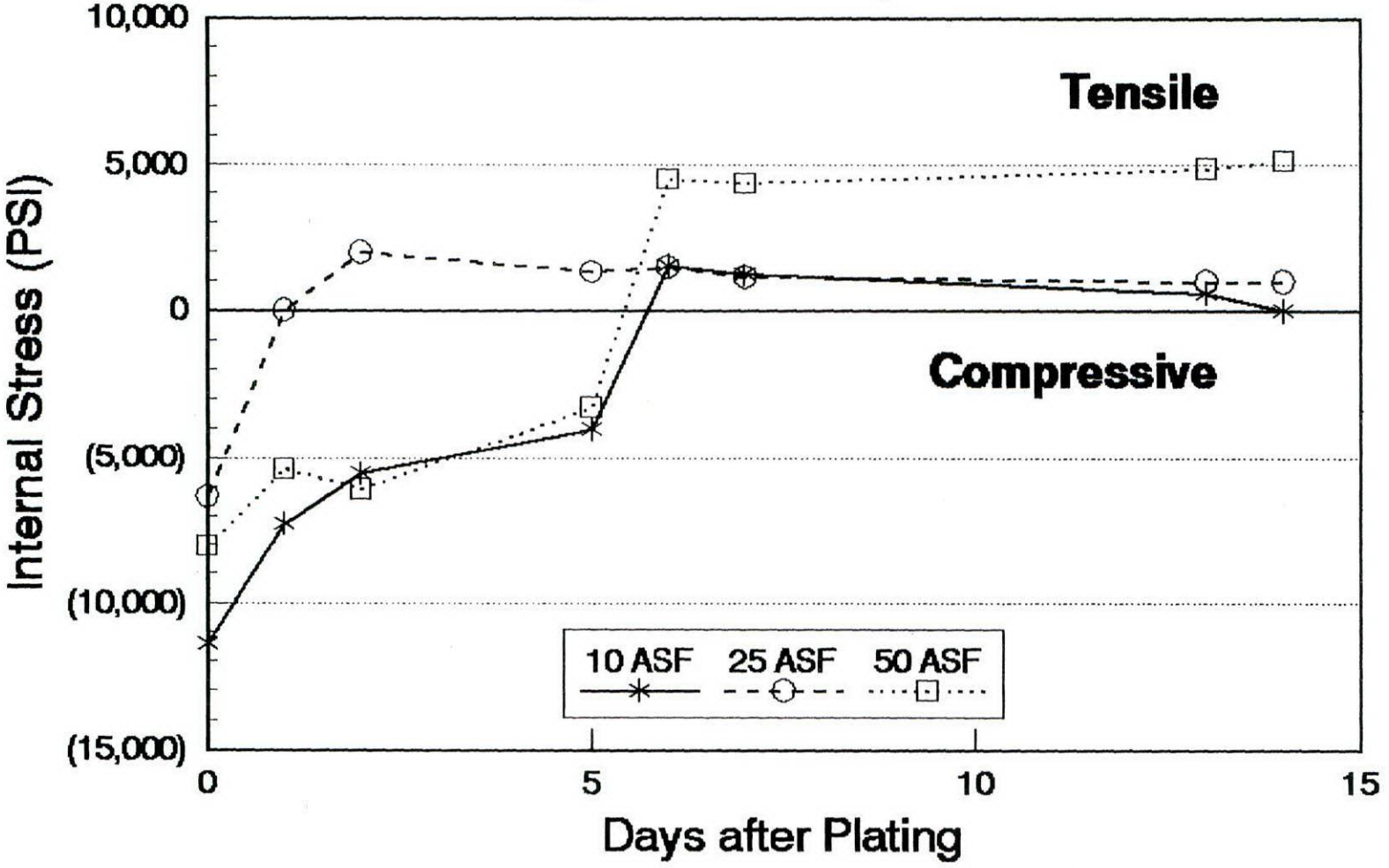


Figure 6
Commercial Non Cyanide Zinc
Additions of Excess Carrier

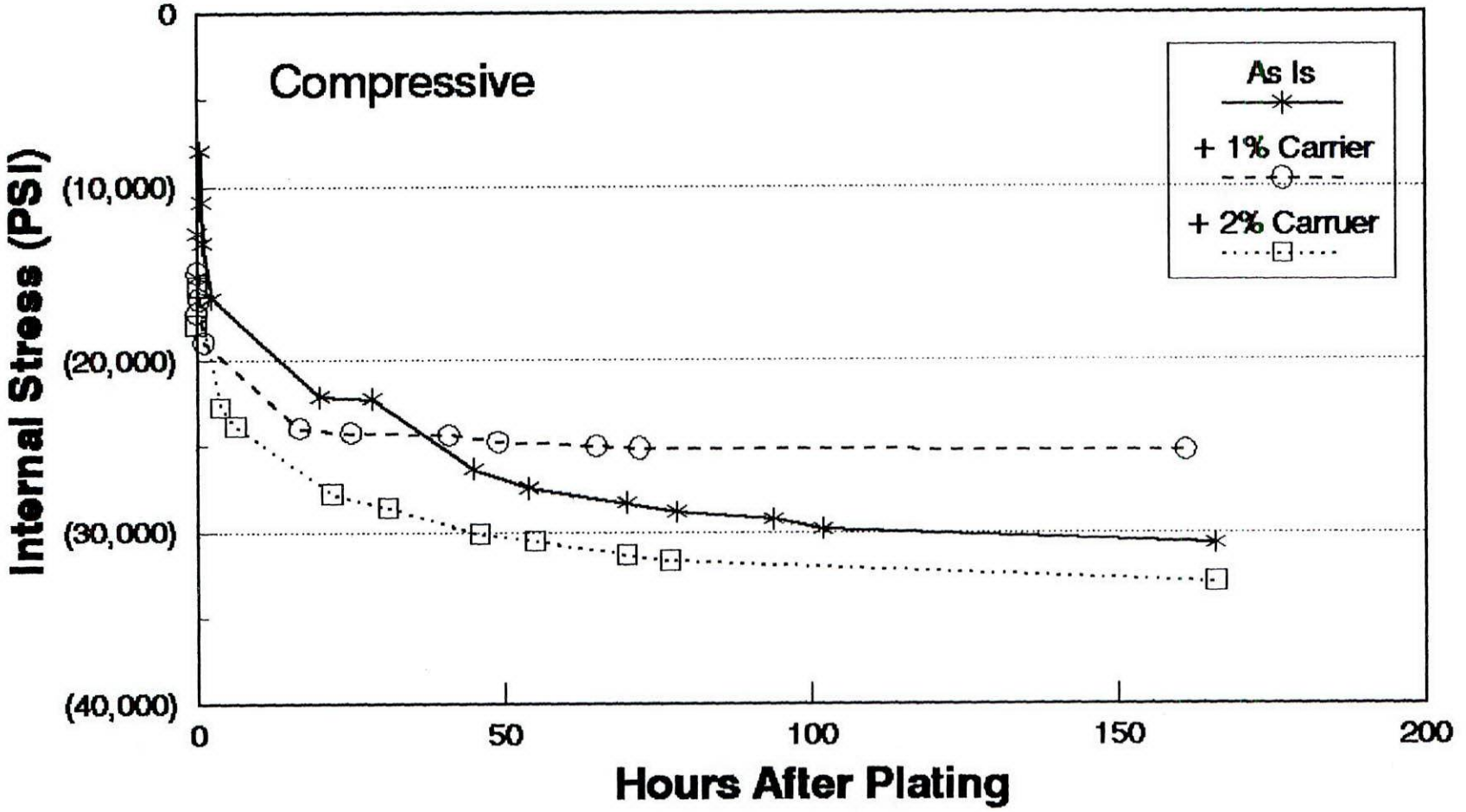


Figure 7
Commercial Non Cyanide Zinc
Excess Brightener Use

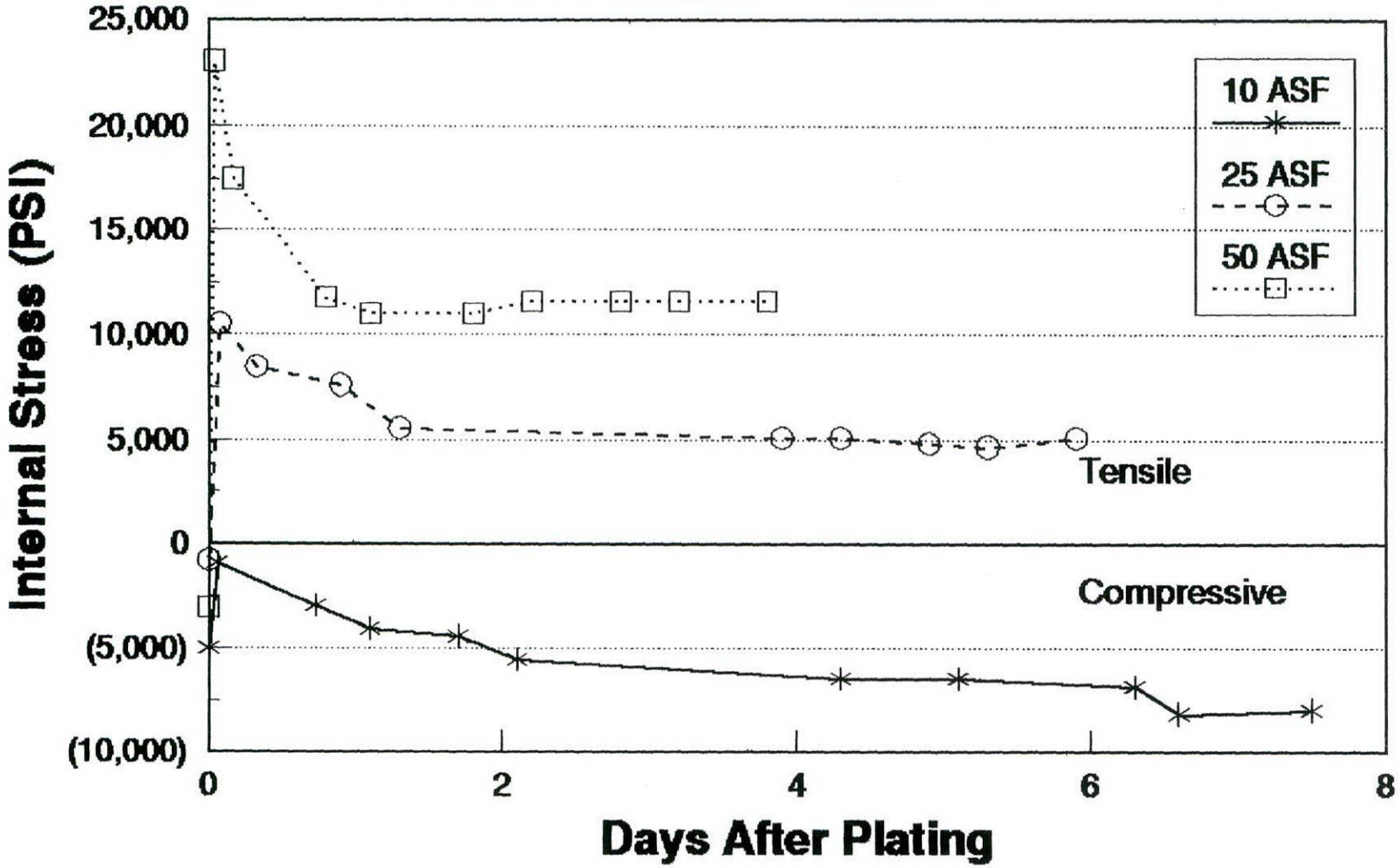
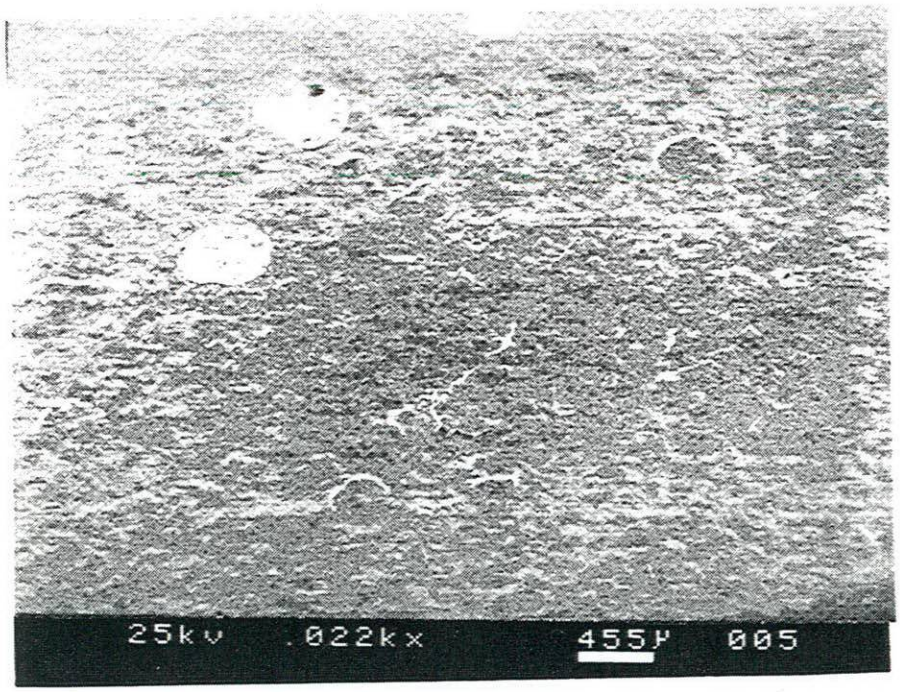


Figure 8

Tensile Adhesion Failure



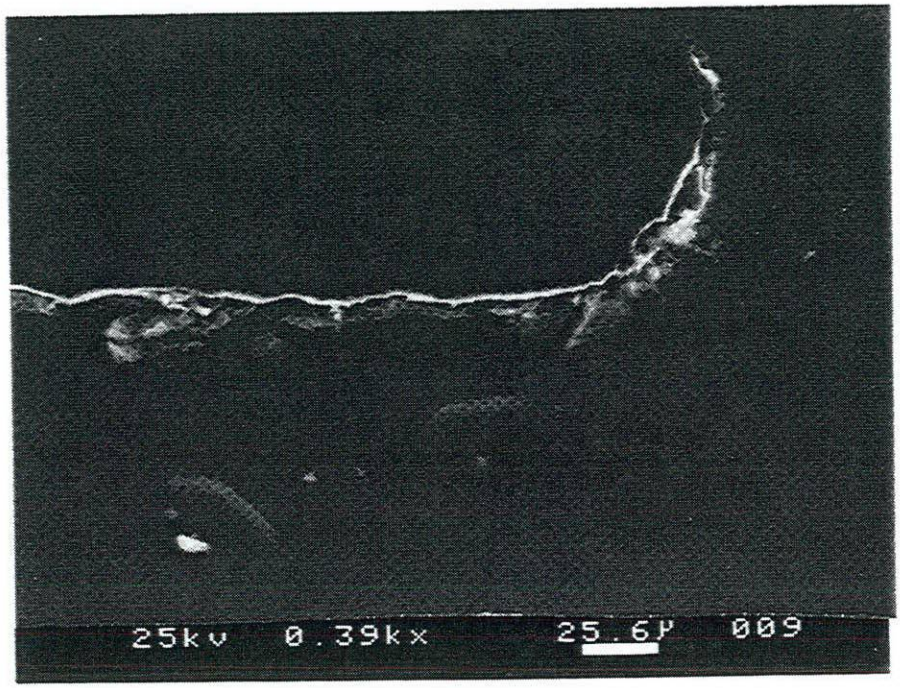


Figure 9

Analysis of Surface Contamination

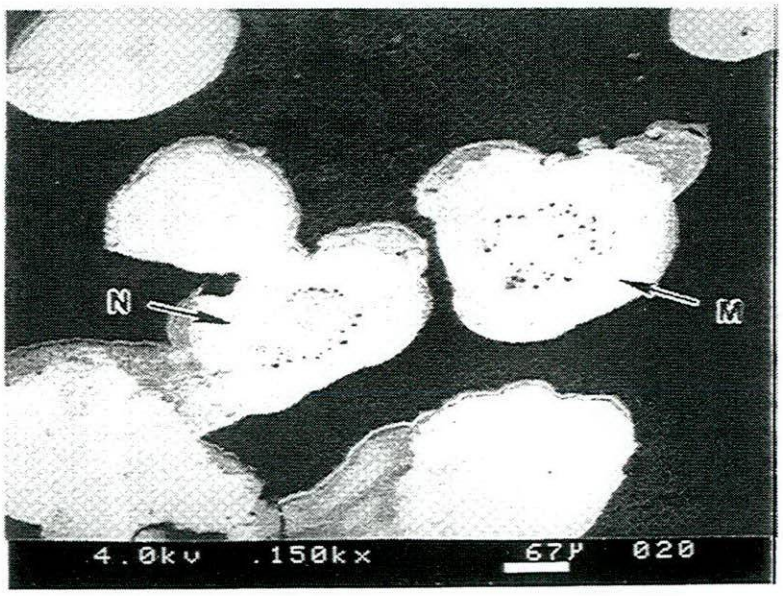


FIG. 19 - AREAS M AND N

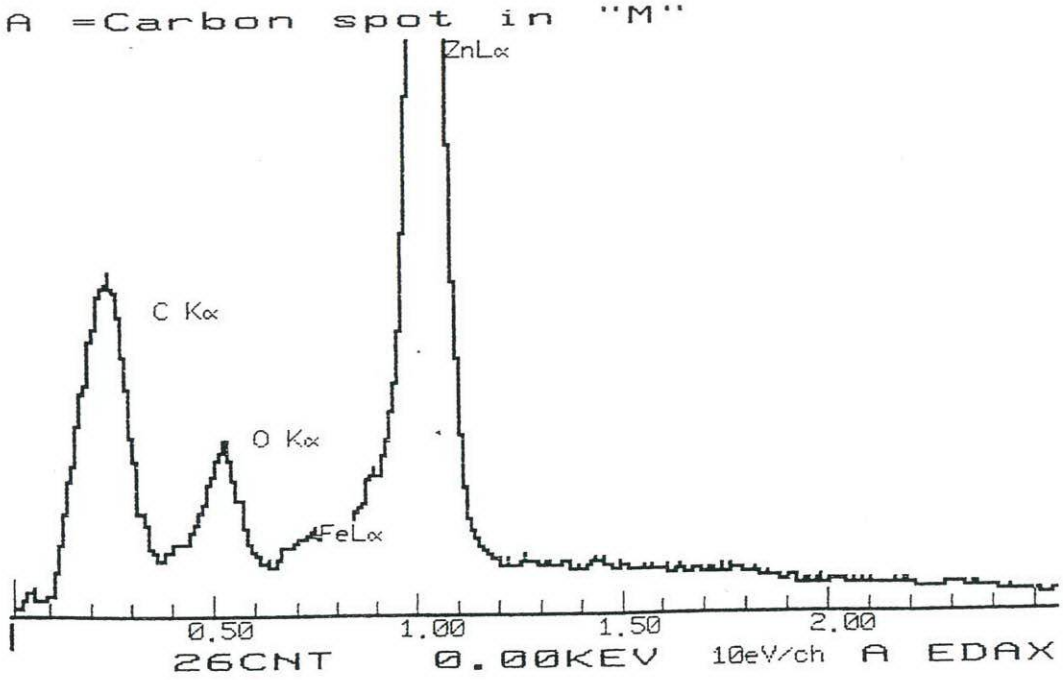
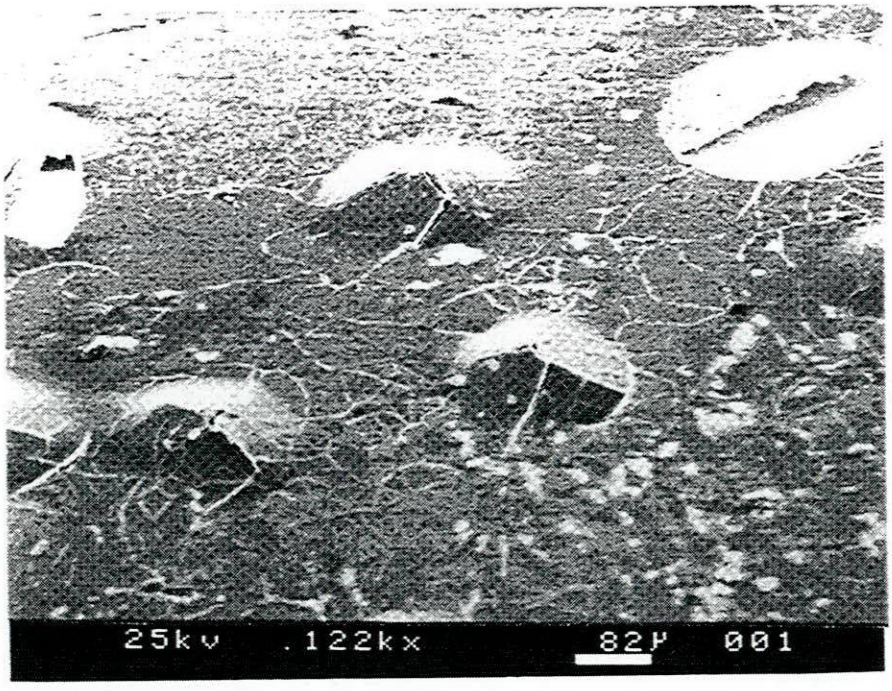


Figure 10

Compressive Adhesion Failure



Paper Not Available In Time For Publication

Study on Hard Chromium Plating from Trivalent Chromium Bath

Shuzhen Duan and Huidong Li, Xin Zhang, University of Science & Technology, Beijing, P. R. China, and Dr. John Dash, Portland State University, Portland, OR

The process and the mechanism of hard chromium plating from a trivalent chromium bath was investigated. The results showed that a hard chromium coating thicker than 50 μm can be obtained from a trivalent chromium bath with a lower pH value and proper composition. The coating consists of columnar crystals and grows up in the manner of transient nucleating.

For copies of this paper please contact:

Ms. Shuzhen Duan
Univ. of Science & Technology
Dept. of Physical Chemistry
Beijing, P.R. China
FAX: 86112017283

The Role of Ultrasonics in Aqueous Cleaning

F. John Fuchs
Applications Engineer

Blackstone Ultrasonics
9 North Main Street
Jamestown, NY 14701
716 665-2340

Introduction -

Chlorinated and fluorinated hydrocarbons used by the finishing industry since its very inception are on the way out, victims of increased regulation, the Montreal Protocol and the "Green" movement in general. It is understandable why these materials achieved their prominent position in metal fininshing -- they are reasonably effective at cleaning and were formerly the least expensive cleaners available. The equipment required for their application is simple and inexpensive, and until recently they were considered environmentally safe.

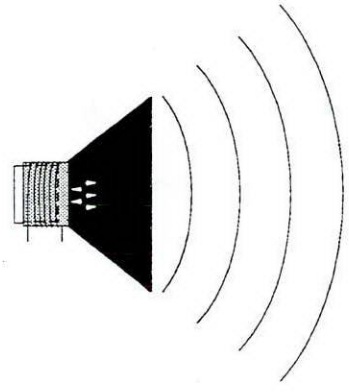
Industry is currently in a struggle to replace solvents with "environmentally friendly" means of cleaning. Although substitute water-based, semi-aqueous and petroleum based cleaners are available, they are often somewhat less effective cleaners than the solvents and may require a boost to achieve the required levels of cleanliness. Ultrasonic energy is now used extensively in critical cleaning applications to both speed and enhance the cleaning effect of the alternative cleaners. This paper is intended to familiarize the reader with the basic theory of ultrasonics and how ultrasonic energy can be most effectively applied to a variety of cleaning processes.

The Theory of Ultrasonics -

Ultrasonics is the science of sound waves above the limits of human audibility. Frequencies above 18 Kilohertz are usually considered to be ultrasonic. In order to understand the mechanics of ultrasonics, it is necessary to first have a basic understanding of sound waves, how they are generated and how they travel through a conducting medium.

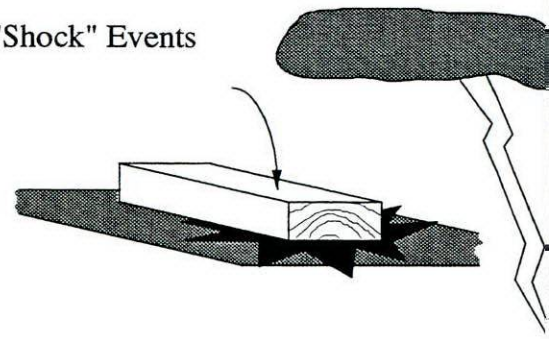
Sound Wave Generation -

A sound wave is produced when an instantaneous displacement is generated in a sound conducting medium, such as by mechanical movement or a "shock" event. The displacement of air by the cone of a radio speaker is a good example of sound waves generated by mechanical movement. As the speaker cone moves back and forth, the air in front of the cone is alternately compressed and rarified to produce sound waves, which travel through the air until they are finally dissipated. We are probably most

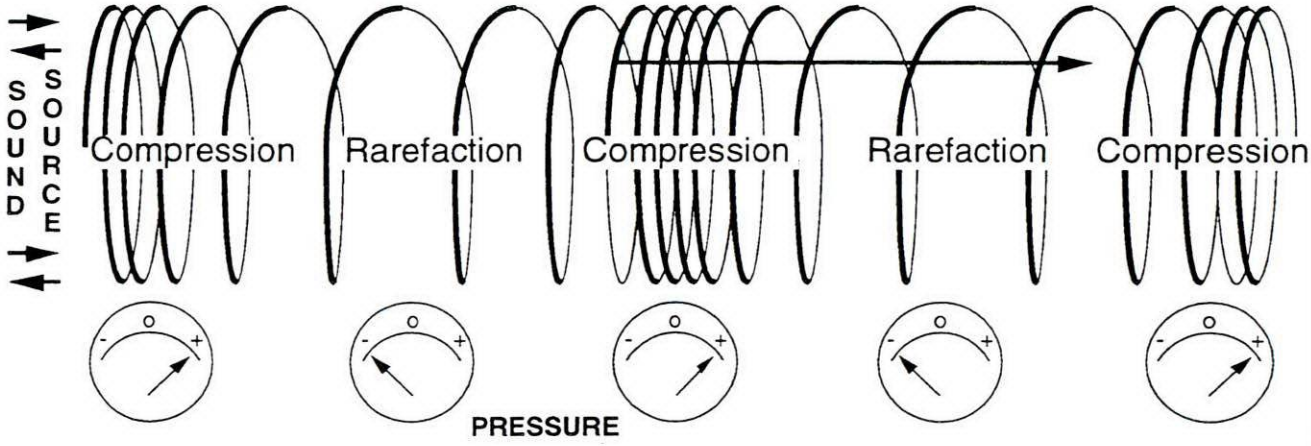


familiar with sound waves generated by alternating mechanical motion. There are also sound waves which are created by a single "shock" event. An example is thunder which is generated as air instantaneously changes volume as a result of an electrical discharge (lightning). Another example of a shock event might be the sound created as a board falls with its face against a cement floor. Shock events are sources of a single compression wave which radiates from the source.

"Shock" Events



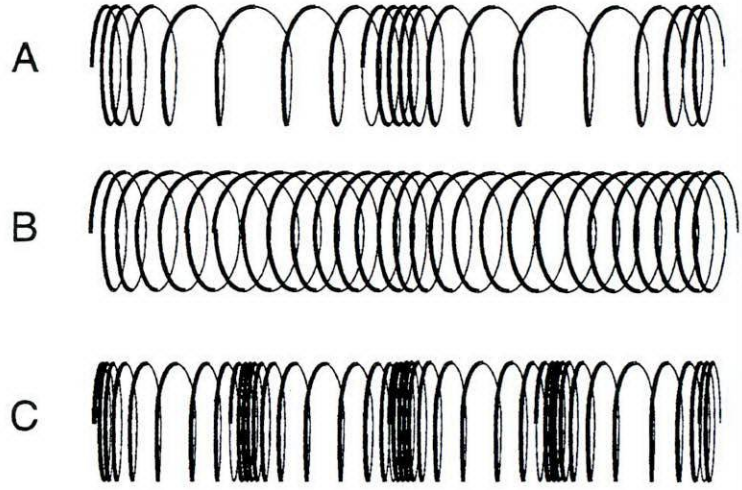
The Nature of Sound Waves -



The diagram above uses the coils of a spring similar to a Slinky® toy to represent individual molecules of a sound conducting medium. The molecules in the medium are influenced by adjacent molecules in much the same way that the coils of the spring influence one another. The source of the sound in the model is at the left. The compression generated by the sound source as it moves propagates down the length of the spring as each adjacent coil of the spring pushes against its neighbor. It is important to note that, although the wave travels from one end of the spring to the other, the individual coils remain in their same relative positions, being displaced first one way and then the other as the sound wave passes. As a result, each coil is first part of a compression as it is pushed toward the next coil and then part of a rarefaction as it receeds from the adjacent coil. In much the same way, any point in a sound conducting medium is alternately subjected to compression and then rarefaction. At a point in the area of a compression, the pressure in the medium is positive. At a point in the area of a rarefaction, the pressure in the medium is negative.

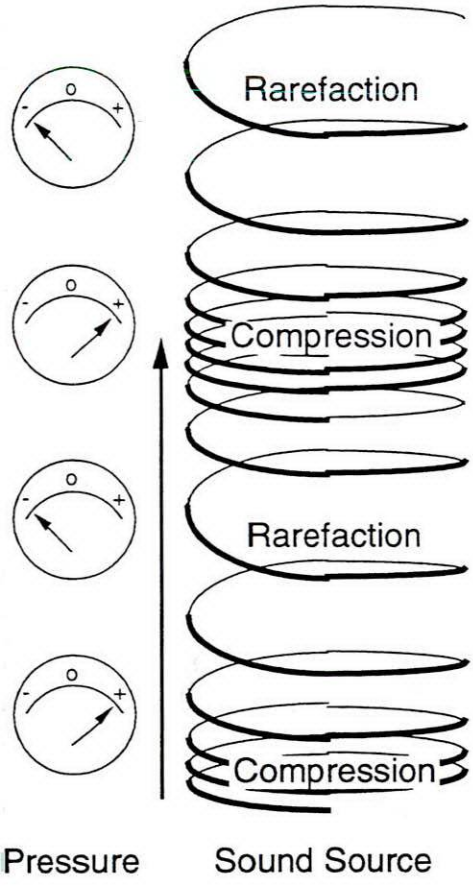
Frequency and Amplitude

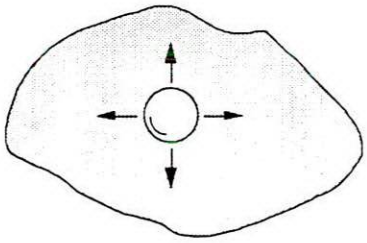
Frequency and amplitude are properties of sound waves. In the diagram at the right, if "A" is the base sound wave, "B" with less displacement of the media (less intense compression and rarefaction) as the wave front passes represents a sound wave of less amplitude or "loudness." "C" represents a sound wave of higher frequency indicated by more wave fronts passing a given point within a given period of time.



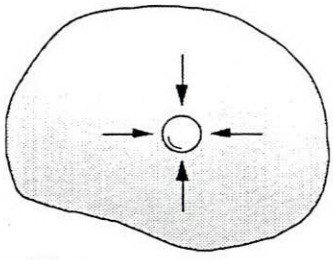
Cavitation -

In elastic media such as air and most solids, there is a continuous transition as a sound wave is transmitted. In non-elastic media such as water and most liquids, there is continuous transition as long as the amplitude or "loudness" of the sound is relatively low. As amplitude is increased, however, the magnitude of the negative pressure in the areas of rarefaction eventually becomes sufficient to cause the liquid to fracture because of the negative pressure, causing a phenomenon known as cavitation.

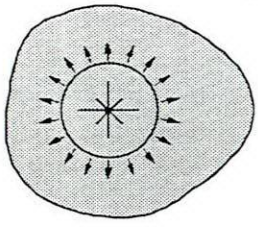




Cavitation "bubbles" are created at sites of rarefaction as the liquid fractures or tears because of the negative pressure of the sound wave in the liquid.



As the wave fronts pass, the cavitation "bubbles" oscillate under the influence of positive pressure, eventually growing to an unstable size.



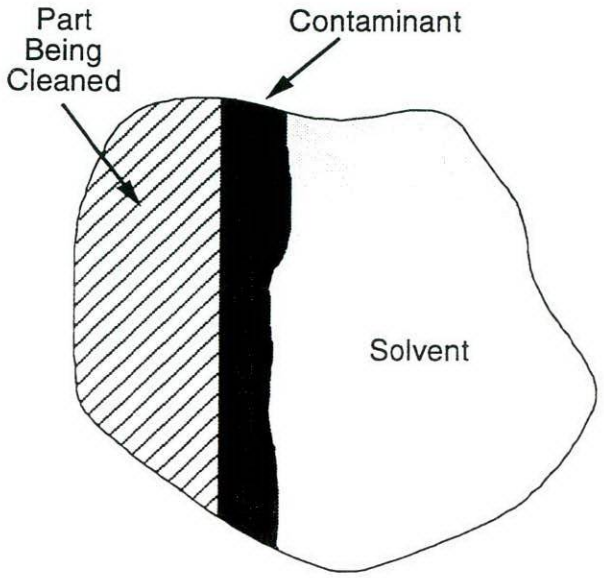
Finally, the violent collapse of the cavitation "bubbles" results in implosions, which cause shock waves to be radiated from the sites of the collapse.

The collapse and implosion of myriad cavitation "bubbles" throughout an ultrasonically activated liquid result in the effect commonly associated with ultrasonics. It has been calculated that temperatures in excess of 10,000°F and pressures in excess of 10,000 PSI are generated at the implosion sites of cavitation bubbles.

Benefits of Ultrasonics in the Cleaning and Rinsing Processes -

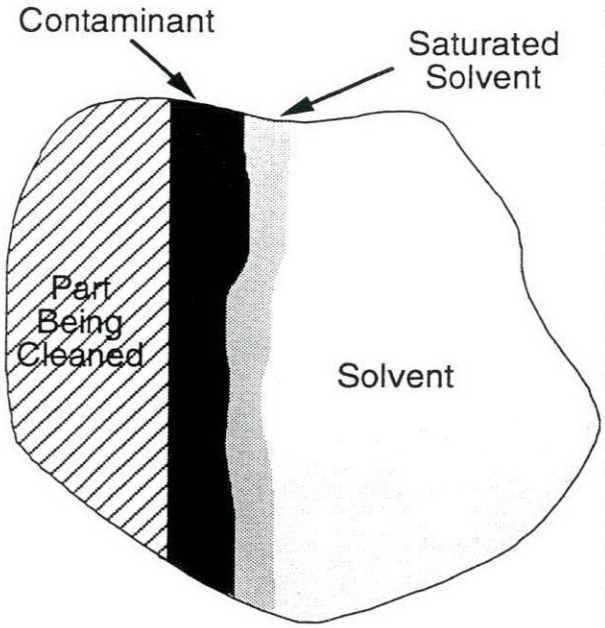
Cleaning in most instances requires that a contaminant be dissolved (as in the case of a soluble soil), displaced (as in the case of a non-soluble soil) or both dissolved and displaced (as in the case of insoluble particles being held by a soluble binder such as oil or grease). The mechanical effect of ultrasonic energy can be helpful in both speeding dissolution and displacing particles. Just as it is beneficial in cleaning, ultrasonics is also beneficial in the rinsing process. Residual cleaning chemicals are removed quickly and completely by ultrasonic rinsing.

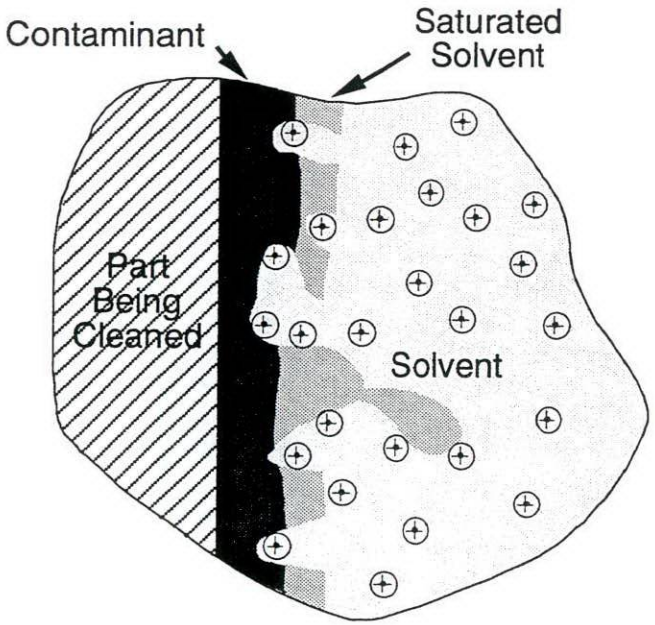
Ultrasonics Speeds Cleaning by Dissolution -



In removing a contaminant by dissolution, it is necessary for the solvent to come into contact with and dissolve the contaminant. The cleaning activity takes place only at the interface between the solvent and the contaminant.

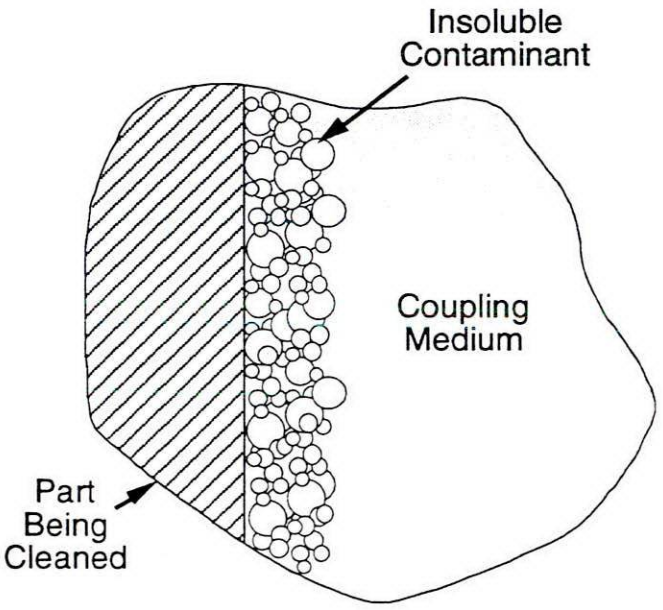
As the solvent dissolves the contaminant, a saturated solvent layer develops at the interface between the solvent and the contaminant. Once this has happened, cleaning action stops as the saturated solvent can no longer attack the contaminant. Fresh solvent cannot reach the contaminant.





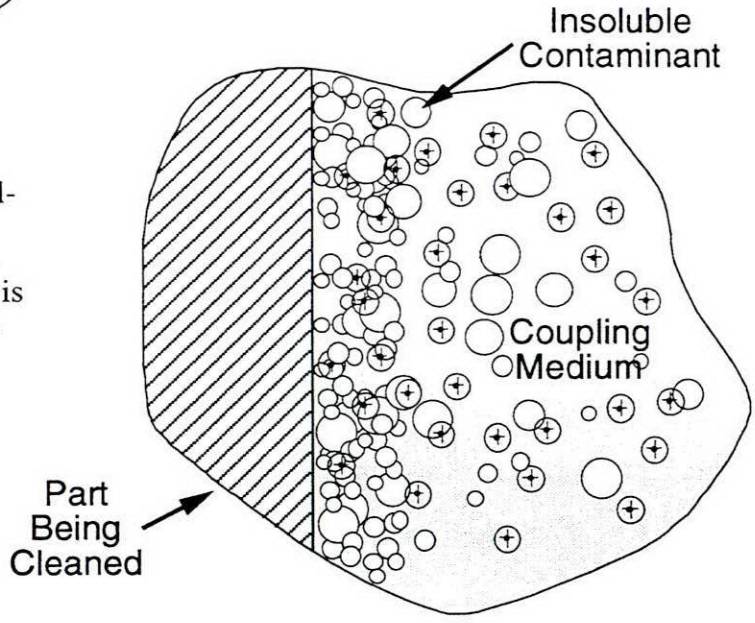
Ultrasonic cavitation and implosion effectively displace the saturated solvent layer to allow fresh solvent to come into contact with the contaminant remaining to be removed. This is especially beneficial when irregular surfaces or internal passageways are to be cleaned.

Ultrasonic Activity Displaces Particles -



Some contaminants are comprised of insoluble particles loosely attached and held in place by ionic or cohesive forces. These particles need only be displaced sufficiently to break the attractive forces to be removed.

Cavitation and implosion as a result of ultrasonic activity displace and remove loosely held contaminants such as dust from surfaces. For this to be effective, it is necessary that the coupling medium be capable of wetting the particles to be removed.



Complex Contaminants -

Contaminations can also, of course, be more complex in nature, consisting of combination soils made up of both soluble and insoluble components. The effect of ultrasonics is substantially the same in these cases, as the mechanical micro-agitation helps speed both the dissolution of soluble contaminants and the displacement of insoluble particles.

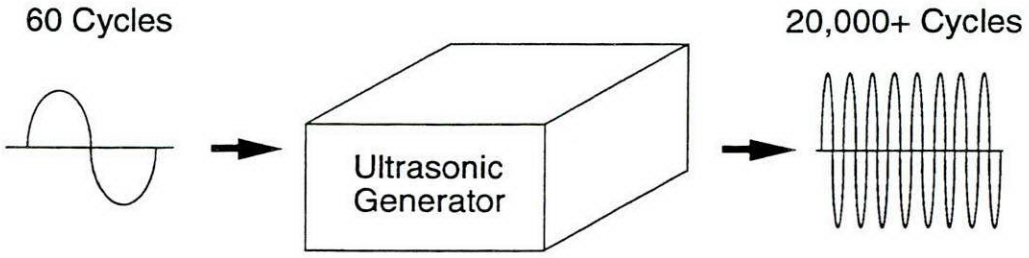
Ultrasonic activity has also been demonstrated to speed or enhance the effect of many chemical reactions. This is probably caused mostly by the high energy levels created as high pressures and temperatures are created at the implosion sites. It is likely that the superior results achieved in many ultrasonic cleaning operations may be at least partially attributed to the sonochemistry effect.

A Superior Process -

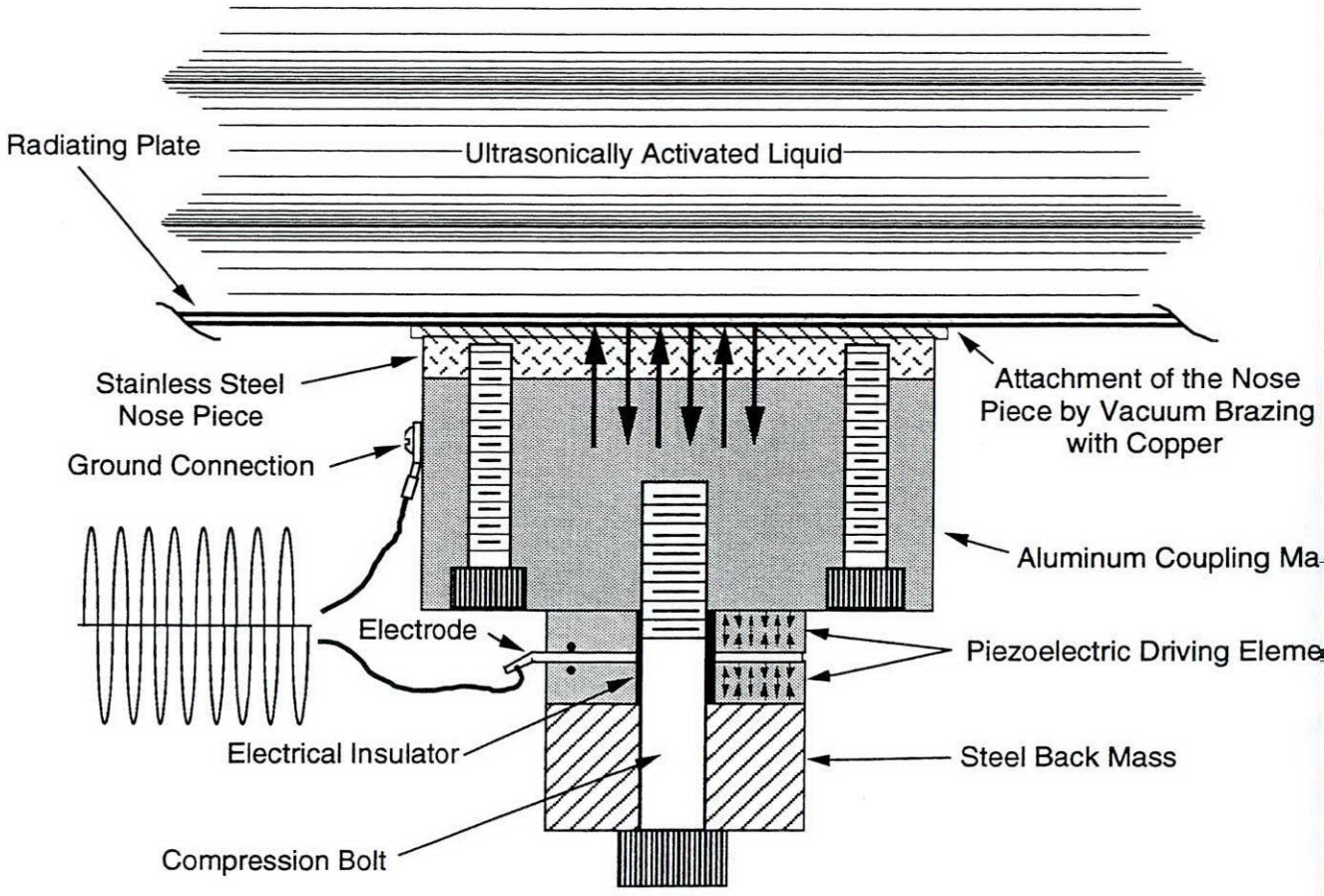
Ultrasonic energy has been proven to be more effective at enhancing cleaning than other alternatives, including spray washing, brushing, turbulation, air agitation, and electro-cleaning in many applications. The ability of ultrasonic activity to penetrate and assist the cleaning of interior surfaces of complex parts is especially noteworthy.

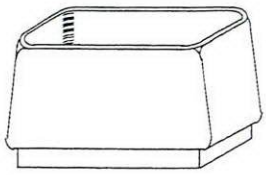
Ultrasonic Equipment -

To introduce ultrasonic energy into a cleaning system requires an ultrasonic transducer and an u trasonic power supply or "generator." The generator converts the 60 cycle power from the power line into alternating current at the desired ultrasonic frequency.



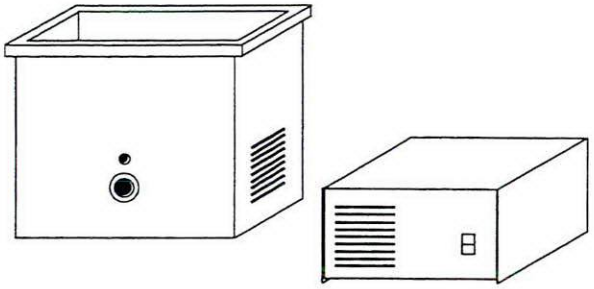
Electrical energy at the ultrasonic frequency is supplied to the transducer by the ultrasonic gener tor. This electrical energy is applied to two piezoelectric elements in the transducer which vibrate. These vibrations are amplified by the resonant masses of the transducer and directed into the liquid through the radiating plate. Transducer elements can be mounted directly on the bottom or sides of metal tanks or can be housed in stainless steel housings which are immersed in the liquid. The immers ible type of transducer can be used to add ultrasonic capability to nearly any cleaning tank.

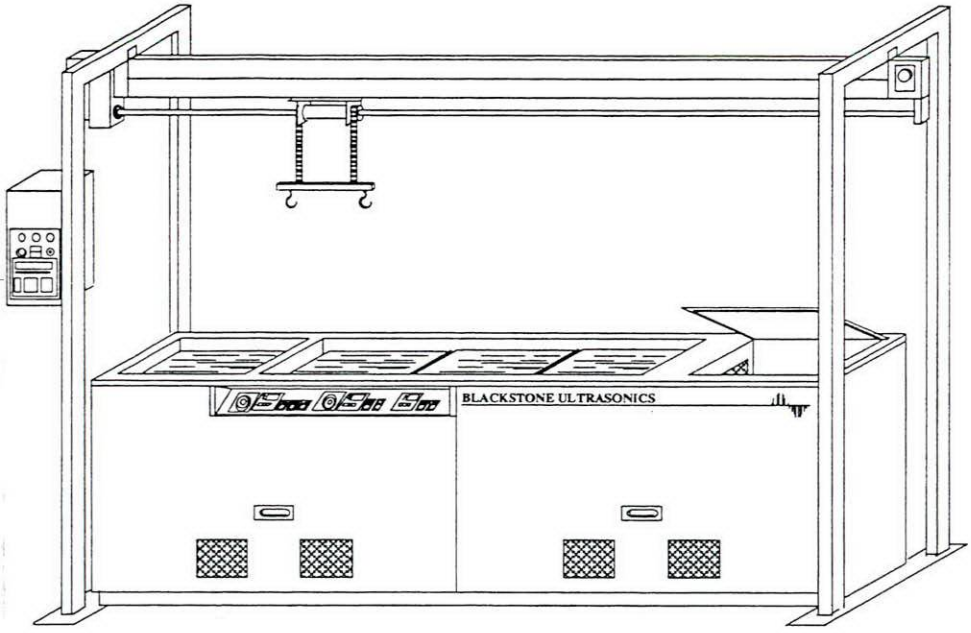




Small, self-contained cleaners are used in doctors' offices and jewelry stores.

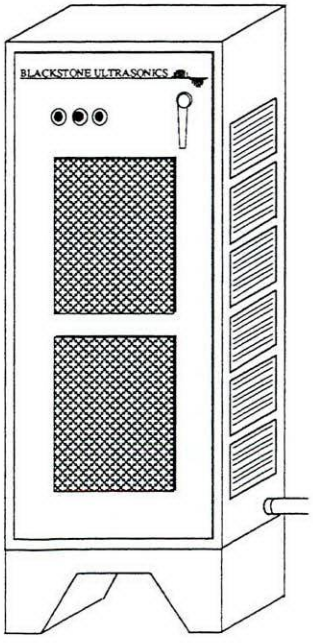
Heated tank cleaning systems are used in laboratories and for small batch cleaning needs.

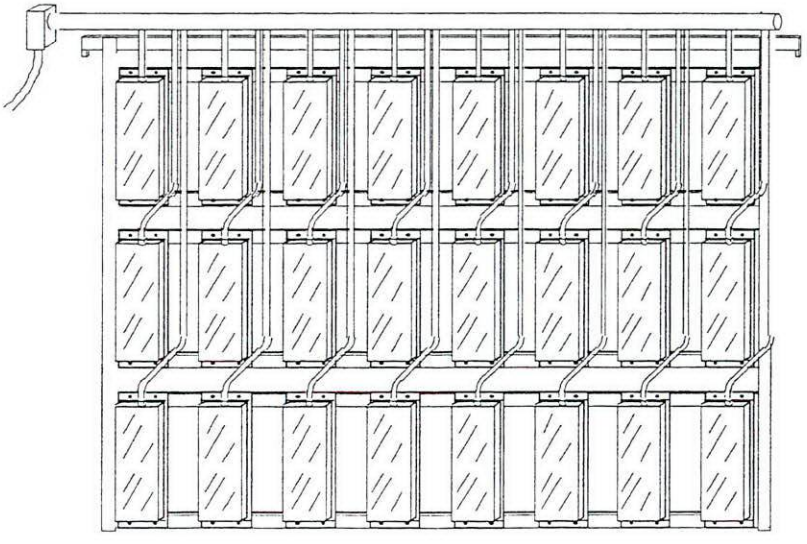




Console cleaning systems integrate ultrasonic cleaning tank(s), rinse tank(s) and a dryer for batch cleaning. Systems can be automated through the use of a PLC controlled material handling system. A wide range of options may be offered in custom designed systems.

Large scale installations or retrofitting of existing tanks in plating lines, etc., can be achieved through the use of modular immersible ultrasonic transducers. Ultrasonic generators are often housed in climate-controlled enclosures.





Maximizing the Ultrasonic Cleaning Process -

Process Parameters -

Effective application of the ultrasonic cleaning process requires consideration of a number of parameters. While time, temperature and chemical remain important in ultrasonic cleaning as they are in other cleaning technologies, there are other factors which must be considered to maximize the effectiveness of the process. Especially important are those variables which affect the intensity of ultrasonic cavitation in the liquid.

Maximizing Cavitation

Maximizing cavitation of the cleaning liquid is obviously very important to the success of the ultrasonic cleaning process. Several variables effect cavitation intensity.

Temperature is the most important single parameter to be considered in maximizing cavitation intensity. This is because so many liquid properties affecting cavitation intensity are related to temperature. Changes in temperature result in changes in viscosity, the solubility of gas in the liquid, the diffusion rate of dissolved gasses in the liquid, and vapor pressure, all of which affect cavitation intensity. In pure water, the cavitation effect is maximized at approximately 160°F.

The viscosity of a liquid must be minimized for maximum cavitation effect. Viscous liquids are sluggish and cannot respond quickly enough to form cavitation bubbles. The viscosity of most liquids is reduced as temperature is increased.

For most effective cavitation, the cleaning liquid must contain as little dissolved gas as possible. Gas dissolved in the liquid is released during the bubble growth phase of cavitation and prevents the violent implosion of the cavitation bubble which is required for the desired ultrasonic effect. The amount of dissolved gas in a liquid is reduced as the liquid temperature is increased.

The diffusion rate of dissolved gasses in a liquid is increased at higher temperatures. This means that liquids at higher temperatures give up dissolved gasses more readily than those at lower temperatures, which aids in minimizing the amount of dissolved gas in the liquid.

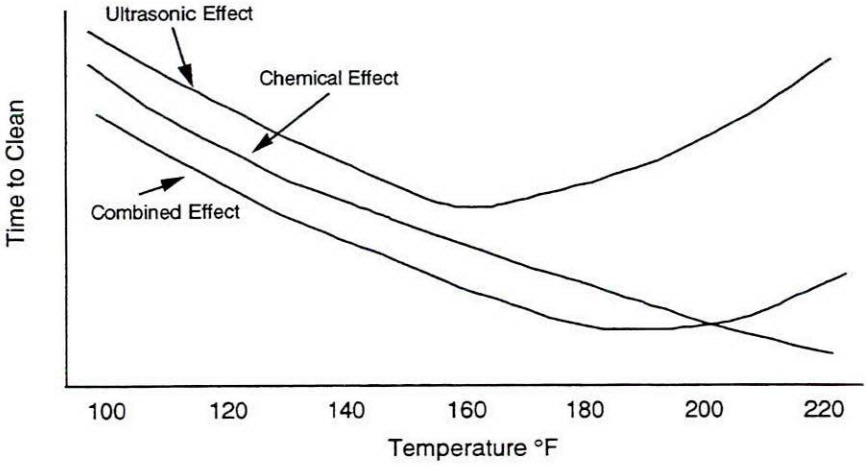
A moderate increase in the temperature of a liquid brings it closer to its vapor pressure, meaning that vaporous cavitation is more easily achieved. Vaporous cavitation, in which the cavitation bubbles are filled with the vapor of the cavitating liquid, is the most effective form of cavitation. As the boiling temperature is approached, however, the cavitation intensity is reduced as the liquid starts to boil at the cavitation sites.

Cavitation intensity is directly related to Ultrasonic Power at the power levels generally used in ultrasonic cleaning systems. As power is increased substantially above the cavitation threshold, cavitation intensity levels off and can only be further increased through the use of focusing techniques.

Cavitation intensity is inversely related to Ultrasonic Frequency. As the ultrasonic frequency is increased, cavitation intensity is reduced because of the smaller size of the cavitation bubbles and their resultant less violent implosion. The reduction in cavitation effect at higher freqencies may be overcome by increasing the ultrasonic power.

Maximizing Overall Cleaning Effect

Cleaning Chemical selection is extremely important to the overall success of the ultrasonic cleaning process. The selected chemical must be compatible with the base metal being cleaned and have the capablility to remove the soils which are present. It must also cavitate well. Most cleaning chemicals can be used satisfactorily with ultrasonics. Some are formulated especially for use with ultrasonics. However, Avoid the non-foaming formulations normally used in spray washing applications. Highly wetted formulations are preferred. Many of the new petroleum cleaners, as well as petroleum and terpene based semi-aqueous cleaners, are compatible with ultrasonics. Use of these formulations may require some special equipment considerations, including increased ultrasonic power, to be effective.



Temperature was mentioned earlier as being important to achieving maximum cavitation. The effectiveness of the cleaning chemical is also related to temperature. Although the cavitation effect is maximized in pure water at a temperature of approximately 160°F, optimum cleaning is often seen at higher or lower temperatures because of the effect that temperature has on the cleaning chemical. As a general rule, each chemical will perform best at its recommended process temperature regardless of the temperature effect on the ultrasonics. For example, although the maximum ultrasonic effect is achieved at 160°F, most highly caustic cleaners are used at a temperatures of 180°F to 190°F because the chemical effect is greatly enhanced by the added temperature. Other cleaners may be found to break down and lose their effectiveness if used at temperatures in excess of as low as 140°F. The best practice is to use a chemical at its maximum recommended temperature not exceeding 190°F.

Degassing of cleaning solutions is extremely important in achieving satisfactory cleaning results. Fresh solutions or solutions which have cooled must be degassed before proceeding with cleaning. Degassing is done after the chemical is added and is accomplished by operating the ultrasonic energy and raising the solution temperature. The time required for degassing varies considerably, based on tank capacity and solution temperature, and may range from several minutes for a small tank to an hour or more for a large tank. An unheated tank may require several hours to degass. Degassing is complete when small bubbles of gas cannot be seen rising to the surface of the liquid and a pattern of ripples can be seen.

The Ultrasonic Power delivered to the cleaning tank must be adequate to cavitate the entire volume of liquid with the workload in place. Watts per gallon is a unit of measure often used to measure the level of ultrasonic power in a cleaning tank. As tank volume is increased, the number of watts per gallon required to achieve the required performance is reduced. Cleaning parts that are very massive or that have a high ratio of surface to mass may require additional ultrasonic power. Excessive power may cause cavitation erosion or "burning" on soft metal parts. If a wide variety of parts is to be cleaned in a single cleaning system, an ultrasonic power control is recommended to allow the power to be adjusted as required for various cleaning needs.

Part Exposure to both the cleaning chemical and ultrasonic energy is important for effective cleaning. Care must be taken to ensure that all areas of the parts being cleaned are flooded with the cleaning liquid. Parts baskets and fixtures must be designed to allow penetration of ultrasonic energy and position the parts to assure that they are exposed to the ultrasonic energy. It is often necessary to individually rack parts in a specific orientation or rotate them during the cleaning process to thoroughly clean internal passages and blind holes.

Conclusion -

Properly utilized, ultrasonic energy can contribute significantly to the speed and effectiveness of many immersion cleaning and rinsing processes. It is especially beneficial in increasing the effectiveness of today's preferred aqueous cleaning chemistries and, in fact, is necessary in many applications to achieve the desired level of cleanliness. With ultrasonics, aqueous chemistries can often give results surpassing those previously achieved using solvents. Ultrasonics is not a technology of the future -- it is very much a technology of today.

Paper Not Available In Time For Publication

Managing Regulatory Change for Small Business: The Cadmium, Nickel and Chromium Standards and Their Impact on Occupational Health and Safety Program Management in Metal Finishing Companies

Michael Ziskin, CHCM, CHMM, and Mary A. Healy, CIH,
Field Safety Corporation, Stamford, CT

This presentation will be an examination of a proactive approach to health and safety management. In light of the more stringent requirements of the cadmium standard, managers of smaller-sized companies need to examine ways to incorporate these changes into their programs, which will allow them to maximize use of limited resources and minimize administrative load and downtime. Methods for meeting the requirements of the cadmium standard, as well as the nickel and chromium standards while streamlining various programs, will be discussed. For example: (1) Consolidation of training programs into training tiers or levels that include Hazard Communication, Training, Hazardous Waste and Emergency Response Operations, and Process Safety Management; (2) comprehensive medical surveillance for metal finishing for cadmium, chromium and nickel, with biological monitoring criteria for cadmium based on employee exposure; and (3) the "Compliance Hierarchy" as corporate policy for dealing with all operations involving hazardous materials; focusing on engineering out exposure as a long-term objective, thereby reducing exposure and biological monitoring requirements.

For copies of this paper please contact:

Michael Ziskin
Field Safety Corp.
28 Mazee Ave.
Stamford, CT 06902
203/964-9199
FAX: 203/969-1325

COMPETENCY-BASED TRAINING IN ELECTROPLATING

& SURFACE FINISHING FACILITIES

PRESENTED BY

MICHAEL H. ZISKIN, CHCM, CHMM
PRESIDENT

FIELD SAFETY CORP.
28 MAGEE AVENUE
STAMFORD, CT 06902
(203) 964-9199



TYPES OF TRAINING

REGULATORY COMPLIANCE
- Environmental (EPA, State Environmental)
- Occupational (State and Federal)
- Transportation (DOT)

LOSS CONTROL
- Worker's Compensation Claims
- Insurance Premiums

LIABILITY
- Corporate Exposure
- Personal Exposure
- Toxic Torts

CORPORATE MANDATE
- Beyond Minimum Compliance
- Community Relations

ORGANIZATIONAL STANDARDS
- Industrial - AESF, ABIH, IHMM, Etc.
- Labor - AFL-CIO, Etc.

APPLICABLE LAWS (PARTIAL LIST)

OSHA'S HAZARDOUS WASTE OPERATIONS AND EMERGENCY RESPONSE (HAZWOPER) 29 CFR PART 1910.120

OSHA'S HAZARD COMMUNICATION STANDARD (HCS) OR "WORKER RIGHT-TO-KNOW" LAW 29 CFR PART 1010.1200

OSHA'S BLOODBORNE PATHOGENS STANDARD 29 CFR PART 1910.1030

OSHA'S PROCESS SAFETY MANAGEMENT OF HIGHLY HAZARDOUS CHEMICALS (PSM) 29 CFR PART 1910.119

EPA'S RESOURCE CONSERVATION AND RECOVERY ACT (RCRA) - 40 CFR PART 265.16

EPA'S SPILL PREVENTION CONTROL AND COUNTERMEASURE (SPCC) PLAN 40 CFR PART 112

DOT'S HAZARDOUS MATERIALS TRAINING - 49 CFR PART 172 SUBPART H

ASSIGNING TRAINING

1. WHAT TYPES OF TRAINING ARE NEEDED?
2. WHO SHOULD BE TRAINED?
3. WHAT MATERIAL SHOULD BE RECOMMENDED FOR INCLUSION?
4. WHAT LEVELS OF TRAINING ARE NECESSARY?
5. HOW SHOULD TRAINING BE ADMINISTERED?
6. HOW CAN PROFICIENCY BE DEMONSTRATED?

JOB DESCRIPTION

JOB TITLE FOR EACH POSITION

JOB DESCRIPTION FOR EACH POSITION INCLUDING:

- THE BASIC DUTIES OF EACH EMPLOYEE
- REQUISITE SKILLS
- EDUCATION
- OTHER QUALIFICATIONS

WRITTEN DESCRIPTION OF THE TYPE AND AMOUNT OF TRAINING

DOCUMENTATION OF TRAINING COMPLETED

CHARACTERISTICS OF AN ADULT LEARNER

- ABLE TO LEARN - "CAN'T TEACH AN OLD DOG NEW TRICKS" - DOESN'T APPLY
- MUST KNOW "WHY IS IT IMPORTANT?" "HOW CAN I APPLY IT?"
- DESIRES TO PARTICIPATE IN THE DECISION MAKING PROCESS ABOUT LEARNING
- MUST HAVE SPECIFIC OBJECTIVES

- DOESN'T LIKE TO BE TREATED AS A CHILD
- LIKES ORGANIZATION/TO KNOW THE "BIG PICTURE"
- HAS EXPERIENCED LEARNING SITUATIONS - BOTH GOOD & BAD
- HAS WEALTH OF INDIVIDUAL EXPERIENCES - "LIFE"
- RECOGNIZES GOOD/BAD TRAINING
- MORE REALISTIC
- RESPONDS MORE TO FIRST IMPRESSIONS
- MAY BE MORE RIGID IN THEIR THINKING
- MAY NOT ACCEPT CRITICISM EASILY
- MAY BE MORE CONCERNED WITH USE OF TIME
- MAY BE MORE WILLING TO CHALLENGE THE INSTRUCTOR
- RESPONDS MORE TO INTERNAL MOTIVATION FOR LEARNING
- MAY PARTICIPATE IN LEARNING ACTIVITIES WITH MIXED EMOTIONS
- WANT TO USE WHAT THEY LEARN RIGHT AWAY

THE ADULT LEARNER MUST SEE THE RELEVANCE IN TRAINING

COMMITMENT FROM UPPER MANAGEMENT - BY EXAMPLE

HOW DO THEY FIT INTO THE PROGRAM

- JOB DESCRIPTION
- JOB REVIEW/REWARD SYSTEM
- RESPECT FOR THEMSELVES
- RESPECT FOR FELLOW WORKERS
- RESPECT FOR THE COMPANY

HOW WILL THEIR TIME BE SPENT

SIT DOWN - CLASSROOM STYLE

DEMONSTRATION
- I DO
- WE DO
- YOU DO

HANDS ON SKILL DEVELOPMENT

PUT TO PRACTICE WHAT IS LEARNED SPECIFIC AND CLEAR APPLICATION:

- THE CHEMICAL THEY WORK WITH
- THE WORK PLACE THEY WORK IN
- WITH THE RESOURCES AVAILABLE TO THEM: HUMAN EQUIPMENT

FIRST IMPRESSIONS COUNT FOR A LOT WITH THE ADULT LEARNER

WHY ARE WE HERE?

WHAT ARE WE GOING TO ACCOMPLISH?

HOW DO YOU FIT INTO THE BIG PICTURE?

THE OBJECTIVES OF THE TRAINING PROGRAM

WHAT ARE YOUR PERSONAL NEEDS IN RELATION TO THE TRAINING PROGRAM TOPIC?

WHAT DO YOU EXPECT TO GET OUT OF THIS TRAINING PROGRAM?

PERCEPTION OF DEFINED ROLE

PERCEPTION OF A HAZARDOUS MATERIAL OR HAZARDOUS EVENT

ESTABLISHING A COMMON PURPOSE WITH THE CLASS

ESTABLISHING A SET OF TERMS, DEFINITIONS AND COMMON UNDERSTANDING OF THE GOAL OF THE TRAINING PROGRAM

IF IT HASN'T HAPPENED HERE YET, WHAT MAKES YOU SO CERTAIN IT WILL IN THE FUTURE?

- INEFFECTIVE

IF IT HAPPENED BEFORE - IT COULD VERY LIKELY HAPPEN AGAIN - LET'S DISCUSS WHY?

- VERY EFFECTIVE

EMERGENCY RESPONSE OPERATIONS AT OTHER THAN RCRA SITES OR UNCONTROLLED HAZARDOUS WASTE SITE CLEAN-UPS. DIFFERENT LEVELS OF INITIAL TRAINING ARE REQUIRED DEPENDING ON THE DUTIES AND FUNCTIONS OF EACH RESPONDER PLUS DEMONSTRATED COMPETENCE OR ANNUAL REFRESHER TRAINING SUFFICIENT TO MAINTAIN COMPETENCE.

1. **FIRST RESPONDERS "AWARENESS LEVEL"**
   (INDIVIDUALS LIKELY TO WITNESS OR DISCOVER A HAZARDOUS SUBSTANCE RELEASE AND INITIATE THE EMERGENCY RESPONSE) MUST DEMONSTRATE COMPETENCY IN SUCH AREAS AS RECOGNIZING THE PRESENCE OF HAZARDOUS MATERIALS IN AN EMERGENCY, THE RISKS INVOLVED, AND THE ROLE THEY SHOULD PERFORM.

2. **FIRST RESPONDERS "OPERATIONS LEVEL"**
   (INDIVIDUALS WHO RESPOND FOR THE PURPOSE OF PROTECTING PROPERTY, PERSONS OR THE NEARBY ENVIRONMENT WITHOUT ACTUALLY TRYING TO STOP THE RELEASE) MUST HAVE 8 HOURS OF TRAINING PLUS "AWARENESS LEVEL" COMPETENCY OR DEMONSTRATE COMPETENCE IN THEIR ROLE.

3. **HAZARDOUS MATERIALS TECHNICIANS**
   (INDIVIDUALS WHO RESPOND TO STOP THE RELEASE) MUST HAVE **24** HOURS OF TRAINING EQUAL TO THE "OPERATIONS LEVEL" AND DEMONSTRATE COMPETENCE IN SEVERAL SPECIFIC AREAS.

4. **HAZARDOUS MATERIALS SPECIALISTS** (THOSE WHO SUPPORT THE TECHNICIANS BUT REQUIRE A MORE SPECIFIC KNOWLEDGE OF THE SUBSTANCES TO BE CONTAINED) MUST HAVE **24** HOURS OF TRAINING EQUAL TO THE TECHNICIAN LEVEL AND DEMONSTRATE COMPETENCE IN CERTAIN AREAS.

5. **ON-SCENE INCIDENT COMMANDERS** (WHO ASSUME CONTROL OF THE INCIDENT SCENE BEYOND THE "AWARENESS LEVEL") MUST HAVE **24** HOURS OF TRAINING EQUAL TO THE "OPERATIONS LEVEL" AND DEMONSTRATE COMPETENCE IN SPECIFIC AREAS.

DEFINITION

COMPETENCE - POSSESSING KNOWLEDGE, SKILLS AND JUDGEMENT NEEDED TO PERFORM INDICATED OBJECTIVES SATISFACTORILY (NFPA 472)

FIRST RESPONDER AWARENESS LEVEL

THE GOAL AT THE FIRST RESPONDER AWARENESS LEVEL SHALL BE TO PROVIDE THOSE PERSONS, WHO IN THE COURSE OF THEIR NORMAL DUTIES MAY BE THE FIRST ON THE SCENE OF A HAZARDOUS MATERIALS INCIDENT, WITH THE FOLLOWING COMPETENCIES TO RESPOND IN A SAFE MANNER WHEN CONFRONTED WITH A HAZARDOUS MATERIALS INCIDENT. THESE PERSONNEL ARE NOT EXPECTED TO TAKE ANY ACTIONS OTHER THAN TO RECOGNIZE THAT A HAZARD EXISTS, CALL FOR TRAINED PERSONNEL, AND SECURE THE AREA.

- AN UNDERSTANDING OF WHAT HAZARDOUS MATERIALS ARE, AND THE RISKS ASSOCIATED WITH THEM IN AN INCIDENT
- AN UNDERSTANDING OF THE POTENTIAL OUTCOMES ASSOCIATED WITH AN EMERGENCY CREATED WHEN HAZARDOUS MATERIALS ARE PRESENT
- THE ABILITY TO RECOGNIZE THE PRESENCE OF HAZARDOUS MATERIALS IN AN EMERGENCY
- THE ABILITY TO IDENTIFY THE HAZARDOUS MATERIALS AND DETERMINE BASIC HAZARD AND RESPONSE INFORMATION
- AN UNDERSTANDING OF THE ROLE OF THE FIRST RESPONDER ON THE SCENE OF A HAZARDOUS MATERIALS INCIDENT AS IDENTIFIED IN THE LOCAL CONTINGENCY PLAN FOR HAZARDOUS MATERIALS INCIDENTS
- THE ABILITY TO RECOGNIZE THE NEED FOR ADDITIONAL RESOURCES AND MAKE APPROPRIATE NOTIFICATIONS
- THE ABILITY TO INITIATE SCENE MANAGEMENT (I.E., IMPLEMENT THE INCIDENT COMMAND SYSTEM, ISOLATE THE IMMEDIATE SITE, DENY ENTRY TO UNAUTHORIZED PERSONS, AND EVACUATE)

LEVELS OF TRAINING

OVERVIEW (BROAD)

SITE SPECIFIC (LIMITED)

DISCIPLINE - INTENSIVE (LIMITED)

METHODS OF TRAINING

LECTURE

DISCUSSION

ON-THE-JOB (O-J-T)

CASE STUDY

EXERCISES

PROGRAMMED INSTRUCTION

TYPES OF EXERCISES

TABLE - TOPS

FUNCTIONAL (INCLUDING SIMULATION)

FIELD

THE GOAL OF A RESPONSE TEAM IS NEVER NEEDING TO RESPOND - EXPAND THE ROLE AND PURPOSE OF THE TEAM -BE PROACTIVE INSTEAD OF REACTIVE

MODULES FOR HAZMAT TRAINING

HAZARD RECOGNITION

HAZARD EVALUATION

PERSONAL PROTECTIVE EQUIPMENT

DECONTAMINATION

INCIDENT COMMAND AND SITE MANAGEMENT

SITE CONTROL OPERATIONS

SPILL CONTROL AND CLEAN UP

SIMULATION AND EXERCISES

CASE STUDY

CHEMICAL SPECIFIC RESPONSE PROCEDURES DEVELOPMENT

TRIAL-RUN OF PROCEDURES

REFINEMENT OF PROCEDURES AND TEAM MEMBER ROLES AND RESPONSIBILITIES

CONTINUED CRITIQUE, REFINEMENT AND EVALUATION OF PROGRAM

TRAINERS NEED

- HUMAN RELATIONS SKILLS NECESSARY TO EVALUATE PEOPLE
- TECHNICAL SKILLS TO ASSESS PROGRAM STRENGTHS
- CONCEPTUAL SKILLS TO HANDLE THE DEMANDS OF THEIR POSITIONS
- EFFECTIVE TEACHING AND COMMUNICATION SKILLS

TRAINERS MUST BE KNOWLEDGEABLE

IN THE SUBJECT MATTER

HAZARD COMMUNICATION: TAKING IT ALL IN STRIDE

Vicki P. Sherwood
DuPont Electronic Materials
14 Alexander Drive
RTP, NC 27709

Abstract

OSHA's Hazard Communication Standard has seen its tenth anniversary. Some companies are still struggling with compliance to this performance based standard. Others have established model hazard communication programs. Meanwhile the standard itself gives very little direct guidance as to how to establish a program that meets the letter of the law. Instead OSHA has set general guidelines as to how companies are to meet the intent of the law which is to inform American workers about the chemical hazards they may face on the job and how they can protect themselves. This paper is an attempt to alleviate some of the struggle of compliance by sharing ideas for meeting compliance issues.

The Regulation

One of the most far-reaching of the OSHA regulations is the Hazard Communication Standard, 29 CFR 1910.1200. The standard is intended to ensure workplace safety by providing workers with necessary training and information regarding hazardous chemicals they work with. Originally the standard was enacted to cover Standard Industrial Codes 20 -39 which apply to all manufacturing industries. In August of 1988, OSHA revisited this law and decided that all industries, even non-manufacturing industries, should be covered by the standard. The standard itself is often referred to as a performance based standard--which means OSHA determines the objectives and allows the employer to decide the best way to achieve those objectives. This leaves some flexibility in how the standard is implemented in the workplace.

Hazard Determination

In order to have an effective Hazard Communication Program, accurate determination of the physical and health hazards of chemicals must take place. There are no specific methods to follow for hazard determination. However, a good starting point is OSHA's Table Z, a specific OSHA chemical standard or the American Conference of Governmental Industrial Hygienists (ACGIH) list of Threshold Limit Values (TLV). Appendix B of the Hazard Communication Standard gives criteria for the types of information to review for hazard evaluation. Additionally, Appendix C of the standard lists many excellent references for researching chemical hazards. A few of the references listed are as follows:

• *Condensed Chemical Dictionary*
Van Norstrand Reinhold Co., 135 West 50th Street, New York, NY 10020.

• *The Merck Index: An Encyclopedia of Chemicals and Drugs*
Merck and Company, Inc., 126 E. Lincoln Ave., Rahway, NJ 07065

•*Industrial Hygiene and Toxicology, by F.A. Patty*
John Wiley & Sons, Inc., New York, NY (multivolume set)

• *Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment and Biological Exposure Indices with Intended Changes*
American Conference of Governmental Industrial Hygienists (ACGIH).
6500 Glenway Avenue, Bldg. D-5, Cincinnati, OH 45211.

• *NIOSH Pocket Guide to Chemical Hazards*

NIOSH Pub. No. 85-114.

A good resource not listed in Appendix C of the Hazard Communication Standard for reviewing health hazard studies is:

•*Taber's Cyclopedic Medical Dictionary*
F.A. Davis Company 1915 Arch St., Philadelphia, PA 19103.

Screening Chemical Purchases

Since every chemical that is brought into the workplace must go through hazard evaluation, it is a good idea to keep the responsibility of hazard evaluation within one working group or job function. Having one employee responsible for evaluating the hazards of chemicals will help ensure consistent evaluation. Additionally, chemical purchases should be coordinated through that employee. It is helpful if there is a chemical purchase approval system prior to bringing a chemical into the workplace. Such a system would have checks in place to ensure that the chemical can be handled properly and that the appropriate personal protective equipment is in place or ordered at the same time of the chemical purchase.

At DuPont Electronic Materials in Research Triangle Park, NC, for example, the purchasing agent screens all requisitions for chemicals to insure that a chemical hazard identification approval rating has been assigned by the safety office. This rating is the same rating system that is used on the in-house labeling system and is to be placed on all requisitions for chemicals. As established in the Chemical Purchase Screening Procedure, all employees are made aware that this rating must be assigned before a chemical can be purchased. If a purchase requisition arrives without the required rating the purchasing agent holds the order until the rating is provided. After the chemical is ordered and it arrives at the loading dock, the receiving agent double checks the rating prior to delivering the chemical to the requisitioner of the chemical. If the rating is not available, the shipment is held until the rating is provided.

Labeling

Once a method of evaluating chemical hazards has been established, the hazards must be communicated to the employees who work with or may be exposed to those chemicals. One method that is called for in the Hazard Communication Standard is labeling. The Standard maintains that all containers of hazardous chemicals must be labeled as to the hazard posed by the chemical. There are two types of labels that may be applied.

Shipping Labels. A manufacturer, importer or distributor that ships chemicals must label containers of chemicals. These labels must provide the following information:

- identity of chemical
- identity of manufacturer, distributor or importer
- address of manufacturer, distributor or importer
- physical and health hazards of the chemical
- specific organs or body systems that may be affected

The last item is better known as target organ effects. In most cases, these effects show up only after chronic or long term exposure to a hazardous chemical. Some target organ effects such as hepatotoxins(liver), neurotoxins (nervous system) and nephrotoxins (kidneys) are described in Appendix A of the Hazard Communication Standard.

In-house labels. The shipping label must remain intact after the chemical container has reached its destination. In addition to this, there may be reason to add in-house

labels to containers of hazardous chemicals. An example when this is appropriate is when the contents of a larger container are dispensed into smaller containers used at individual workstations. If the container of the hazardous chemical does not remain in immediate control of the person who filled it then it must be labeled as to the hazards of the chemical it contains. If the secondary container remains in control of the person who filled it, the container does not have to be labeled. However, the secondary container rule sometimes receives wide interpretation from OSHA inspectors. It is prudent to label all secondary containers with in-house labels.

Material Safety Data Sheets

Every hazardous chemical present at the workplace must have an up-to-date material safety data sheet (MSDS) to provide employees with additional hazard information beyond chemical labeling. Employers need to know that these MSDS's must be readily available. This may be accomplished by keeping notebooks of MSDS's throughout the workplace or even a centralized unlocked file. Some larger corporations keep MSDS's in an electronic database accessible at any computer terminal. Providing MSDS's through electronic means is acceptable by OSHA. However, it is advisable to keep paper copies of all MSDS's handy in case of power outages or computer glitches.

The Chemical Inventory

Another requirement of the Hazard Communication Standard is the hazardous chemicals inventory. This inventory should contain a listing of all the materials and chemicals in the workplace that are considered hazardous. Like MSDS's, this inventory must be kept up-to-date and available to employees. This list was intended to be included in the written hazard communication program. However, some employers may find that their list is exceedingly long and difficult to manage within the written program. To overcome some of the struggle, some companies may find it easier to keep the inventory in an electronic database accessible by all employees. Other companies may choose to station personal computers around the workplace with the inventory in an easily accessible program. In cases where the inventory is kept electronically, instructions on how to access the inventory should be posted nearby or within the written Hazard Communication Program.

Another positive issue toward informing employees about the hazards of the chemicals in the workplace, the chemical inventory can work for the employer in many ways. At DuPont Electronic Materials for example, the hazardous chemicals list includes the hazard identification ratings for the in-house labels of approved chemicals. Any employee can access the list to determine which label to apply to chemical containers. The chemical inventory is also used as a basis for reporting to local emergency planning committees.

Training and Information

The most vital part of the Hazard Communication Standard is the training and information requirement. Training is the main tool for disseminating the elements of the Hazard Communication Program to the employees. Training is required at or before an employee's initial work assignment. The standard also requires retraining any time a new hazard is introduced to the workplace. It is also prudent to have retraining on an annual basis. Further, some companies have found mini training sessions on an on-going basis very helpful.

Among the elements of information and training required by the standard are:

- the requirements of the Hazard Communication Standard

- any operations in the work area where hazardous chemicals are present
- the location of the written Hazard Communication Program
- methods and observations used to detect the presence or release of hazardous chemicals
- physical and health hazards of chemicals in the workplace
- measures employees can take to protect themselves
- details of the written Hazard Communication Program
- hazards of non-routine tasks
- hazards posed to and by contract employees

As well as training on the location of the MSDS's, the employer must also train the employees on how to read the MSDS's. This is key to understanding the hazards that chemicals possess and how to protect themselves. MSDS's usually contain helpful information on personal protective equipment (PPE). Some, however, lack specific information on assignment of PPE based different usage or volumes of the chemical. Many MSDS's are written with tank car or drum quantities in mind. The PPE listed on the MSDS may not always be appropriate for the application used in the workplace.

One method of training employees on the proper selection of PPE is by developing a spreadsheet or matrix listing the chemical, its different uses and volumes and the PPE assigned for specific tasks. If the PPE is realistic for the job and selection is made easy for employees, its acceptance and proper use could increase.

Another avenue for training and information dissemination is the Standard Operating Procedure (SOP). The SOP can be used to reiterate hazards of chemicals associated with a process and promote use of proper personal protective equipment.

Additional aspects that must be covered during training are the hazards present during non-routine tasks. Good examples of non-routine tasks are tank cleaning or line flushing in preparation for maintenance work. Whether information about the specific tasks takes place in a scheduled training session or if it will occur just prior to undertaking a non-routine task, it must be covered.

Finally, when planning training it is important to consider the hazards posed to employees by contract employees. Additionally, when considering contract employees, it's important to inform them of the hazards they may face while working in the facility. Some of this information can be included in a written contract. However, it's also a good idea to invite contractors and subcontractors to hazard communication training sessions.

Written Hazard Communication Program

Besides training, the most important requirement of the Hazard Communication Standard is the written hazard communication program that pulls together all of the required elements of the standard. This document, written by the employer, is intended to spell out how the employer intends to meet all of the requirements of the Hazard Communication Standard. This important document needs to be kept up-to-date. An out-of-date compliance program can pose safety risks and lead to fines if discovered by OSHA. Some facilities place their programs on a one to two year cycle for review. The program should be reviewed or revised when organization changes occur at the workplace. This is particularly important if individuals' names or positions are documented within the program as having responsibility for some aspect of compliance.

Although there may be very good intentions written into the hazard communication program, anything put in writing that is not fulfilled can be considered as a willful violation and usually carries a heavier penalty should there be a citation. This paper was intended to be an overview of the federal

Hazard Communication Standard. To ensure accurate compliance, requirements of local and state regulations that may be stricter than the federal standard should be reviewed.

References

29 CFR 1910.1200 Hazard Communication

Weinstock, Matthew P., "Hazard Communication: Clearing Up the Confusion," Occupational Hazards, Vol 55, Oct 1993, pp 35-39.

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American Electroplaters &
Surface Finishers Society, Inc.

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CONTROL OF HAZARDOUS ENERGY
Lockout/Tagout/Test

Bob Napolitano, CEF

Hi-G Company
A Subsidiary of Nytronics, Inc.
85 Nutmeg Road
South Windsor, CT 06074

Control of Hazardous Energy Lockout/Tagout/Test

Bob Napolitano, CEF

Introduction

On September 1, 1989 the Occupational Safety and Health Administration (OSHA) issued the final rule on the control of Hazardous Energy commonly referred to as Lockout/Tagout. This standard establishes safeguards to protect employees from hazardous energy releases while they are performing service or maintenance on machines and equipment. The standard covers proper shutdown procedures, employee training and inspection practices.

We need to make sure our facilities have complied with the Lockout/Tagout Standard to avoid fines and prevent injuries. We can learn how to implement requirements for establishing a energy control program, employee training and periodic review.

Scope and Application

The Lockout/Tagout Standard (29 CFR 1910.147) requires all general industrial facilities, including both captive and job electroplating facilities, to have a written program covering documented energy control procedures, employee training and periodic inspection of the procedures. The key element of the program is the procedure for servicing and maintenance of machines and equipment in which the unexpected start up or the release of stored energy could cause injury to employees or contractors.

Exception

The standard does not apply to servicing and maintenance of cord and plug connected electrical equipment, or during hot tap operations on pressurized pipelines where continuity of service is essential and shutdown of the system in impractical such as on gas, steam or water lines.

Requirements of the Standard

Energy Control Program

The lockout/tagout standard requires the employer to establish an energy control program that includes: documented energy control procedures; employee training program; and periodic inspections of the procedures. Employers must establish a program to ensure that machines and equipment are isolated and inoperative before any employee performs servicing or maintenance.

Employers are given flexibility to develop a program and procedures that meet the needs of their specific work place, machinery and equipment.

Energy Control Procedure

The standard requires written procedures to identify the information that authorized employees must know in order to control hazardous energy during servicing or maintenance. A single energy control procedure may be sufficient if the information is the same for similar machinery or equipment. If other conditions exist such as multiple energy sources, different connecting means, or specific shut down sequence. The employer must develop separate energy control procedures to protect employees.

Maintenance procedures which mandate the use of the lockout/tagout system could include the following:

Equipment lubrication
Unjamming equipment
Equipment installation/construction
Equipment adjustments
Electrical repairs

Equipment cleaning
Tank cleaning
Equipment inspections
Equipment modifications
Tool changes
General maintenance activities

The procedure must include the following steps:

1. Preparing for shutdown, notification of employees
2. Shutting down the machine(s) or equipment
3. Isolating the machine or equipment from the energy sources
4. Applying lockout and/or tagout devices to the energy isolating devices
5. Safely releasing all potentially stored or residual energy
6. Verifying the isolation of the machine or equipment prior to the start of servicing or maintenance work

Testing for ZERO Energy

To make sure that there is zero energy, the authorized employee tries to turn the equipment on. If it comes on, the steps in the isolation procedure must be completed again until the machine doesn't energize.

Examples of the Control of Stored Energy

Install ground wires
Relieve trapped pressure
Release tension on springs or block movement
Block hydraulic and pneumatic systems which could move
Block or brace to prevent falling objects
Drain process piping and close valves
Dissipate extreme temperatures

Removal of Locks and Tags

In addition, certain steps must be taken prior to reenergizing and restarting equipment after servicing is completed including:

1. Assuring that the machines or equipment is operationally intact;
2. Assuring that lockout/tagout devices are removed from each energy isolating device by the employee who applied the device;
3. Notifying affected employees that lockout/tagout devices have been removed, assuring all employees are safely positioned or out of the way;
4. Make sure that locks or tags are removed only by those employees who attached them.

In the event this is not possible, then the device may be removed under the direction of the employer who adheres to the specific procedures outlined in the standard.

Testing or Positioning of Machines

OSHA allows the temporary removal of locks or tags and the reenergization of the machine or equipment only when necessary under special conditions. The following steps must be followed:

1. Clear the machine of tools and materials.
2. Remove employees from the machine.
3. Remove the lockout or tagout device.
4. Energize and proceed with testing or positioning.
5. Deenergize all systems, isolate the machine from the energy source and reapply lockout or tagout devices.

Energy Isolating Devices

The employer's primary tool for providing employee protection is the energy isolating device to which all locks and tags are attached. This device guards against the accidental start up or energizing of equipment during servicing or maintenance. There are two types of energy isolating devices:

the preferred are those capable of being locked out, and the least preferred are those that cannot be locked out.

When energy isolating devices cannot be locked out the employer must use tagout. The employer may chose to modify or replace the device to make it capable of being locked out. When using tagout the employer must comply with all tagout provisions of the standard and provide additional training to employees on the limitations of the tagout system.

Tags are essentially warning devices and do not provide the physical restraint of a lock. Furthermore, they provide a false sense of security.

If the energy isolating device is lockable, the employer will use locks unless they can prove that the use of tags would provide protection at least as effective as locks and would assure full employee protection. Full employee protection would require tagging and the additional work associated with removing a valve handle or pulling a circuit breaker or blocking a control switch.

Equipment Must Be Upgraded

When an employer makes a major replacement, repair, renovations, or modifications of machines or equipment, and when new equipment is installed, the ability to lockout all hazardous energy must be available.

Lockout/Tagout Devices

When attached to an energy isolating device, both lockout and tagout devices are tools that the employer can use in accordance with the requirements of the standard to help protect employees from hazardous energy. The lockout device provides protection by holding the energy isolating device in the safe position, thus preventing the machine or equipment from becoming energized. The tagout device does so by identifying the energy isolating device as a source of potential danger; and an indicator that the equipment may not be operated until the tagout device is removed.

Steps to Compliance

Step 1. Conduct a Survey

Use area supervisors, group leaders, foremen and members of the safety committee to conduct the basic survey and gather data. Tailor the survey form to the facility's system of identifying the machine or equipment. They will collect data on the type of energy and energy isolating devices. The data collected might be similar to the following:

Machine: XYZ ID# 123
Location: Machine Shop
Energy Types: electrical and pneumatic
Energy Isolation Device(s): electrical disconnect box and valves for pneumatic system.

Step 2. Compile the Data

Once the survey has been completed, then the data should be compiled. The survey data will determine the Energy Control Procedure(s), identify lockout/tagout devices, and determine if single or multiple procedures are required for each piece of equipment. Once identified these procedures must be written and incorporated into the general document governing lockout/tagout.

Step 3. Train the Employees

Employee Training and Recordkeeping

The employer must provide effective initial training and retraining as necessary and must certify that such training has been given to all employees covered by the standard. The certification must contain the name and dates of training for each

employee.

For the purposes of the standard, there are three types of employees: authorized, affected and other. The amount and kind of training is based upon the relationship of the employee's job to the machine and the degree of knowledge relevant to hazardous energy that the employee must possess. Authorized employees are those charged with the responsibility for implementing the energy control procedures and performing the servicing or maintenance to the lockout/tagout equipment. Generally these employees are maintenance personnel and area supervisors.

Training for authorized employees must include, at a minimum, the following:

1. details about the type and magnitude of the hazardous energy sources present in the workplace, and (For example, electrical, hydraulic, pneumatic, heat or cold, stored residual energy.)

2. the methods and means necessary to isolate and control those energy sources such as locks, blocks, etc.

Because an "affected" employee is not the person who is performing the servicing or maintenance, that employee's responsibilities under the energy control program are simple: Whenever there is a lockout or tagout device in place on an energy-isolating device, the affected employee leaves it alone and does not attempt to operate the equipment.

Training programs must ensure that all employees understand the purpose, function, and restrictions of the energy control program and that authorized employees possess the knowledge and skill necessary for the safe application, use, and removal of energy controls.

Retraining Required

Employees must be retrained whenever there is a change in job assignment or new equipment is added. In addition, if the employer has a reason to believe there are deviations from proper lockout/tagout procedures, then retraining must be implemented. Along with the issue of retraining goes discipline practices for not following lockout/tagout procedure. If employees do not follow the instructions and training, then the employer must have some vehicle for disciplinary measures. During an OSHA investigation of a recent fatality, employees told the inspector that they had lockout/tagout training but the employer did not make them use it. Statements such as this can lead to increased employer liability.

Periodic Inspections and Recordkeeping

Periodic inspections must be performed at least annually to assure the energy control procedures continue to be implemented properly and that the employees are familiar with their responsibilities under the program. After performing the inspection, the employer must certify by identifying the machine or equipment, date of inspection, employees included and the name of the inspector. The content of the inspection must include a review of the authorized employees responsibilities and the capabilities of the lockout and tagout devices.

Outside Contractors

The employer and the outside contractor must communicate with each other concerning lockout or tagout procedures before work can begin.

Group Lockout or Tagout

During all group lockout/tagout operations each employee shall be protected by the application of

his or her personal lockout or tagout device.

Shift Changes

During shift changes there must be procedures to provide continuity from one shift to the next concerning lockout or tagout protection.

Conclusion

We need to make sure our facilities have complied with the Lockout/Tagout Standard to avoid fines and prevent senseless injuries. We can learn to comply with the requirements for establishing a energy control program, employee training and periodic review by conducting the survey and identifying the elements of the program.

PROCESS SAFETY MANAGEMENT

OF

HIGHLY HAZARDOUS MATERIALS

29 CFR 1910.119

By

Robert F. Lee, CEF, REA
Manager Corporate Environmental
and Safety Engineering Department

Rogers Corporation

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INTRODUCTION

The prime objective of the Process Safety Management standard is to prevent the uncontrolled release of hazardous chemicals into either the work place where employees can be exposed or the environment where the general public can be affected. A sound and well engineered Process Safety Management Plan for hazardous chemicals if properly followed can and will greatly reduce the risk of uncontrolled releases and subsequent human exposure potentials. A proper Process Safety Management Plan will incorporate risk evaluations encompassing process development, design, implementation, operation, maintenance, and modification or dismantlement under both "normal" manufacturing conditions and under rationally selected "emergency" conditions.

This standard targets a number of highly hazardous chemicals used by industry that have potential for catastrophic impact if they are uncontrollably released. Additionally, the EPA under the auspices of the Clean Air Act, Clean Water Act, and RCRA also has requirements for industry to prevent the uncontrolled release of these and other chemicals into the environment. Thus, it makes considerable sense to develop your Process Safety Management Plan to comply to both OSHA and EPA mandates.

Before going any further, it is important to define the regulatory definition of what constitutes a PROCESS. "Process means any activity involving a highly hazardous chemical including any use, storage, manufacturing, handling, or the on-site movement of such chemicals, or combination of these activities. For purposes of this definition, any group of vessels which are interconnected and separate vessels which are located such that highly hazardous chemical could be involved in a potential release shall be considered a single process."

29 CFR 1910.119 (a) APPLICABILITY

Who Is Covered?

A. Any operation that utilizes, at or above the threshold quantities, any of the chemicals listed in the attached Appendix "I".

B. Any operation that uses or processes more than 10,000 pounds (4535.9 kg) of flammable liquid or gas, as determined under 29 CFR 1910.1200(c), except hydrocarbon fuel used for work place consumption as a fuel that is not part of the process containing another listed highly hazardous chemical, or flammable liquids that are stored in atmospheric tanks or that are transferred below their normal boiling point without chilling or refrigeration.

C. Any operation that manufactures or otherwise processes explosive or pyrotechnic devices.

Who Is Exempt?

D. Any retail establishment.

E. Any oil or gas drilling or servicing organization.

F. Any normally unoccupied remote facility.

29 CFR 1910.119 (b) DEFINITIONS

See Appendix "II".

29 CFR 1910.119 (c) EMPLOYEE PARTICIPATION

This section of the standard is very similar to some requirements of the Clean Air Act Amendments; thus, one comprehensive plan will meet both needs. Basically, this standard states that employers must develop a written plan with employee consultation and that plan must provide employee access to process hazard analyses and to all other information used to develop plan.

29 CFR 1910.119 (d) PROCESS SAFETY INFORMATION

This requirement states that a written compilation of process safety information must be done before conducting any process hazard analysis. This information will enable the employer and employee to identify and understand the hazards posed by the process involving highly hazardous chemicals. This compilation shall include information on the hazards, technology and equipment used, or produced, in the processing of highly hazardous chemicals. This compilation shall include the following information, at a minimum:

A. Hazards

1. Toxicity data on chemicals used or produced.
2. OSHA Permissible Exposure Limits (PEL's) for these chemicals.
3. Physical properties of these chemicals.
4. Reactivity data for these chemicals.
5. Corrosivity data for these chemicals.
6. Thermal and chemical stability data for these chemicals.
7. Data on hazards associated with inadvertent mixing of these chemicals and potential incompatibility reactions.

NOTE: Properly prepared Material Safety Data Sheets (MSDS's) containing the above information may be used to comply to this requirement.

B. Technology

1. Simplified flow diagram of process.
2. Process chemistry or chemistries.
3. Maximum intended inventory of chemicals for use in process.
4. Safe upper/lower limits for process temperatures, pressures, flows and/or compositions.
5. An evaluation of the consequences of deviations from normal operation upon safety and health considerations.

C. Equipment

1. Materials of construction.
2. Instrument and piping schematics.
3. Electrical classification.
4. Layout of relief systems and a description of their function in the process.
5. Exhaust and ventilation system schematics and specifications.
6. Identification of design codes and standards employed.
7. Material and energy balances for processes installed after May 26, 1992.
8. Safety systems employed (such as interlocks, detectors or suppression devices.
9. Documentation: Employer to document that equipment complies with recognized and generally accepted engineering practices and that for equipment designed and installed to codes and standards no longer in effect that such equipment is designed, maintained, inspected, tested, and operated in a safe manner.

29 CFR 1910.119 (e) PROCESS HAZARD ANALYSIS

Employers are required to do an initial process safety analysis on processes covered under this standard. That analysis shall be appropriate to the nature of the process used and shall identify, evaluate, and control the hazards involved. Employers are to prioritize processes according to hazard potential and set a schedule for completing the hazard analyses according to the following time frames:

Schedule

1. No less than 25% of initial process hazard analyses to be completed by May 26, 1994.
2. No less than 50% by May 26, 1995.
3. No less than 75% by May 26, 1996.
4. All processes shall be done by May 26, 1997.

Methodology

The employer is to use one or more of the following methodologies for this analysis:

1. What-if analysis.
2. Checklists.
3. Combination what-if and checklist analysis.
4. Hazard and operability study.
5. Fault tree analysis.
6. Any equivalent method.

NOTE: The key is that whatever methodology used must be formally written and easily understood by employees.

Process Hazard Analysis

The actual process hazard analysis must address the following:

1. The hazards of the process.
2. A written documentation and evaluation of any previous incident with the process that had potential for catastrophic consequences in the work place.
3. Description of engineering and administrative controls in place on the process and an explanation of their use and recognition.
4. A discussion of the consequences of failure of either engineering or administrative controls.
5. Facility siting (layout showing fire and safety equipment locations, safe havens, evacuation routes, location of hazardous chemical storage and usage, etc.).
6. Human factors.
7. A qualitative study of the varying range of potential safety and health effects, that could ensue following the failure of controls, upon employees in the work place.

Process Hazard Analysis Team

All process hazard analyses shall be conducted by a team with experience in engineering and process operations. At least one employee with experience and knowledge of the process shall be included, and at least one member of the team must be familiar with the methodology of process hazard analysis.

Process Analysis Deficiencies

Employer to act promptly to correct any deficiencies found as a result of these process hazard analyses. Document action taken and date completed, communicate these actions to operating, maintenance and administrative employees whose work assignments in the process area may be affected.

Process Hazard Aaalysis Frequency

Each initial, or follow-on, process hazard analysis done must be updated at least every five (5) years by a qualified team.

Record Retention

All process hazard analyses, revisions and updates must be kept for the life of the process; this also includes all documentation of modifications and maintenance performed on the process.

29 CFR 1910.119 (f) OPERATING PROCEDURES

Employers are required to develop and implement clearly written operational instructions, for employees, for all processes covered by this standard. These instructions shall include the following at a minimum:

Steps For Each Phase Of Operation

1. Normal operations sequence including normal start-up.
2. Temporary, or modified, operations sequence.
3. Emergency shutdown procedure, with clear assignment of responsibility to qualified operators.
4. Emergency operations sequence, if appropriate.
5. Normal shutdown procedures.
6. Start-up sequence after emergency shutdown or changeover.

Operating Limits

1. Consequences of process deviation.
2. Requirements to avoid or correct probable deviations.

Safety and Health Issues

1. Properties of, and hazards with, use of process chemicals.
2. Precautions needed to prevent exposure such as engineering controls, administrative controls and personal protective equipment.
3. Response procedures in the advent of physical contact or airborne exposure to chemicals.
4. Quality control procedures for raw materials and inventory management.
5. Any unique or special hazards associated with process.

Safety Controls

1. A written plan for calibration and testing of safety controls and alarms on a scheduled basis.

2. Current operating procedures shall be readily available to employees who work or maintain process.

3. Operating procedures shall be reviewed as necessary to insure they reflect current operations sequence and employer is to certify annually that they are accurate.

4. Safe work practices are to be developed to control hazards during operations and maintenance such as LOCKOUT/TAGOUT, CONFINED SPACE ENTRY, opening process equipment or piping, and control of process area access by maintenance, contractor, laboratory or other support personnel.

29 CFR 1910.119 (g) TRAINING

Initial Training

Each employee who works with a covered process shall be trained in the safe work practices, operational procedures, health and safety hazards, and emergency operations. This includes current workers and newly assigned workers before they actually start assignment in the process area.

Refresher Training

This refresher training should be given whenever necessary and at a frequency not to be less than every three (3) years.

Training Documentation

The employer is responsible to maintain a record for each applicable employee that identifies the employee, establishes the dates of various training sessions given and explains the method used to determine that the employee understood the training.

29 CFR 1910.119 (h) CONTRACTORS

Outside Contractors: (Employer Responsibilities)

This standard holds the employer responsible for certain aspects of these requirements, such as evaluating the contractor's safety performance and programs, notifying contractor's employees of known fire/explosion/toxic release hazards associated with contractor's work on the process, informing contractor's employees of employer's Emergency Action Plan (discussed later), establish safe work practices for contractor's employees that control their entrance/ presence/exit from the process area, periodically evaluate contractor's employees compliance to their responsibilities under this standard, and maintain a contract employee log of accidents and illness with their work in the process area.

Outside Contractors: (Contractor Responsibilities)

This standard requires the contractor, in these situations, to insure that all their employees are trained in the work practices necessary to perform work in the process area, to insure that their employees are instructed in the known potential hazards associated with the process area as well as provisions of the employer's Emergency Action Plan, to document each employee's training record and verify that employees understand content thereof, to insure that all their employees follow all applicable safety rules of the facility in which they are working, and to notify employer of any unique hazards presented by the contractor's work or of any hazards found by contractor's employees.

29 CFR 1910.119 (i) PRE-START-UP PROCESS SAFETY REVIEW

The employer is required to conduct and document a pre-start-up safety review for new process installations and following significant process modification that require a change in process safety information. This review conducted before introduction of highly hazardous chemical(s) to the process, shall confirm the following:

1. Construction and equipment installation is according to design specifications.

2. Safety, operations, maintenance, and emergency procedures are in place and are adequate.

3. A Process Hazard Analysis has been done for the process and that any outstanding corrective recommendations have been resolved or implemented before start-up.

29 CFR 1910.119 (j) MECHANICAL INTEGRITY

This section applies only to Pressure Vessels, Storage Tanks, Piping Systems (including Valves), Relief and Venting Systems, Emergency Shutdown Systems, Controls (including Alarms, Interlocks, Monitoring Devices and Sensors), and Pumps.

Procedures:

Employer shall establish and implement written procedures for the on-going maintenance and integrity of process equipment.

Training

Employer shall insure each maintenance employee is trained in an overview of the process and it's hazards and in the procedures needed to perform tasks to assure they are done in a safe manner.

Inspection and Testing

This standard requires the following actions by the employer:

1. Inspection and testing procedures shall follow accepted and recognized good engineering principles.

2. Frequency of inspections and testing shall be in accordance with manufacturer's recommendations, recognized engineering practices and/or more frequently if determined to be necessary by prior operational history.

3. Each inspection and test shall be documented with the date of the action, the name of the employee doing the action, the serial number or other identifier of the equipment action was done on or with, a description of the action done and the results of the inspection or test.

Equipment Deficiencies

The employer shall correct deficiencies that are outside of acceptable process limits, as defined by the Process Safety Information, before further use or in a safe and timely manner when appropriate means are employed to assure continued safe operation.

Quality Assurance

The employer shall insure that during construction of new plants and installations of equipment that they be suitable for intended process use. Appropriate checks and inspections shall be undertaken to insure that equipment is installed correctly and that all components are as specified in the design criteria. Maintenance materials, spare parts, and equipment must be suitable for the process they are intended for.

29 CFR 1910.119 (k) HOT WORK PERMIT

The employer shall institute a Hot Work Permit requirement and issue said permit for hot work done on or near covered processes. That permit shall document that the Fire Prevention and Protection requirements of 29 CFR 1910.252(a) have been implemented prior to commencement of hot work. That permit shall have the date of permit issuance, identify the equipment or object that hot work is to be done on and the name of the issuer. That permit is to be retained until hot work is completed.

29 CFR 1910.119 (l) MANAGEMENT OF CHANGE

Employer is to establish and implement a written procedure for the management of changes on the process or equipment associated with said process. That procedure is to address the following:

1. The technical basis for said change.
2. The impact of said change upon safety and health.
3. Modifications necessary to existing operations procedures.
4. Necessary time frame for said change.
5. Authorization(s) requirement(s) for the change.

Employees and contractors affected by said change shall be informed of and trained in the change(s) prior to start-up of the changed process or part thereof. If said change affects the Process Hazard Analysis data, such information shall be immediately updated.

29 CFR 1910.119 (m) INCIDENT INVESTIGATION

The employer shall investigate each incident which resulted in, or could have reasonably resulted in, a catastrophic release of highly hazardous chemical(s) in the work place. This investigation shall be initiated within 48 hours of it's occurrence. The incident investigation team shall have at least one person knowledgeable in the process, including a contract employee if said incident involved contract work, as well as other knowledgeable persons with relevant experience. The team will issue an incident report at the conclusion of the investigation, and that report shall contain the following information at a minimum:

INCIDENT REPORT

1. Date of incident.
2. Date investigation began.
3. A description of incident.
4. The factor(s) contributing to the incident.
5. Appropriate recommendations to correct and prevent a recurrence of incidence.

The employer shall promptly address and resolve the investigation report findings and recommendations. This report is to be reviewed with all affected employees and contractor employees where applicable.

RECORD RETENTION

Incident investigation reports shall be retained for at least five years.

29 CFR 1910.119 (n) EMERGENCY PLANNING AND RESPONSE

Employer shall prepare and implement an Emergency Action Plan for the entire facility in accordance with the requirements of 29 CFR 1910.38(a). Said plan shall include procedures for dealing with small releases. Additionally, some employers may be required to meet the hazardous waste and emergency response requirements of 29 CFR 1910.120(a), (p), and (q).

29 CFR 1910.119 (o) COMPLIANCE AUDITS

Employer shall certify that they have evaluated their compliance to the requirements of this standard at least every three (3) years. This audit must be conducted by at least one individual knowledgeable in the process. This audit must result in the issuance of a report.

Employer is responsible to insure that appropriate action was taken to correct any noted deficiencies, and that such action is documented. Employer shall retain the two most recent compliance reports.

29 CFR 1910.119 (p) TRADE SECRETS

This standard requires the employer to make available to all individuals involved with, or affected by the standard, all relevant information necessary to insure compliance. Nothing in this standard shall preclude the employer from requiring persons to whom information is released to enter into confidentiality agreements not to disclose said information as set forth in 29 CFR 1910.1200.

As set forth in 29 CFR 1910.1200(i)(1) through 1910.1200(i)(12), employees and their representatives shall have access to trade secret information contained in the Process Hazard Analysis and other documents required to be developed under this standard.

APPENDIX I - Highly Hazardous Chemicals, Toxics & Reactives
(Reference: 29 CFR 1910.119 Appendix A)

CHEMICAL NAME	CAS*	TQ**
Acetaldehyde	75-07-0	2500
Acrolein (2-Propenal)	107-02-8	150
Acrylyl Chloride	814-68-6	250
Allyl Chloride	107-05-1	1000
Allylamine	107-11-9	1000
Alkylaluminms	Varies	5000
Ammonia, Anhydrous	7664-41-7	10000
Ammonia Solutions (>44% Ammonia by Wt.)	7664-41-7	15000
Ammonium Perchlorate	7790-98-9	7500
Ammonium Permanganate	7787-36-2	7500
Arsine (Arsenic Hydride)	7784-42-1	100
Bis(Chloromethyl) Ether	542-88-1	100
Boron Trichloride	10294-34-5	2500
Boron Trifluoride	7637-07-2	250
Bromine	7726-95-6	1500
Bromine Chloride	13863-41-7	1500
Bromine Pentafluoride	7789-30-2	2500
Bromine Trifluoride	7787-71-5	15000
3-Bromopropyne (Propargyl Bromide)	106-96-7	100
Butyl Hydroperoxide (Tertiary)	75-91-2	5000
Butyl Perbenzoate (Tertiary)	614-45-9	7500
Carbonyl Chloride (Phosgene)	75-44-5	100
Carbonyl Fluoride	353-50-4	2500
Cellulose Nitrate (Conc. >12.5% N)	9004-70-0	2500
Chlorine	7782-50-5	1500
Chlorine Dioxide	10049-04-4	1000
Chlorine Pentafluoride	13637-63-3	1000
Chlorine Trifluoride	7790-91-2	1000
Chlorodiethylaluminum (Diethylaluminum Chloride)	96-10-6	5000
1-Chloro-2,4-Dinitrobenzene	97-00-7	5000
Chloromethyl Methyl Ether	107-30-2	500
Chloropicrin	76-06-2	500
Chloropicrin & Methyl Bromide Mixture	None	1500
Chloropicrin & Methyl Chloride Mixture	None	1500
Cumene Hydroperoxide	80-15-9	5000
Cyanogen	460-19-5	2500
Cyanogen Chloride	506-77-4	500
Cyanuric Fluoride	675-14-9	100
Diacetyl Peroxide (Conc. >70%)	110-22-5	5000
Diazomethane	334-88-3	500
Dibenzoyl Peroxide	94-36-0	7500
Diborane	19287-45-7	100
Dibutyl Peroxide (Tertiary)	110-05-4	5000
Dichloro Acetylene	7572-29-4	250
Dichlorosilane	4109-96-0	2500

Diethylzinc	557-20-0	10000
Diisopropyl Peroxydicarbonate	105-64-6	7500
Dilauroyl Peroxide	105-74-8	7500
Dimethyldichlorosilane	75-78-5	1000
Dimethylhydrazine, 1,1-	57-14-7	1000
Dimethylamine, Anhydrous	124-40-3	2500
2,4-Dinitroaniline	97-02-9	5000
Ethyl Methyl Ketone Peroxide (Methyl Ethyl Ketone Peroxide) (Conc. >60%)	1338-23-4	5000
Ethyl Nitrite	109-95-5	5000
Ethylamine	75-04-7	7500
Ethylene Fluorohydrin	371-62-0	100
Ethylene Oxide	75-21-8	5000
Ethyleneimine	151-56-4	1000
Fluorine	7782-41-4	1000
Formaldehyde (Formalin)	50-00-0	1000
Furan	110-00-9	500
Hexafluoroacetone	684-16-2	5000
Hydrochloric Acid, Anhydrous	7647-01-0	5000
Hydrofluoric Acid, Anhydrous	7664-39-3	1000
Hydrogen Bromide	10035-10-6	5000
Hydrogen Chloride	7647-01-0	5000
Hydrogen Cyanide, Anhydrous	74-90-8	1000
Hydrogen Fluoride	7664-39-3	1000
Hydrogen Peroxide (>52% by Weight)	7722-84-1	7500
Hydrogen Selenide	7783-07-5	150
Hydrogen Sulfide	7783-06-4	1500
Hydroxylamine	7803-49-8	2500
Iron, Pentacarbonyl	13463-40-6	250
Isopropylamine	75-31-0	5000
Ketene	463-51-4	100
Methacrylaldehyde	78-85-3	1000
Methacryloyl Chloride	920-46-7	150
Methacryloyloxyethyl Isocyanate	30674-80-7	100
Methyl Acrylonitrile	126-98-7	250
Methylamine, Anhydrous	74-89-5	1000
Methyl Bromide	74-83-9	2500
Methyl Chloride	74-87-3	15000
Methyl Chloroformate	79-22-1	500
Methyl Ethyl Ketone Peroxide (Ethyl Methyl Ketone Peroxide) (Conc. >60%)	1338-23-4	5000
Methyl Fluoroacetate	453-18-9	100
Methyl Fluorosulfate	412-20-5	100
Methyl Hydrazine	60-34-4	100
Methyl Iodide	74-88-4	7500
Methyl Isocyanate	624-83-9	250
Methyl Mercaptan	74-93-1	5000
Methyl Vinyl Ketone	79-84-4	100
Methyltrichlorosilane	75-79-6	500

Nickel Carbonyl (Nickel Tetracarbonyl)	13463-39-3	150
Nitric Acid (>94.5% by Weight)	7697-37-2	500
Nitric Oxide	10102-43-9	250
Nitroaniline (Para Nitroaniline)	100-01-6	5000
Nitromethane	75-52-5	2500
Nitrogen Dioxide	10102-44-0	250
Nitrogen Oxides (NO, NO2, N2O4, N2O3)	10102-44-0	250
Nitrogen Tetroxide (Nitrogen Peroxide)	10544-72-6	250
Nitrogen Trifluoride	7783-54-2	5000
Nitrogen Trioxide	10544-73-7	250
Oleum (Fuming Sulfuric Acid) (Conc. >65% by Weight)	8014-94-7	1000
Osmium Tetroxide	20816-12-0	100
Oxygen Difluoride (Fluorine Monoxide)	7783-41-7	100
Ozone	10028-15-6	100
Pentaborane	19624-22-7	100
Peracetic Acid (Peroxyacetic Acid) (Conc. >60% Acetic Acid)	79-21-0	1000
Perchloric Acid (Conc. >60% by Weight)	7601-90-3	5000
Perchloromethyl Mercaptan	594-42-3	150
Perchloryl Fluoride	7616-94-6	5000
Peroxyacetic Acid (Peracetic Acid) (Conc. >60% Acetic Acid)	79-21-0	1000
Phosgene (Carbonyl Chloride)	75-44-5	100
Phosphine (Hydrogen Phosphide)	7803-51-2	100
Phosphorous Oxychloride (Phosphoryl Chloride)	10025-87-3	1000
Phosphorous Trichloride	7719-12-2	1000
Phosphoryl Chloride (Phosphorous Oxychloride)	10025-87-3	1000
Propargyl Bromide	106-96-7	100
Propyl Nitrate	627-03-4	2500
Sarin	107-44-8	100
Selenium Hexafluoride	7783-79-1	1000
Stibine (Antimony Hydride)	7803-52-3	500
Sulfur Dioxide (Liquid)	7446-09-5	1000
Sulfur Pentafluoride	5714-22-7	250
Sulfur Tetrafluoride	7783-60-0	250
Sulfur Trioxide (Sulfuric Anhydride)	7446-11-9	1000
Sulfuric Anhydride (Sulfur Trioxide)	7446-11-9	1000
Tellurium Hexafluoride	7783-80-4	250
Tetrafluoroethylene	116-14-3	5000
Tetrafluorohydrazine	10036-47-2	5000
Tetramethyl Lead	75-74-1	1000
Thionyl Chloride	7719-09-7	250
Trichloro (Chloromethyl) Silane	1558-25-4	100
Trichloro (Dichlorophenyl) Silane	27137-85-5	2500

Trichlorosilane	10025-78-2	5000
Trifluorochloroethylene	79-38-9	10000
Trimethoxysilane	2487-90-3	1500

* = Chemical Abstract Service Number ** = In Pounds

APPENDIX II - Definitions

1. ATMOSPHERIC TANK. A storage tank which is designed to operate at pressures from atmospheric through 0.5 p.s.i.g. (Pounds per square inch guage).

BOILING POINT. The boiling point of a liquid at a pressure of 14.7 p.s.i.a. (Pounds per square inch absolute). For materials where this is unknown, or for mixtures without a constant boiling point, ASTM D-86-62, Standard Method for Petroleum Product Distillation may be used.

CATASTROPHIC RELEASE. A major uncontrolled emission, fire or explosion, involving one or more highly hazardous chemicals, that presents a serious danger to employees in the work place.

FACILITY. The buildings, containers or equipment that contain the process.

HIGHLY HAZARDOUS CHEMICAL. A substance possessing toxic, reactive, flammable or explosive properties that is listed in Appendix I and meets the threshold quantity amount.

HOT WORK. Work that involves electric or gas welding, cutting, brazing or similar flame or spark producing operations.

NORMALLY UNOCCUPIED REMOTE FACILITY. A site that is operated, maintained or serviced by employees who visit its operation and perform needed work only periodically. No employees are permanently stationed at the facility. Facilities meeting this definition must be geographically remote from all other buildings, processes and/or persons.

TRADE SECRET. Any confidential formula, pattern, process, device, information or compilation of data that is used by an employer, which gives that employer an opportunity to obtain a competitive advantage over other manufacturers who do not know of or use it.

American Electroplaters &
Surface Finishers Society, Inc.

81st ANNUAL CONFERENCE & EXPOSITION
INDIANAPOLIS, INDIANA U.S.A.
JUNE 20 - 23, 1994

LABELING REQUIREMENTS

Martha S. Martin, CEF

Delta Compliance Consultants, Div.
Delta Chemicals & Equipment, Inc.
3675 Newgate Lane
Indianapolis, IN 46236
(317) 898-6446

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Abstract

A few years ago, several young men lost their lives in a plating shop accident by combining cyanide and acid. Was this tragedy the result of improper container labeling? Under Occupational Safety & Health Administration (OSHA's) Hazard Communication Standard (HCS) containers must be labeled if they contain potentially hazardous chemicals. A survey revealed that most facilities fall far short of this requirement for labeling on intermediate containers such as transport, mixing, storage or process tanks. This paper will address the types of labels and the requirements, exceptions, exemptions, and types pertaining to the surface finishing industry.

Introduction

Proper labeling is critical to the success of a hazard communication program. Labels tell your employees if the contents are hazardous and what the hazards are. Employees depend upon the label as a fast, easy way to determine how to handle chemicals. Few employees will take the time to read Material Safety Data Sheets (MSDS) about specific chemical hazards. In fact, they rely on the manufacturer to summarize these hazards on the label of the product. This paper will examine the container labels required by the hazard communication standard as it pertains to the hazards found in a typical metal finishing shop - specifically transfer containers, process tanks and wastewater treatment reactor vessels. Along with this will be an explanation of the different standardized labeling systems such as American National Standards Institute (ANSI), National Fire Protection Association (NFPA), Hazard Material Identification System (HMIS), and Chemical Hazard Inventory Program (CHIP).

We need to make sure containers of hazardous chemicals are properly labeled in order to comply with the OSHA standard, avoid fines, and prevent injuries.

The key ideal this paper presents is that it's easy to comply with the labeling requirements because the requirements are published, standardized labeling systems are available, and hazards can be identified.

Key words: labeling, health hazards, hazardous waste, hazardous chemicals

Requirements are Published

Labeling requirements are published in The OSHA Hazard Communication Standard (29 CFR 1910.1200)

Scope and Application

Employers must inform employees about the hazardous chemicals they are exposed to by:

Hazard Communication Program
Labels
Other forms of warnings
Material Safety Data Sheets
Information
Training

Definitions

Label - any written, printed, or graphic material, displayed on or affixed to containers of hazardous chemicals.

Identity - any chemical or common name which is on the MSDS

Immediate use - only one person will use within the work shift

Mixture - any combination of two or more chemicals if the combination is not the result of a chemical reaction. For example, a nickel plating bath is a mixture containing nickel salts, boric acid, nickel brighteners, wetting agents, hydrochloric acid and nickel anodes

Oxidizer - a chemical other than a blasting agent or explosive that initiates or promotes combustion in materials

Physical hazard - a chemical for which there is scientific validity that it is a combustible liquid, compressed gas, explosive, flammable, organic peroxide, pyrophoric, unstable (reactive) or water-reactive

Use - means to package, handle, react, or transfer

Work area - a room or defined space where hazardous chemicals are produced or used and where employees are present

HMR - 181 Hazardous Material Definition

Any article, material, substance or chemical which poses a danger to the handler of the material, to the general public, or to the environment.

Mixtures

If a mixture has not been tested as a whole to determine whether the mixture is a health hazard, the mixture shall be assumed to present the same health hazards as do the components which comprise one percent (by weight or volume) or greater of the mixture, except that the mixture shall be assumed to present a carcinogenic hazard if it contains a component in concentrations of 0.1 percent or greater which is considered to be a carcinogen.

Employers shall describe in writing the procedures they use to determine the hazards of the chemical they evaluate. The written procedures are to be made available to the employee on request.

Employers shall ensure that each container of hazardous chemicals is labeled, tagged or marked with the following information:

Identity of the hazardous chemical
Appropriate hazard warnings

Label stationary containers such as plating tanks with any of the following:

signs
placards
process sheets (see example in appendix)
batch tickets
operating procedures
other written material

Some state laws may also require additional information such as phone #, Chemical Abstract Service (CAS) number, and the five components with the highest concentration.

Hazard information must be **readily accessible** to the employees **in their work area** throughout **each work shift**.

What must be labeled?

1. Each container of hazardous chemicals leaving the workplace

Hazardous waste transported to Treatment Storage Disposal Facility (TSDF) from finishing operations

F006 - Wastewater treatment sludges from electroplating operations
F007 - Spent cyanide plating bath solutions
F008 - Spent cyanide plating bath residues
F009 - Spent stripping and cleaning bath solutions from electroplating
D001 - Ignitable waste (paint waste, lubricating oil waste)
D002 - Corrosive waste
D003 - Reactive waste
D006 - Cadmium waste
D007 - Chromium waste

2. Solid metal products, such as a steel beam or casting, are exempt from labeling as long as the required label is sent to customer prior to or with the initial shipment.

3. Labels on hazardous chemicals cannot conflict with Department of Transportation (D.O.T.) labeling requirements. This past year, October 1, 1993, we experienced a change in labeling requirements moving F006 from the "ORM-E" category to a "Class 9" material. The proper shipping label is "Hazardous Waste Solid, N.O.S., 9 NA3077, PGIII, (F006)". A "Class 9" placard should appear on each side of bulk containers.

4. Containers holding hazardous chemicals subject to OSHA substance specific health standard must be labeled in accordance with that standard.

5. Each container of hazardous chemical in the workplace must be labeled, tagged, or marked with the following:

Chemical or common name of potential hazardous chemical
Name and address of manufacturer
Appropriate hazard warning - Physical and Health

Warnings in the form of :

signs
placards
process sheets
batch tickets
operating procedures

Also, other written material may be used instead of labels for individual stationary process containers such as plating lines or clarifiers. (see examples in Appendix 1)

6. An existing label on incoming containers of hazardous chemicals may not be removed or defaced unless it is immediately replaced.

Note: *Proposed Rule* - Hazardous Materials Transportation Act Sect. 29 of Act of 1990 regulations require no removal of labels on packages, containers, motor vehicles, rail freight cars aircraft and vessels containing hazardous material until all contents are removed.

7. Labels must be in English, prominently displayed on containers or readily available in the work area during each work shift.

8. New labels are not required if existing labels convey the required information.

Containers that must be labeled

All containers - intermediate, smaller storage, process and transport containers must be labeled.

Common examples include buckets, barrels, boxes, tanks, reactor vessels, cans, cylinders, drums, roll-offs, hoppers, bags, barrels, bottles.

Frequently, operators overlook labeling con-

tainers that are not so obvious. For example, clarifiers(confined space), propane tanks, mixing vessels, boxes of anodes, pressurized gas cylinders, bulk storage tanks for nitric and hydrochloric acid, holding treatment tanks and confined spaces.

If you "manufacture" any potentially hazardous chemical (this means mix, distill, blend) all the containers used must be labeled. This would apply to making up a process bath or a reagent tank for wastewater treatment.

Exceptions

Pipes or piping systems, engines, fuel tanks, or other operating systems in a vehicle, are not considered to be containers and are exempted from labeling requirements.

Labeling of portable containers:

Not required if only for the immediate use of the employee who performs the transfer during one shift. The inherent danger in this practice is containers are seldom left empty, and they may contain a residue of the hazardous material. It is a wise practice to have dedicated transfer containers that are properly labeled.

Hazardous Chemical Labeling Systems

American National Standards Institute (ANSI)
This system rates the levels of hazards by the use of the words Danger, Warning and Caution. Danger signifies the highest level of warning and caution the lowest. For example, these are common examples:

Danger - High Voltage
Warning - Eye Protection Required Beyond This Point
Caution - Wet Floor

National Fire Protection Association (NFPA) System

The National Fire Protection Association (NFPA) label was designed to help fire-fighters. This system uses a diamond label divided into four smaller colored diamonds using numeric values from 0 - 4 to denote the level of hazard. The NFPA Placarding Rating is as follows:

Health Hazard - Blue
Fire Hazard - Red
Reactivity Hazard - Yellow
Specific Hazard - White

Health Hazard (Blue Background)

The rating scale is from 0 - 4 with 4 representing the highest degree of hazard

4 Materials which on very short exposure could cause death or major residual injury even though prompt medical treatment were given.
Example: hydrogen cyanide gas, chlorine gas

3 Materials which on short exposure could cause serious temporary or residual injury even though prompt medical treatment were given.
Example: chlorine, chromic acid, nitric acid, sulfuric acid, 111 trichloroethane, liquid oxygen, sodium hydrosulfite, sodium hydroxide

2 Materials which on exposure would cause irritation but only minor residual injury even if no treatment were given.
Example: phosphoric acid, tolulene, formaldehyde, acetone

1 Materials which on exposure would offer no hazard beyond that of ordinary combustible material.
Example: methyl ethyl ketone, potassium per-

manganate

0 Normal material
Example: Fuel Oil No. 1

Fire Hazard (Red Background)

4 Materials which will rapidly or completely vaporize at atmospheric pressure and normal ambient temperature, or which are readily dispersed in air and which will burn readily.
Flash point < 73° F.(22.8° C) and boiling point < 100° F.(37.8° C)
Example: gases, cryogenic materials, gasoline, benzene, toluene, isobutly acetate, acetone

3 Liquids and solids that can be ignited under almost all ambient temperature conditions.
Flash point < 73° F.(22.8° C) and boiling point > 100° F.(37.8° C)
Example: tolulene, organic peroxides, sodium hydrosulfite, methyl ethyl ketone

2 Materials that must be moderately heated or exposed to relatively high ambient temperatures before ignition can occur.
Flash point > 100° F.(37.8° C) and < 200° F.(93.4° C)
Example: No.2 fuel oil, formaldehyde, acetone

1 Materials that must be preheated before ignition can occur.
Flash point > 200° F. (93.4° C)
Example: ethylene glycol, 111 trichloroethane

0 Materials that will not burn
Example: sodium hydroxide

Reactivity Hazard (Yellow Background)

4 Materials which in themselves are readily capable of detonation or of explosive decomposition or reaction at normal temperatures and pressures.
Example: nitroglycerin

3 Materials which in themselves are capable of detonation or explosive reactions but require a strong initiating source or which must be heated under confinement before initiation or which react explosively with water.
Example: acetylene

2 Materials which in themselves are normally unstable and readily undergo violent chemical change but do not detonate. Also, materials which may react violently with water or which may form potentially explosive mixtures with water.
Example: sulfuric acid, sodium metal

1 Materials which in themselves are normally stable, but which can become unstable at elevated temperatures and pressures or which may react with water with some release of en -ergy but not violently.
Example: Muriatic Acid, chromic acid, 111 trichloroethane, sodium hydrosulfite, acetone

0 Materials which in themselves are normally stable, even under fire exposure conditions, and which are not reactive with water.
Example: General Degreasers

Specific Hazard (White Background)

OX - Oxidizing Properties
Example: oxygen, chlorine, nitric acid, potassium permanganate

ACID - Acid

ALK - Alkali

COR - Corrosive

~~W~~ - Use no water

Example: sulfuric acid, sodium metal, sodium hydrosulfite, acetone

The primary strength of the NFPA label is that it is easy to represent the hazard through the numeric code. However, the inherent weakness is it is often difficult for the person assigning the numbers to decide which is appropriate just from reading the MSDS sheet. Secondly, while the label conveys information about the severity of the hazard, it doesn't tell what kind of hazard (such as a health hazard because it's corrosive or can cause cancer.)

National Paints and Coatings Association Hazardous Materials Information System (HMIS) System

The Hazardous Materials Identification System uses color coded bands on the label. Like the NFPA label, hazards are described by their severity using numeric designations. The strong point of the label is the level of personal protective equipment can be indicated on the white band. A pictogram cross references the letter (A, B, C, D, etc.) of personal protection index required.

The hazard index is as follows:

4 Severe Hazard
3 Serious Hazard
2 Moderate Hazard
1 Slight Hazard
0 Minimal Hazard

The advantage of this system is that it tells what the Physical and Health Hazard levels are. However, the system requires a pocket card or wall chart to tell what the letters mean in order to select the proper equipment for personal protection.

Chemical Hazard Identification Program (CHIP Label)

The Chemical Hazard Identification Program (CHIP) uses symbols to convey hazard warnings. It is easy for employees to recognize the hazard and is good for employees who have English as a second language. The weakness of the system is the amount of time it takes to make up the label.

Written Label

On the written label, all the information is presented in writing. It gives great detail but is very difficult and time consuming to read.

Department of Transportation Labeling System (D.O.T.)

The Department of Transportation Labeling System uses a diamond shape label organized by color and class. D.O.T. is important to the surface finisher if the firm transports or offers for transport any hazardous material. Under this class would fall some of the common hazardous wastes from metal hydroxide wastewater treatment systems, paint solvent residues, poison cyanide waste and others. The class system developed under the HM 181 law is as follows:

Class 1 - Explosive and Blasting Agents- Orange Label
Class 2 - Flammable Gas - Red Label
Non Flammable Gas - Green Label
Oxygen - Yellow Label
Poison Gas - White Label
Class 3 - Flammable Liquid - Red Label
Class 4 - Flammable Solid - Red/White Striped Label Combustible - White on Top/Red on Bottom Label
Dangerous - Blue Label
Class 5 - Oxidizer - Yellow Label 5.1

Organic Peroxide - Yellow Label 5.2
Class 6 - Poison - White Label
Harmful Store Away From Foodstuffs- White Label
Infectious Substance - White Label
Biomedical Material - Red on White Label
Class 7 - Radioactive I- White Label
Radioactive II - Yellow/White Label
Radioactive III - Yellow/White Label
Class 8 - Corrosive - White/Black Label
Class 9 - Miscellaneous Black/White Stripes on top/ White on Bottom

Labeling

Before offering hazardous waste for transportation, a generator must label each package in accordance with D.O.T. Regulations under 49 CFR Part 172.401 - 172.404.

1. Shipper must furnish and attach appropriate label(s) to each package of hazardous material offered for shipment unless exempted from labeling requirements.

2. If the material in a package has more than one hazard classification, the package must be labeled for each hazard.

3. When two or more hazardous materials of different classes are packed within the same packaging or outer enclosure, the outside of the package must be labeled for each material involved.

4. Labels must not be applied to a package containing only material which is not subject to Parts 170 - 189 of this subchapter or which is exempted therefrom. This does not prohibit the use of labels in conformance with U.N. recommendations.

Marking

In addition to the type of waste, the container must also contain the following information:

Hazardous Waste - Federal Law Prohibits Improper Disposal
If found contact the nearest police or public safety authority or the U.S. Environmental Protection Agency
Generator's name and address
Manifest Document Number

Accumulation Time

The accumulation start time must be marked on accumulation containers. A large quantity generator may accumulate hazardous waste for 90 days. Beyond this time the generator is considered an operator of a storage facility. In some cases a 30 day extension may be granted by the Regional Administrator. Resource Conservation & Recovery Act (RCRA) inspectors are typically collecting fines in excess of $100,000 for violation of storage time. This is one area of improper labeling that can be very costly to the company.

Don't Forget to Identify and Label These Hazards

Cleaner Bath
Chrome Bath
Nickel Bath
Cyanide Copper Bath
Wastewater Treatment Clarifier
Hazardous Waste
F006 - Wastewater treatment sludges from electroplating operations
F007 - Spent cyanide plating bath solutions
F008 - Spent cyanide plating bath residues
F009 - Spent stripping and cleaning bath solutions from electroplating
D001 - Ignitable waste (paint waste, lubricat-

ing oil waste)
D002 - Corrosive waste
D003 - Reactive waste
D006 - Cadmium waste
D007 - Chromium waste

Health Hazard Definition

Although safety hazards related to physical characteristics can be defined readily in terms of testing (flammable, reactive) health hazard definitions are less precise and more subjective. Health hazards cause measurable changes in the body - such as decreased pulmonary function. Employees must be apprised of both the change in body function and the signs and symptoms that may occur to signal a change.

There have been many attempts to categorize effects and to define them in various ways. Generally the terms "acute" and "chronic" are used to delineate between effects on the basis of severity or duration.

Acute
Acute effects usually occur rapidly as a result of short-term exposures. Overexposure to hydrogen cyanide gas would be an example of an acute effect.

Chronic
Chronic effects generally occur as a result of long-term exposure and are of long-term duration. Overexposure to asbestos leading to lung cancer would be an example of a chronic effect.

The American National Standards Institute (ANSI) developed definitions for precautionary labeling of Hazardous Industrial Chemicals (Z129.1-1982). These are irritation, corrosivity, sensitization and lethal dose. These are important but do not cover the range of acute effects as a result of occupational exposure.

For OSHA Purposes (29 CFR 1910.1200 A) the following characteristics of chemicals are considered health hazards.

Carcinogen - causes cancer, a potential to cause cancer or is regulated as a carcinogen.

Corrosive - causes visible destruction in living tissue on contact. The material is applied to the skin of an Albino rabbit for four hours. If the tissue is destroyed or has irreversible changes it is corrosive. Chemicals are also classified as corrosive if they have a pH < 2 or > 12.5.

Highly toxic - causes death
1. median lethal dose (LD50) of 50 milligrams or less per kilogram of body weight administered to albino rats or 200 mg for 24 hours or gas or vapor 2 mg/L for 1 hour.
Example: nerve gas

Toxic - chemical has a median lethal dose (LD50) of > 50 and < 500 mg/kg or 200 mg/kg in 24 hours or LC50 of 200 ppm to < 2000 ppm resulting in death in 1 hour.
Example: cyanide

Irritants - cause a reversible inflammatory effect on living tissue.
Example: Sodium Hydroxide

Sensitizer - causes an allergic reaction in some people after repeated exposure.
Example: poison ivy

Target Organ Effects From Health Hazards

Hepatotoxins - Produce liver damage
Symptoms: jaundice, liver enlargement
Chemicals: nitrosamines, carbon tetrachlorides

Nephrotoxins - Produce kidney damage

Symptoms: edema, proteinuria
Chemicals: halogenated hydrocarbons, uranium

Neurotoxins - Nervous System
Symptoms: Narcosis, behavior changes, decrease in motor function
Chemicals: nerve gas, mercury, carbon disulfide

Blood - Decrease hemoglobin function, Oxygen deprivation
Symptoms: cyanosis, loss of consciousness
Chemicals: carbon monoxide (tow motors), cyanides

Lung - Irritates and damages lungs and pulmonary tissue
Symptoms: cough, tightness in chest, shortness of breath
Chemicals: nitric acid (anodizing bright dip), silica, asbestos

Reproduction Toxins - Chromosomal damage (mutations) effect on fetus and reproduction
Symptoms: sterility, birth defects
Chemicals: lead (battery manufacturers, chrome plating)

Cutaneous - Affect dermal layer
Symptoms: defatting of skin, rashes, irritation
Chemicals: ketones (paint dept.) chlorinated compounds (wastewater treatment)

Eye - Affect eyes or vision acuity
Symptoms: conjunctivitis, corneal damage
Chemicals: organic solvents (paint dept.) acids (plating, wastewater treatment)

Physical Hazards

Combustible liquids
Compressed gas
Explosive
Flammable
Organic peroxide
Pyrophoric
Unstable (reactive)
Water reactive
Reactive

Exemptions (No labeling Required)

Federal Insecticide, Fungicide, and Rodenticide Act (7 U.S.C. 136 et seq.)
Pesticides

Federal Food, Drug, and Cosmetic Act (21 U.S.C. 301 et seq.)
Food or Food Additives

Federal Alcohol Administration Act (27 U.S.C. 201 et seq)
Distilled Spirits

Consumer Product Safety Act (15 U.S.C. 2051 et seq)
Consumer Products
Tobacco
Wood
Articles
Food, drugs cosmetics or alcohol

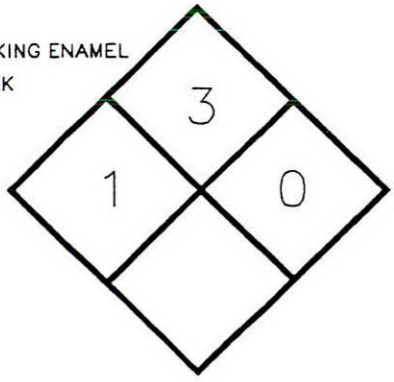
A cross reference listing of some of the common chemicals occurring in finishing plants has been complied for your convenience. However, an examination should be made of the material safety data sheets to determine your particular Health and Physical Hazards for labeling purposes.

The key point to remember is it's easy to comply with the labeling requirements because the requirements are published, there are standardized labeling systems available, and we can identify the hazards.

NFPA AND HMIS TELL LEVEL OF HAZARD

NFPA LABEL

BAKING ENAMEL
MEK

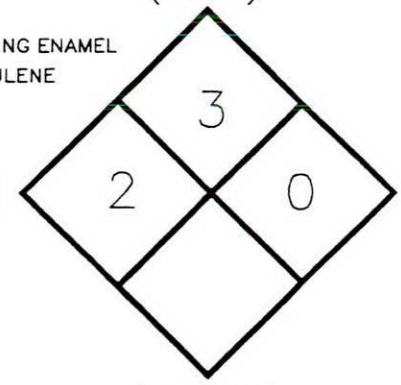


BAKING ENAMEL
MEK
TOLULENE

FLAMMABILITY
(RED)

* BAKING ENAMEL
TOLULENE

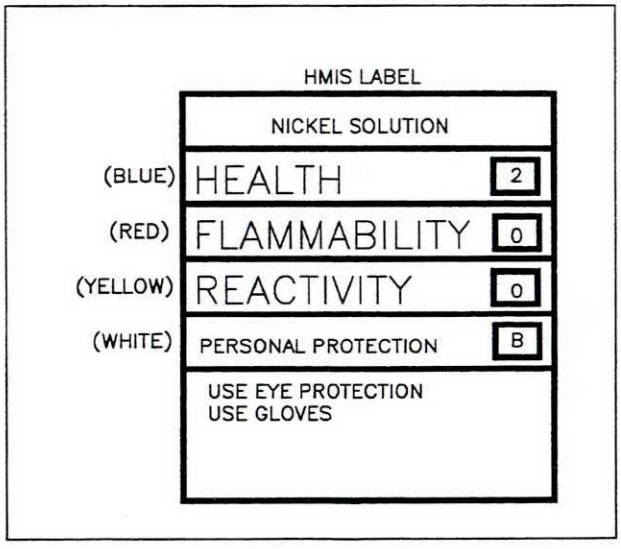
HEALTH
(BLUE)



REACTIVITY
(YELLOW)

(WHITE)
SPECIAL

* When a mixture contains two or more chemicals, label to the highest level of warning.



LIMITATION: THE HAZARD IS UNKNOWN

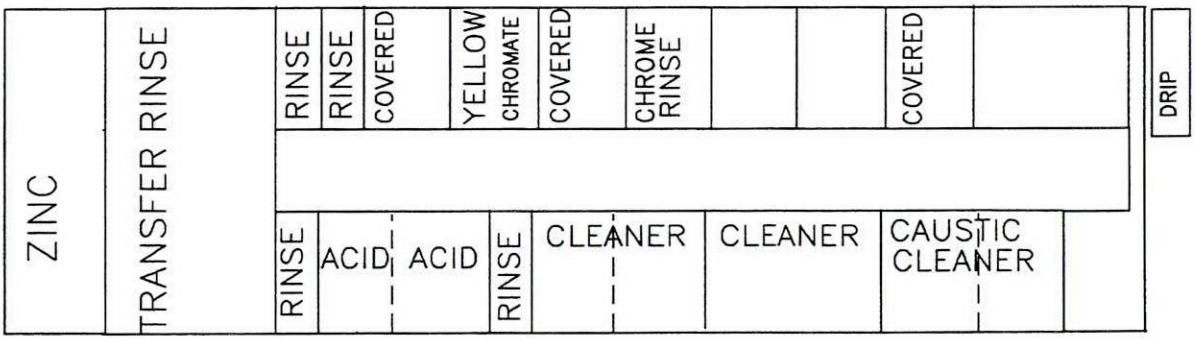
PROCESS SHEET

CLEANER TANKS
CAUSTIC SODA, LYE, SODIUM HYDROXIDE
HEALTH HAZARD – IRRITATION – EYE, NOSE, THROAT, SKIN –– MARKED
SYMPTOMS
NOSE IRRITATION, PNEUMONITIS, EYE, SKIN BURNS, TEMPORARY LOSS OF HAIR
TARGET ORGANS
EYES, RESPIRATORY SYSTEM, SKIN

ZINC TANK
HEALTH HAZARD – IRRITATION –EYE, NOSE, THROAT, SKIN ––– MARKED
SYMPTOMS
RESPIRATORY EFFECTS – ACUTE LUNG DAMAGE/EDEMA
CHRONIC (CUMMULATIVE) TOXICITY – SUSPECT CARCINOGEN OR MUTAGEN

ACID TANKS
MURIATIC ACID
HEALTH HAZARD – IRRITATION –EYE, NOSE, THROAT, SKIN ––– MARKED
SYMPTOMS
COUGHING AND CHOKING SENSATION, IRRITATION OF NOSE, AND LUNGS
CAUSES BURNS
TARGET ORGANS
EYES, SKIN, RESPIRATORY SYSTEM

CHROME TANKS
HEALTH HAZARD – CUMMULATIVE LUNG DAMANGE, NASAL PERFORATION, ULCERATION
SYMPTOMS
RESPIRATORY, NASAL SEPTUM IRRITATION, LEUKOCYTOSIS, LEUKOPENIA
MONOCYTOSIS, EOSINOPHILIA, EYE INJURY, CONJUNCTIVITIS, SKIN ULCER
SENSITIZATION DERMATITIS
TARGET ORGANS
BLOOD, RESPIRATORY SYSTEM, LIVER, KIDNEYS, EYES, SKIN



SURFACE FINISHING CHEMICALS AND THEIR HEALTH HAZARDS

	CYA-NIDE	CAD-MIUM	SULFURIC ACID	ZINC	NIC-KEL	CHROMIC ACID & CHROMATES	PHOSPHORIC ACID	2-BUTANONE (MEK)	SODIUM HYDROXIDE	TOLULENE	NITRIC ACID	FORMALDE-HYDE
INOGEN		X		X	X	X						X
OSIVE			X			X	X		X		X	
LY TOXIC	X											
C												
TANT	MI		MI	MI			MI	X	MI	X	MI	X
ITIZER												
ET ORGAN EFFECTS												
TOTOXINS	X					X				X		
ROTOXINS	X					X				X		
OTOXINS												
D						X						
S			X	X	X			X	X			
ODUCTIVE												
NEOUS												
			X	X		X	X		X	X	X	X
				X	X	X				X	X	
AT				X						X	X	
	X							X		X		
	X											
	X		X	X	X	X	X		X	X	X	X
AL			X								X	
IRATORY			X	X		X	X		X		X	X

ARKED IRRITATION
NDICATED
CENTRAL NERVOUS SYSTEM
CARDIO-VASCULAR SYSTEM

e: U.S. Department of Labor, Occupational Safety and Health Administration, OSHA CD-ROM (OSHA A94-1) Retrieval Softward
Compiled from Chemical Fact Sheets

Worker Exposure Assessment: More Than Just Air Testing

By Philip A. Platcow, C.I.H., Sedgwick James, Inc.

Manufacturing employers frequently attempt to address employee health concerns by immediately performing air testing. "Qualitative exposure assessment" is an industrial hygiene approach which evaluates the critical aspects of exposure. Critical aspects include the manufacturing process e.g., electroplating, the employee's location in the process, specific chemicals, safe chemical handling procedures, and ventilation. The results of this evaluation determine the controls. This approach normally requires less time and better utilizes typically limited resources.

Throughout industry, employee concerns over airborne contamination are addressed by immediately conducting industrial hygiene air testing. An experienced industrial hygienist, however, will not rush into air sampling. The following presents a discussion of another industrial hygiene approach, *qualitative exposure assessment*, which should be conducted prior to, and in some cases instead of, *quantitative* air sampling.

Often, the first impulse, if we have any confidence in the employee voicing the concern, is to "run out into the shop" and set-up an air sampling pump on an employee and then pick it up at the end of the shift, send the sample off to the lab for analysis, and finally communicate the result to the employee/union. But let us slow down and first consider qualitative exposure assessment.

There are a number of reasons why workplace exposure assessments should be conducted:

- To address employee/union concerns;
- To protect employee health;
- To measure compliance with OSHA standards, e.g. the Respiratory Protection Standard 29 CFR 1910.134, Process Safety Standard 29 CFR 1910.119, Confined Space Entry Standard 29 CFR 1910.146; and
- To consider future process modifications or to measure the effect of new processes after installation.

The Qualitative Approach

Where to begin?

Qualitative assessments should be performed in a logical, step-by-step manner. It is appropriate to begin by examining the air quality concern. Figure 1 provides a questionnaire which can be utilized in approaching this assessment.

Do we believe the employee?

A thorough assessment of the employee's concern is almost always in order. If an employee believes there is a health threat, the concern should automatically be considered legitimate. If not addressed quickly, an employee's perception can be spread throughout the workforce, and become a "real" business problem.

Who solves the problem?

Industrial hygiene concerns overlap various departments and staff functions For example, looking at an operation may involve the process engineer. Evaluating maintenance procedures will involve the maintenance supervisor. Chemical substitution may involve flammable materials and thus the safety director. Employee concerns may necessitate the involvement of the human resources director. The industrial hygiene process is therefore a team building endeavor.

How do we evaluate the process?

The process allegedly creating airborne emissions, *and where the employee fits into it* is usually where the evaluation must begin. Consider the following:

- What chemicals are used in the process? Have substitutes been sought? Although the suggestion of substitutes often disturbs some companies, it is still the best way to eliminate hazards. Furthermore, substitution of a chemical can create another hazard, e.g., replacing the degreasing solvent 1,1,1-trichloroethane (a health hazard), with another solvent which may be less of a health hazard, but then creates a fire hazard.

- Are there chemicals, e.g., cleaning chemicals used in proximity to a process, that are being misconstrued as being part of a process? Often, time is wasted reviewing a process line when the agent causing the concern is associated with cleaning or another process altogether.
- Where does the employee fit into the operation? Can the process be automated to eliminate or reduce exposure? Is it possible to reduce the duration of employee exposure? Can the employee be physically separated from the operation by installation of a wall and remote controls? It should be remembered that engineering changes are always preferable to administrative changes.
- Are actual work procedures in accordance with good industrial hygiene practices? Is housekeeping well-addressed? Messy procedures e.g., not closing chemical or dirty rag containers, careless splashing of the chemicals by poorly tuned "dip apparatus", and poor housekeeping, in general, can create unnecessary airborne concentrations of chemicals and aggravate existing concentrations. If these procedures are not "tight," buttoning them up will reduce airborne chemical concentrations.
- Is equipment well maintained? This refers not only to repairing damaged equipment, but also to preventative maintenance.
- Is the process a closed circuit or totally contained? If the process is *truly* contained, emissions are usually not possible. If the process is not fully enclosed, can it be? If this is possible, and it is practical to do so, then this maybe the answer to the concern, and air sampling may *not be necessary*.
- Is local exhaust ventilation employed with the process? If not, consideration should be given to installing local exhaust to capture the emission directly from the source. If ventilation is used and there are still odors or excessive concentrations, the local exhaust should be evaluated to determine if it is operating properly: e.g., is there a slipping fan belt? is a filter blocked? is the exhaust properly located and sized to be adequate for the volume of emission to be controlled? General room ventilation is usually not a good solution to an airborne chemical problem.

Experience shows that when these questions are addressed, that the means for controlling the hazard is almost always obvious. The effect of the mitigation process employed will depend on the implementation of appropriate controls.

These controls can be expensive; are they really required?

Controlling emissions from large processes can be expensive and time consuming, but consider the advantages discussed below. And remember, OSHA wants an employer to "engineer-out" a recognized health hazard. Personal protective equipment, such as respirators, should be the *last resort.*

- Substitution of the hazardous material with a less hazardous one may significantly improve employee health since the cause of impaired health is diminished or eliminated. This will improve employee and maybe even community relations, especially if the replaced material was a carcinogen or produced reproductive effects. This must be done carefully, however, in order to maintain product quality. This can be a vital consideration in electroplating and other finishing operations which require extremely clean surfaces and tight tolerances.
- A well organized equipment maintenance program has a number of benefits: reduced downtime and resulting higher productivity, extended equipment longevity, reduced accident potential, less chemical splashing, less waste generation, and a lower potential to increase airborne chemical exposure.
- The installation of exhaust ventilation could eliminate the need for respiratory protection. This means a savings on annual pulmonary function exams; respirator fit-tests; purchase, sanitation, restoration, and replacement of personal protective equipment such as respirators; annual refresher training; Exhaust ventilation will therefore usually result in a more productive workforce.

Figure 2[1] illustrates a typical ventilation scheme for electroplating. Ventilation specifications will depend on the dimensions of the tank and the hazard potential of the solutions involved.

- The containing of a process will result in less airborne chemical exposure and could mean the creation of less waste. Recycling also translates into less hazardous waste dollars, less wasted product, and good ecological citizenship.
- Better housekeeping and more careful use of hazardous compounds again means less dollars spent on waste removal and disposal, less wasted product, reduced purchases to replace "spent" materials, and in some situations, perhaps the elimination of respiratory protection.

The examples above are just a few of the benefits that may result from qualitatively assessing employee exposures in lieu of immediate air sampling. Process and procedural changes, borne out of qualitative assessment, may cost some money, but they often save more money in the long run. It will "take some money to make money," but it is likely that over time, money will be saved, employees will be better protected and more productive, morale will be higher because employees will see actual employer dedication to their health and safety, and the workplace will be cleaner and safer.

If the exposure assessment discussed above is conducted, and it results in controls being installed, will we ever have to take air samples again?

Performing qualitative worker exposure assessment does not entirely eliminate the need for air sampling altogether. Consider the following:

- If there is a concern that exposure may still approach an OSHA action limit, then air sampling should be conducted for compliance purposes. Chances are, however, the concentrations measured will be significantly reduced, and the need for future air sampling may be reduced, if not eliminated.
- Air sampling may be performed to check the improvement resulting from installing controls, "a sort of before and after check." This would imply that air sampling should be conducted prior to making the engineering change. This may be a good idea because it shows "doubters"that controls *do* work. If an improvement is not detected, the process should be re-evaluated because some of the confounders described earlier may have come into play.
- Air sampling may also be required to alleviate employee concerns. These concerns may come at any time and, as mentioned above, need to be taken seriously. As a rule though, if management takes the pro-active approach outlined throughout this discussion, employee challenges should be reduced because employees will be witnessing employer action, not rhetoric.

In summary, addressing air contamination concerns does not always require immediate air sampling. Qualitative exposure assessment is often preferable to quantitative analysis, at least as an initial response. Qualitative analysis requires an interdisciplinary approach involving in the evaluation several departments, or fields of expertise, to ensure that a consensus is developed and that all those involved "buy into" the solution.

The entire operation generating an emission must be considered. Controls or solutions could include containment, exhaust ventilation, personal protective equipment, and chemical reduction or substitution. Other related sources of airborne contamination will also be evaluated. These include housekeeping, maintenance procedures, and other safe chemical handling procedures. The qualitative assessment approach will best utilize typically limited resources and in most cases reduce employee exposures for the long term.

Acknowledgments

The author wishes to thank Gary Slepp of Sedgwick and Michael Hill for editorial assistance. The author would also like to thank Dr. Margaret Quinn of the University of Massachusetts Work Environment Program for providing background information and assistance on this paper's topic.

Reference

1. American Conference of Governmental Industrial Hygienists., *Industrial Ventilation,* 19th Edition, 5-61 - 5-73, Edward Brothers, Ann Arbor, MI (1986)

Qualitative Worker Exposure Assessment Questionnaire

Respond to the following requests for information. Attach additional pages and documents as necessary.

1. Describe the employee's concern:

2. Develop the team to address the concern
   - Industrial Hygienist _____
   - Safety Manager _____
   - Occupational Nurse _____
   - Human Resources Director _____
   - Process Engineer _____
   - Maintenance Supervisor _____

3. Describe the process allegedly producing the airborne contaminant (include: process name, hours of operation, number of employees involved, seasonal impacts, schedule of equipment maintenance, are the process chemicals in a closed loop system, etc. Include maps, drawings, and pictures of the work area and process):

4. What chemicals are involved in the process?

5. Have alternative chemicals been explored? If yes, what were they and what decisions were made and why?

Are new alternatives now available?

6. Describe how the employee fits into the process. Note the number of hours per day, shifts per week, "routine-ness" of the work, distance from the points of emission, personal protective equipment used. Refer to question 3 above as necessary.

Is it possible to reduce employee involvement in, or increase his/her distance from the process? Consider remote controls, complete automation, enclosing the process.

7. Describe the nature of any ventilation system in the work area. Include the type of system, e.g., local vs. general, canopy hood, wall mounted slot hood, flexible duct, volume of air moved in CFM, capture velocity, type of fan. Provide a diagram of the system.

Is it possible to improve ventilation?_____

8. Is a better maintenance schedule required to make the process run more efficiently? Describe.

9. Is major renovation of the process in order? This means replacing > 15-25% of the equipment involved, or an expenditure of a level considered significant to your company.

Fig. 1-Sample Qualitative Worker Exposure Assessment Questionnaire.

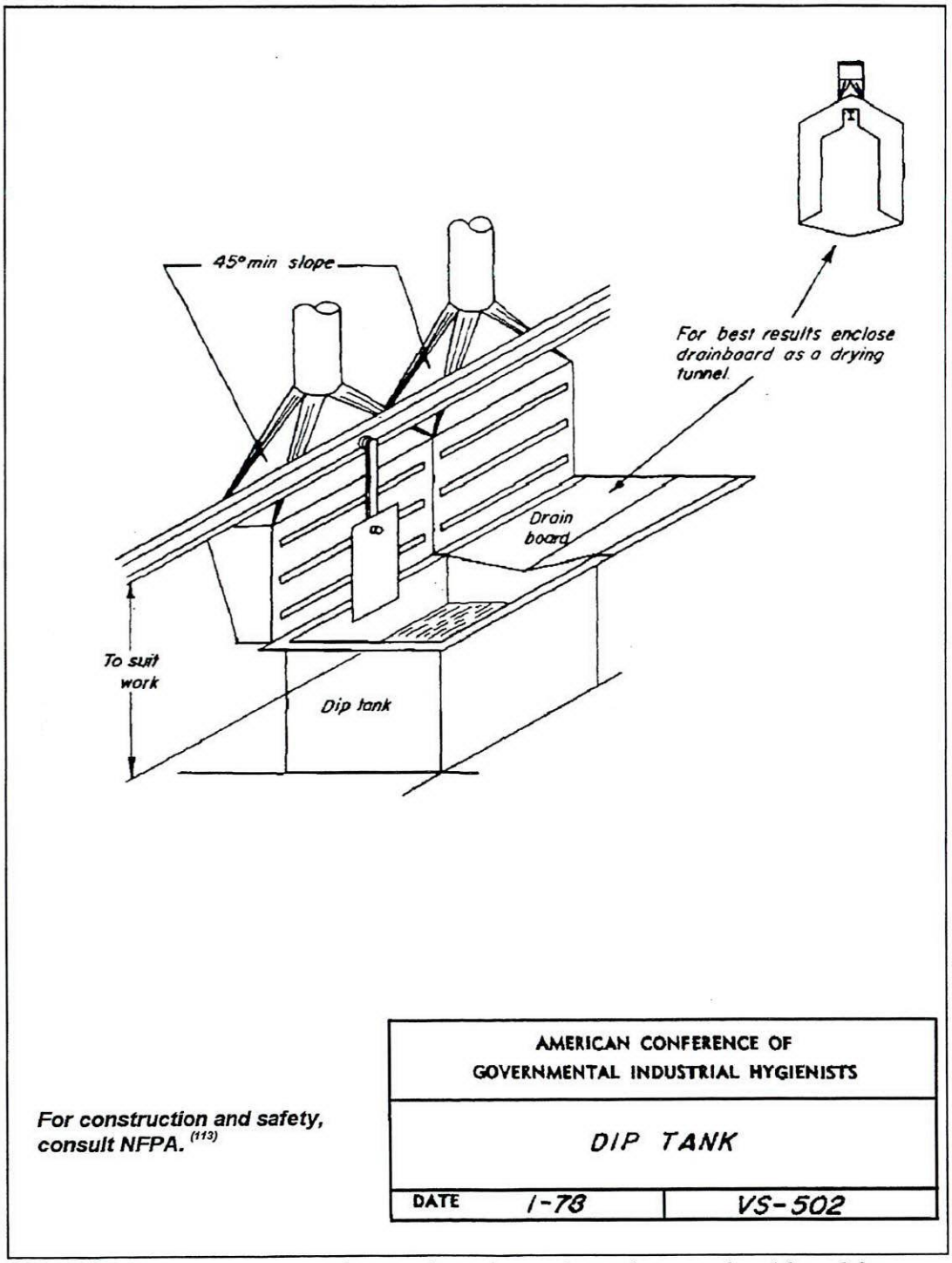


Fig. 2-Typical local exhaust ventilation scheme for an electroplating tank . Adapted from American Conference of Governmental Industrial Hygienists.

Pulse-Plated Pb-Sn Alloys from a Methane Sulfonate Electrolyte

(AESF Project 88)

By K.G. Sheppard and Q. Lin

Materials Sci. & Eng., Stevens Institute of Technology, Hoboken, NJ 07030

In AESF Project 88 we have investigated the application of pulse plating to electrodeposited lead-tin solder alloys from methane sulfonate electrolytes. We have shown that the amount of surfactant additive needed to suppress dendritic growth can be reduced by an order of magnitude compared to D.C plating. In this paper we describe the mechanical properties of the pulse plated solder alloys, both before and after reflow. The tensile behavior was measured using a mini-tensile tester developed at Stevens under previous AESF sponsorship.

Introduction

Electrodeposition of lead-tin solder alloys is important in a variety of electronic packaging applications[1,2]. The fluoborate electrolytes have dominated lead-tin plating technology for many years because of their stability and ability to allow high speed deposition[3]. Concern over environmental impact has resulted in a demand for a less toxic and corrosive electrolyte for lead-tin deposition. Recently, proprietary electrolytes based on sulfonates of lead and tin have been introduced.

As with the fluoborate baths, organic additives are needed to promote desirable deposition characteristics, i.e. dendrite suppression and improved throwing power[4]. The objective of the present study is to evaluate pulse plating as a means to produce uniform deposition characteristics over a wide range of current density while reducing the organic additive requirements.

Pulse-plating, because it provides a measure of control over both mass transport and the crystallization process, offers the possibility of influencing deposit composition and morphology without additives or with significantly reduced additive amounts[5]. Codeposition of impurities can be significantly reduced by pulse-plating, for example in gold[6], because during the off-time desorption from the surface can occur. Pulse plating will influence the deposition process in a manner which will be specific to the particular system being considered.

A further important consideration in electrodeposition that can be influenced by pulse plating is current distribution and hence throwing power and surface roughness. Current distribution is categorized as primary, secondary and tertiary depending on whether it is dominated by electrolyte resistance, activation polarization or a combination of activation and mass transport polarizations respectively. Pulse plating has no influence under primary current distribution and can produce a less desirable distribution than direct current plating under secondary conditions. However, it is tertiary current control that can provide the most desirable current distribution in terms of uniformity. With pulse plating in combination with suitable hydrodynamic conditions it is possible to promote a transition to a tertiary type of distribution by influencing the diffusion layer thickness[7].

Related to the above, the beneficial effects of pulse plating on the distribution of gold deposits plated through a photoresist mask have been described[8]. The incorporation of anodic pulses into the pulse sequence can also have beneficial effects on deposit uniformity[9] and surface roughness.

There has been little published on the pulse-plating of lead-tin alloys and none on deposits from the sulfonate electrolytes. Knodler et al.[10] have investigated the effects of pulse parameters on alloy composition and deposition efficiency from fluoroborate bath. Cheh[11] also studied the effects of pulse plating on composition from a fluoborate bath as experimental verification of a model to predict the composition of pulse-plated alloys. Interestingly he found that the tin dissolves during the off-period while the lead continues to deposit. Chin has used high current pulses to promote localized deposition of solder[12].

Experimental

The electrolyte compositions chosen for the present work were based on the results of previous studies at Stevens in which we investigated the effects of a number of additives and a range of d.c. plating conditions on deposition from methane sulfonate

electrolytes. For many of the experiments to evaluate plating variables, the electrolyte contained 40 g/l Sn (0.34M) and 20.25 g/l Pb (0.1M). This we refer to as the 2:1 tin/lead bath. Other metal ratios in the bath were obtained by reducing the lead content. The solution was made up as follows: 130 ml/l methane sulfonic acid (MSA) (70%); 133 ml/l stannous methane sulfonate (SMS) concentrate; 45 ml/l lead methane sulfonate (LMS) concentrate; the balance was deionized water. The lead concentrate contained 53% LMS, 2% MSA and 45% water. The tin concentrate had 50% SMS, 4-5% MSA and the balance water. The as-supplied SMS concentrate contained < 1% of a proprietary anti-oxidant, identified as a di-hydroxy aromatic. This is required to inhibit oxidation of the Sn^{2+} to Sn^{4+} during storage.

An organic additive was employed in this study, namely reagent grade Triton X-100, 5ml/l (used full strength). This is a proprietary (Rohm and Haas) polymeric non-ionic surfactant with the formula $C_8H_{17}(C_6H_4)(OCH_2CH_2)_xOH$ and average molecular weight of 628. Volumetric additions were used for measurement convenience.

Experiments have been performed to measure the effects of different amounts of Triton-X-100 under pulse-plating conditions at a rotating copper disc electrode. The rotating disc electrode was employed to provide controlled transport. All experiments were conducted at 25°C. The deposit characterization was performed in a JEOL 840 scanning electron microscope euipped with an X-ray energy dispersive analyser. The chemical analysis obtained with the latter was calibrated with pure lead and tin samples.

The mechanical properties of pulse-plated solder deposits were measured with a mini-tensile tester developed at Stevens by R. Weil under past AESF sponsorship. This device is able to provide strength and ductility data on thin films with specimen dimensions scaled down to match the film thickness[13]. Eutectic (60Sn/40Pb) and high lead (10Sn/90Pb) solder compositions were deposited for these measurements. As most solder is subject to reflow (melting) during subsequent component processing, the properties of reflowed material have also been tested. In order to produce reflowed samples having the correct shape for the tensile tester, a reflow furnace with temperature controller and argon atmosphere system was constructed. A reflow sample mold was developed using chemical etching of glass through a photoresist mask that defined the tensile specimen shape. The mold, when covered with a weighted glass microscope slide, allows reflow of the solder tensile test specimens without dimension change caused by surface tension effects.

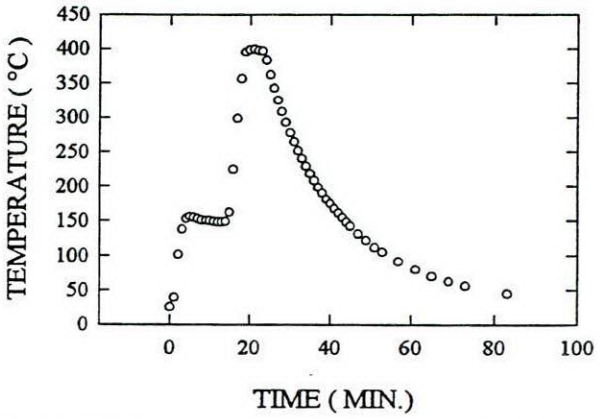


Fig. 1 Reflow temperature profile of Sn/Pb tensile test samples.

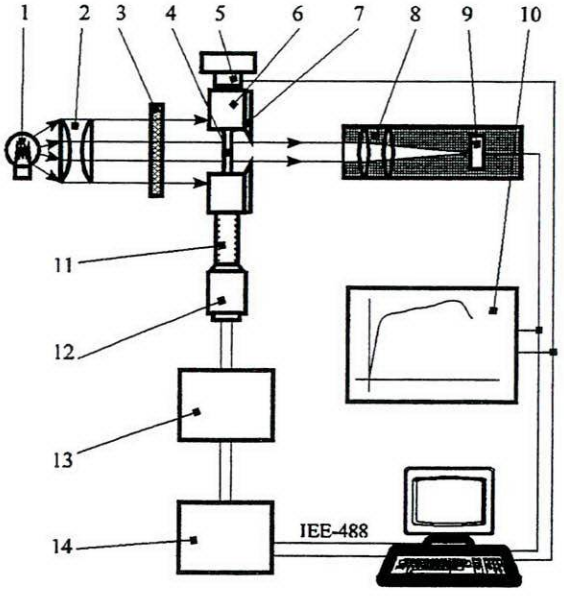


Fig. 2 Computerized mini-tensile test machine.

1. Light Source; 2. Collimating Lenses; 3. Diffuse Screen; 4. Specimen; 5. Load Cell; 6. Grip; 7. Razor Blade; 8. Focusing Lenses; 9. Photo-detector; 10. X-Y Recorder; 11. Load Screw; 12. Stepping Motor; 13. Motor Driver; 14. Indexer.

A reflow temperature profile for the tensile specimens is shown in Fig. 1. Such a temperature profile is used in manufacturing practice. Starting at room temperature, the temperature is raised to 150°C and held at this temperature for 15 minutes. Samples start to melt at about 250°C (eutectic). The peak reflow temperature is about 400°C.

A schematic of the mini-tensile tester is shown in Fig. 2. The amount of light passing between knife edges attached to the specimen grips is used to measure the elastic portion of the tensile curve. This eliminates errors from the elastic distortion of the tensile tester. The larger plastic strains are determined from crosshead displacement. The specimen shape is seen in Fig. 3. This is produced by plating through a photoresist mask onto copper which is subsequently removed by chemical etching. Deposit thickness was approximately 60 μm. The support bar prevents deformation of the gage length during mounting in the grips and is severed just prior to testing.

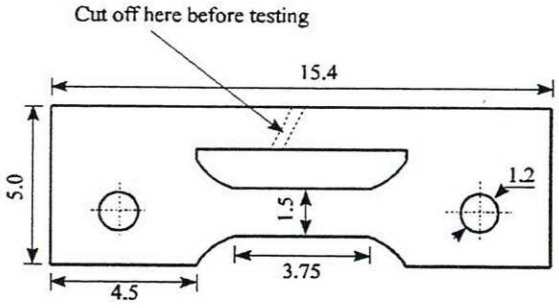


Fig. 3 Schematic of pulse plated Sn/Pb solder alloy tensile test sample. Unit: mm; Total area: 0.667 cm^2; Thickness: 60 μm.

Results and Discussion

Fig. 4 shows how the composition of the d.c. plated alloy varies with current density from approximately 30 to 45% tin in the presence of 5ml/l Triton. It had been found in previous work that 3-5ml/l was the minimum needed to suppress dendritic growth. For d.c. plating the deposit became more grossly nodular as current density was increased. The other curve in Fig. 4 shows the results when pulse plating was employed. It should be noted that these results were obtained with an order of magnitude lower Triton-X concentration in the bath. The tin content is decreased to approximately 10%. Furthermore, there is almost no change in composition over a wide current density range. It should be noted that average current densities, not peak current densities are plotted. The pulse plating produced deposits with good surface morphology (very finely nodular) over the full current density range plotted.

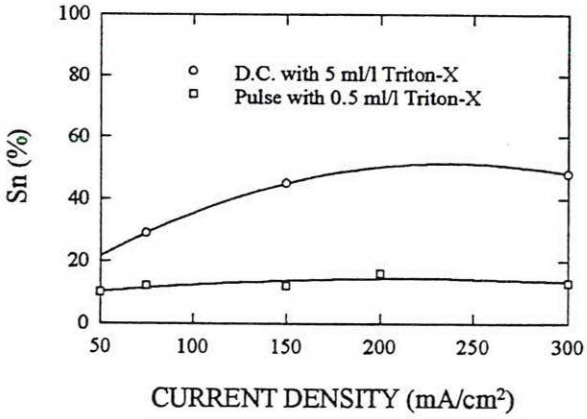


Fig. 4 Effects of average current density on the Sn composition (pulse frequency 100 Hz; duty cycle 10%; Cu disc electrode with 500 rpm).

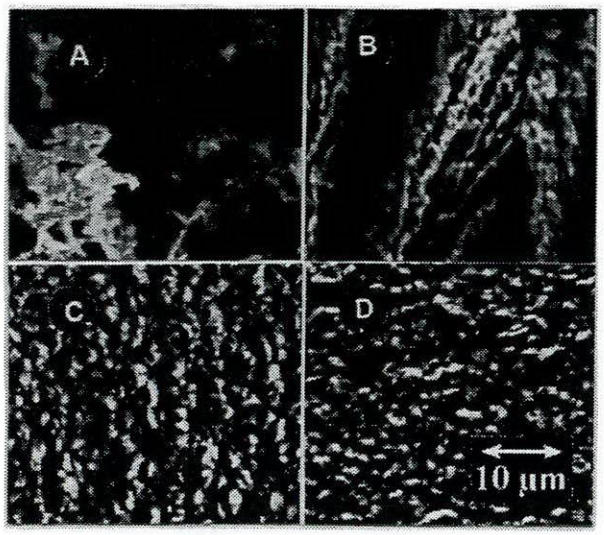


Fig. 5 Effects of Triton-X on the morphology of deposited solder. Sn/Pb (2:1) bath; 75 mA/cm^2; pulse frequency 100 Hz; duty cycle 10%.
(A) no additive; (B) 0.1 ml/l Triton-X; (C) 0.3 ml/l Triton-X; (D) 0.5 ml/l Triton-X.

Pulse plating in the complete absence of the surfactant was not sufficient to completely suppress dendritic growth. Fig. 5A shows a typical morphology. There are no gross dendrites, but at the magnification shown (≈ 1000X) the morphology is clearly dendritic. Adding 0.1 ml/l Triton causes a dramatic change in the dendrite shape (Fig 5B), presumably due to preferential absorption and blockage of certain growth orientations during dendrite branching. The addition of 0.3ml/l Triton is sufficient to completely inhibit the dendrites and little change is observed if more Triton is added. The concentration of Triton needed for full suppression is one tenth of that needed under d.c. plating conditions. Associated with dendrite suppression, a change in deposit composition to much lower tin levels is seen at Triton amounts greater than 0.3 ml/l (Fig. 6). This is to be expected as dendrites are primarily due to tin. However, the tin concentrations are lower than in Triton-suppressed d.c. plating, indicating an additional influence of the pulse plating.

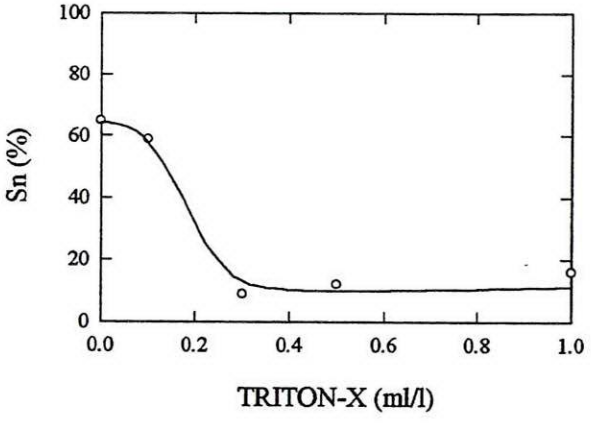


Fig. 6 Effects of Triton-X on the Sn composition of deposited alloy (pulse frequency 100 Hz; 75 mA/cm^2; duty cycle 10%; Cu disc with 500 rpm).

The influence of varying the ratio of tin to lead in the bath for a given set of pulse plating conditions is shown in Fig. 7. Results for d.c plating are included in Fig. 7 for comparison. The pulse plated deposit compositions follow the same trend as those from d.c plating in the presence of the larger Triton concentration. In all cases the pulse plated deposits contained significantly less tin than those from d.c. The morphologies with pulse plating remain good even at high tin content.

Figs. 8 and 9 show the ultimate tensile strength (UTS) for the two compositions, i.e. 60/40 and high lead. The results show that the tensile strength of both alloys is not significantly affected by the average current density used for deposition. Comparing the UTS results at high and low strain rate, the as-plated solder alloys are highly strain rate sensitive. Increase of strain rate from 1.3 x 10^{-3}/sec to 13 x 10^{-3}/sec doubles the ultimate tensile strength of the as-plated alloys. However, such an increase has little effect on the reflowed samples, which have values similar to the as-plated samples tested at the higher strain rate.

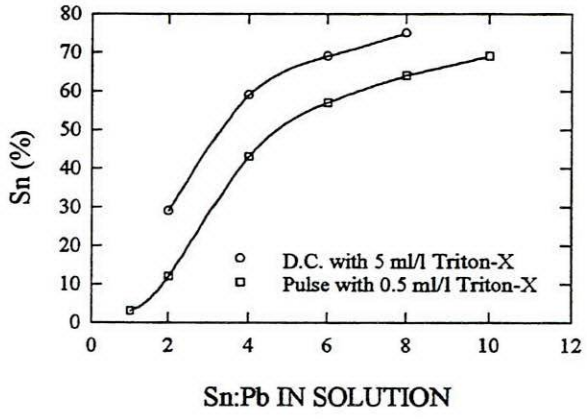


Fig. 7 Effects of solution composition on alloy composition (75 mA/cm^2; duty cycle 10%; frequency 100 Hz; Cu RDE with 500 rpm).

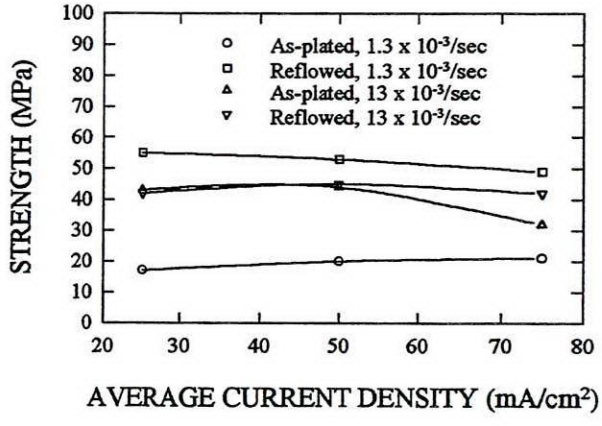


Fig. 8 Effects of average current density on the ultimate tensile strength of 60/ 40 Sn/Pb solder alloy (75 mA/cm^2; duty cycle 10%; frequency 100 Hz; Cu RDE with 500 rpm).

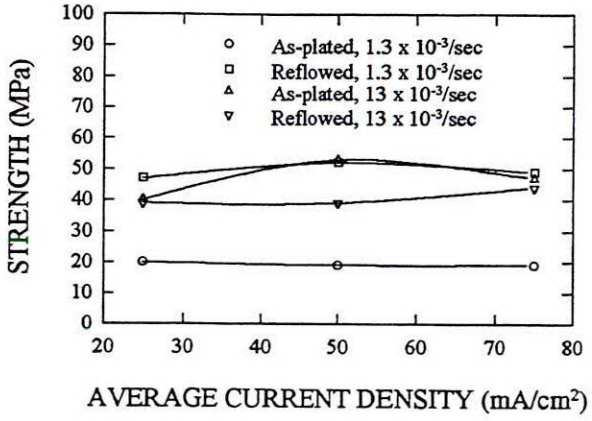


Fig. 9 Effects of average current density on the ultimate tensile strength of 10/ 90 Sn/Pb solder alloy (75 mA/cm^2; duty cycle 10%; frequency 100 Hz; Cu RDE with 500 rpm).

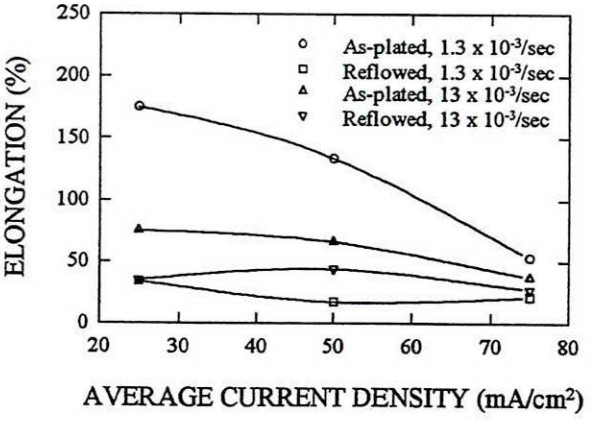


Fig. 10 Effects of strain rate and reflow on the elongation (Sn/Pb 60/40 alloy).

The ductility, as determined from % elongation at failure, is shown in Figs. 10 and 11. Most striking are the very large strains recorded for as-plated material tested at the lower strain rate. This result combined with the low UTS values and strain rate sensitivity, suggests that a degree of superplastic deformation could be occurring at low strain rate. Superplastic behavior is typically associated with a very small grain size. The mechanism is thought to involve grain boundary sliding. The fact that at room temperature lead-tin alloys are at a relatively high homologous temperature (i.e. relative to the melting temperature in °K) means that diffusional processes can enhance grain boundary shear. Large amounts of uniform plastic deformation can then be achieved because the strain rate sensitivity provides a resistance to local necking. Similar superplastic behavior has been reported in fine grained composites made by plating alternating layers of lead and tin[14].

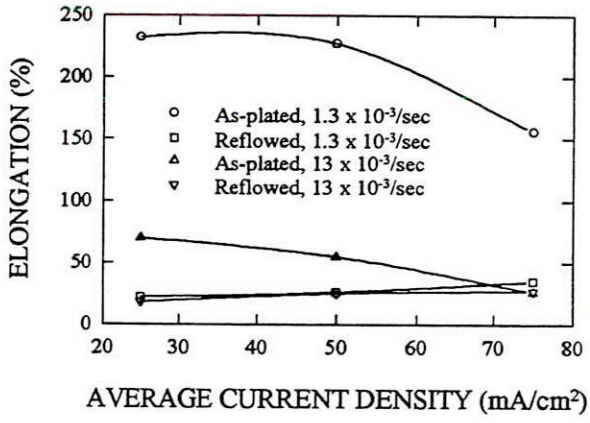


Fig. 11 Effects of strain rate and reflow on the elongation (Sn/Pb 10/90 alloy).

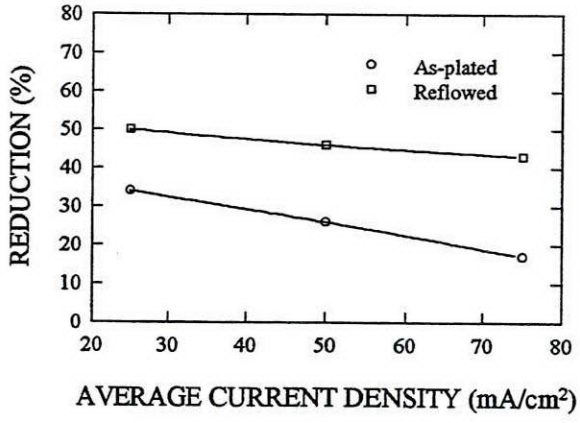


Fig. 12 Effects of average current density on the reduction in cross-section (Sn/Pb 60/40 alloy; strain rate 13 x 10^{-3}).

A second intriguing result is that the ductility of the reflowed material for both alloys, while relatively insensitive to strain rate, is lower than that of the as-plated material. It might reasonably have been expected that melting and solidification would lead to increased grain size and removal of internal defects leading to increased ductility. An explanation for the

results is suggested by Figs. 12-14. Figs. 12 and 13 show the ductility as a percentage reduction in cross-section at the point of fracture rather than as elongation over the gage length. Because of the experimental difficulty, the reductions were estimated from the width change, rather than the true cross-section and therefore probably underestimate the actual reduction in section. It can be seen that by this approach the reflowed samples have greater ductility than as-plated. Thus reflowed material is ductile, however the plastic deformation is highly localized due to the lack of the resistance to necking seen with the as-plated material. The scanning electron microscope photographs of as-plated and reflowed deposits after tensile testing in Fig. 14 clearly shows this difference in necking behavior.

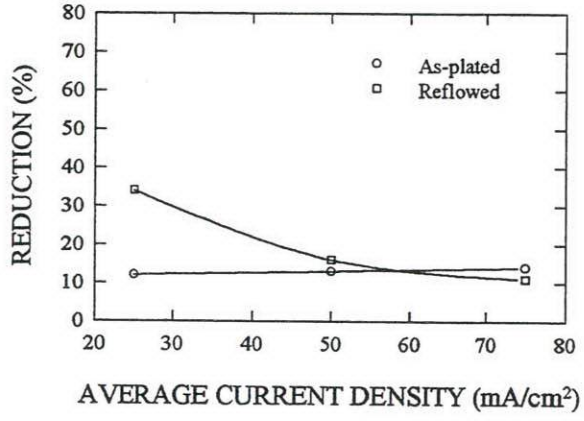


Fig. 13 Effects of average current density on the reduction in cross-section (Sn/Pb 10/90 alloy; strain rate 13 x 10^{-3}).

Conclusions

1. Pulse plating allows deposition of a full range of lead-tin alloys over a wide current density range with good morphology. This is achieved with an additive concentration one tenth that needed to suppress dendritic growth in d.c. plating.

2. As-plated 60Sn/40Pb and 10Sn/90Pb alloys show resistance to necking during tensile testing and thus achieve superplastic levels of elongation.

3. Reflow of the alloys results in material that is more ductile, but only when measured by reduction in area close to the fracture, i.e these materials no longer display resistance to necking and the consequent large elongations.

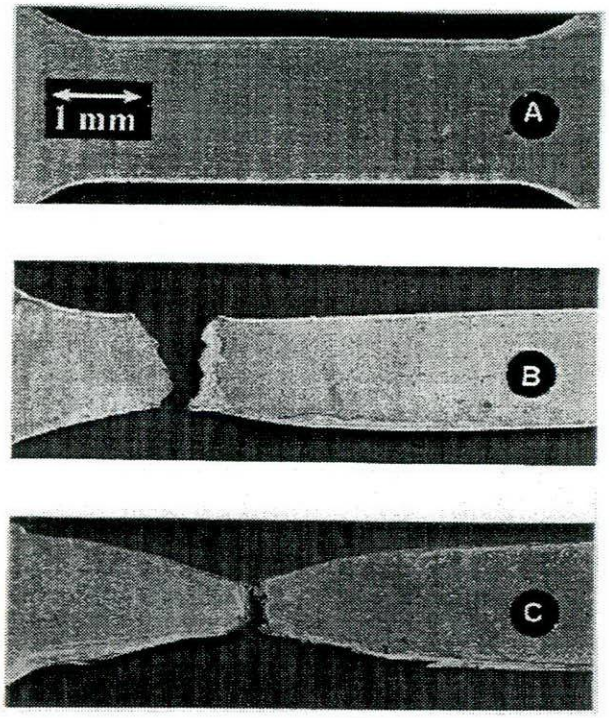


Fig. 14 Photos of tensile test samples.
(A) as-plated;
(B) as-plated and pulled;
(C) reflowed and pulled.

Acknowledgements

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UNDERPOTENTIAL DEPOSITION OF ZINC FOR MITIGATION OF HYDROGEN ABSORPTION AND PENETRATION INTO HY-130 STEEL

B. N. Popov G. Zheng and R. E. White
Department of Chemical Engineering
University of South Carolina
Columbia, SC 29208

ABSTRACT

The underpotential deposition (UPD) of zinc from a plating solution inhibited the discharge of hydrogen on HY-130 steel. In the presence of a monolayer coverage of Zn, hydrogen evolution currents were reduced by 58% compared with values obtained on bare HY-130 steel. The observed effects are due to the kinetic limitations of the hydrogen discharge reaction and the suppression of hydrogen absorption by the deposited monolayers. The hydrogen proton entry mechanism was used and the mass transfer term was introduced in the permeation model to interpret the experimental data. In the presence of zinc monolayers, the hydrogen entry efficiency in the alloy and the hydrogen entry rate constant were reduced by a factor of three and by 74%, respectively.

INTRODUCTION

Various methods have been proposed to decrease hydrogen embrittlement [1–5]. Among these methods are post heat treatment, laser surface modification, and shot peening. Using these methods, it is difficult to reduce hydrogenation of the alloy to a level which eliminates the cracking hazards. Juttner [6] found that as a result of the underpotential deposition (UPD) of lead and thallium on an iron substrate, the active iron dissolution process, as well as the charge transfer, controlled hydrogen evolution are inhibited drastically. The inhibition of the cathodic hydrogen evolution reaction was assumed to result from the lowering of the binding energy of the hydrogen adatoms on Pb and Tl adsorbates [7–9]. Drazic and Vorkapic [10] established that the presence of metal ions (Cd^{+2}, and Zn^{+2}), more electronegative than the cathodic potential for the hydrogen evolution reaction on iron in a 0.25 M H_2SO_4 solution, inhibited hydrogen evolution and corrosion of iron. By comparing cyclic voltammetry results with data derived from the Devanathan - Stachurski method (under identical conditions), the underpotential deposition of zinc, bismuth and lead on AISI 4340 steel [11] and Inconel 718 reduced the amount of both atomic hydrogen adsorbed and the degree of hydrogen ingress in the substrate [12–15].

The objective of this work was to use polarization and permeation techniques to estimate the effectiveness of the UPD of zinc on the reduction of the hydrogen evolution rate on the degree of hydrogen ingress into HY-130 steel.

EXPERIMENTAL

Linear sweep voltammetry and the Tafel method were used to investigate the underpotential deposition of lead on HY-130 steel in the presence and absence of underpotential deposited zinc. The experiments were carried out using stationary HY-130 disc electrodes with a geometric area of 0.5 cm^2 , placed in an electrolyte containing 1M Na_2SO_4 , 0.4 M NaCl and 1M H_3BO_3 in the presence and absence of zinc

ions. Nitrogen was bubbled through the cell and the electrolyte was stirred using a magnetic stirrer. T temperature of the cell was 25°C.

The Devanathan – Stachurski permeation technique [16] was used to investigate both the of hydrogen adsorption and hydrogen permeation through a HY-130 steel membrane with an area approximately 4 cm^2. The permeation experiments were carried out in a system with two compartme separated by a bipolar membrane. The current, due to hydrogen permeation through the membrane, recorded continuously as a function of time and was measured by setting the potential on the anodic s of the membrane (the side from which the hydrogen emerges) at –0.3 V vs a Hg/HgO reference electrc This value corresponds to a practically zero concentration of absorbed atomic hydrogen on the surfa The steel membrane on the cathodic side of the cell was polarized potentiostatically, creating conditi for the underpotential deposition of zinc and hydrogen evolution. The details of the permeation cell the auxiliary equipment have been presented earlier [16, 17, 11–15].

Prior to a permeation experiment, a 0.15 mm thick steel membrane was mechanically polished with micron high purity alumina powder to a mirror finish, cleaned in an ultrasonic cleaning bath and satura with hydrogen in 0.1 N H_2SO_4 by maintaining for 10 hours a cathodic current density of 10 mA/cm^2 the steel membrane while immersed in 0.1M H_2SO_4 in a two electrode cell. Then, the membrane v removed from the cell and etched for 20 seconds in a solution containing methyl alcohol and 1% H_2S rinsed with deionized water, dried in air and fitted into the permeation cell.

To avoid passivation or dissolution, the anodic side of the membrane was electroplated with a t layer (0.15–0.20 μm) of palladium. The electrodeposition was carried out in an electrolyte contain $2x10^{-5}$ M $Na_2Pd(NO_2)_4$ using a current density of 100 $\mu A/cm^2$ for two hours with the membrane in permeation cell. Then, the electrolyte was drained off, and the compartment was washed with deioni water and filled with the anodic solution (0.2M NaOH). To keep the electrolyte impurities in the low possible level, the anodic solution, was pre–electrolyzed for at least 24 hours in a separate electrolytic before being put in the permeation cell. The anolyte was kept at –0.3 V vs a Hg/HgO reference electr until the background current was reduced to $3\mu A/cm^2$ or less.

RESULTS AND DISCUSSION

Cyclic Voltammetry Studies. The potentiodynamic curves obtained for the hydrogen evolution r in the supporting electrolyte containing 1 M Na_2SO_4, 0.4 M NaCl and 1 M H_3BO_3 in the prese and absence of zinc ions are given in Figure (1). The curve with no zinc ions is relatively simple, expected. In the presence of zinc ions in the electrolyte, the hydrogen evolution decreases. When start the cathodic sweep at –0.60 V (SCE), two well defined peaks are observed. The first peak occurs at –0 V and is more noble than the Nernst potential of a zinc electrode [E_{rev} = –1.07 V and –1.04 V (SCE) zinc concentrations of $5x10^{-3}$ M and $5x10^{-2}$ M, respectively]. The second peak is at –1.20V (SCE) corresponds to zinc deposition from the bulk of the electrolyte. The underpotential shift obtained fr the experimental data is therefore, 0.250 V. Using the work function values for iron and zinc [18], under potential shift was calculated to be in the range of 0.180 to 0.310 (V) which is consistent with observed experimental values. In the anodic direction, in the presence of zinc ions in the electrolyte, t stripping peaks were observed and correspond to the zinc dissolution and zinc desorption peak. Accord to Figure (1), the zinc deposition peak increases as the zinc content in the electrolyte is increased. T

phenomena was not observed for the process occurring at a UPD region indicating that the UPD of zinc on HY-130 steel has reached an equilibrium value and does not depend on the amount of the dissolved zinc in the electrolyte. Since the underpotential deposition peak in the potentiodynamic curves given in Figure (1), are not clearly visible, the voltammetric curve obtained for a zinc concentration of $2x10^{-3}$ M was enlarged and is presented in Figure (2). The cathodic peak in Figure (2) at –1.0 V (SCE) indicates that an adsorption process occurred on the HY-130 steel. The peak current corresponds to the underpotential deposition of zinc.

The amount of charge used to deposit zinc was determined by integrating the area under the adsorption current peak and is 500 $\mu C/cm^2$. Assuming that the maximum coverage (one layer of closely packed zinc atoms on the electrode surface) requires a charge of Q_{max} = 450 $\mu C/cm^2$ [19], the degree of coverage of zinc (roughness factor = 1) was estimated to be about 1. The roughness factor could vary from 1.4 for well polished surface to 12 for unpolished surface [20–21].

Polarization measurements. Cathodic polarization curves were carried out using bare HY-130 steel electrodes with an area of 0.5 cm^2 in the absence and presence of $2x10^{-3}$ M zinc ions in an electrolyte containing 1 M Na_2SO_4, 0.4 M H_3BO_3 and 0.4 M NaCl. The electrodes were held at different cathodic potentials for five minutes to ensure that zinc was deposited on the surface. The bulk deposition of zinc occured at –1.10 V (SCE), which is consistent with the results obtained using cyclic voltammetry. Thus, several pre-deposition potentials more positive than –1.10 V (SCE), namely, –1.0 V, –0.95 and –0.90 V (SCE) were applied to obtain various coverages of zinc on the surface. The cathodic polarization curves obtained for the hydrogen evolution reaction (h.e.r.) on bare HY-130 steel and on HY-130 steel with potentiostatically predeposited zinc are shown in Figure (3). The presence of zinc ions on the surface inhibited the h.e.r. The results obtained from the polarization studies are summarized in Figure (4), where the percent reduction in the hydrogen evolution current density at –0.65 V (SCE) in the presence (i_p) and absence (i) of predeposited zinc is plotted as function of the applied potential. Accordingly, the h.e.r. was reduced by 58% at –1.0 V (SCE), compared with the corresponding value obtained on a bare HY-130 steel surface.

Hydrogen Permeation Studies on Cathodically Polarized HY-130 Steel. Permeation experiments were performed to clarify the role of zinc on hydrogen entry kinetics. Zinc was predeposited on a HY-130 steel membrane from the same electrolyte used in the polarization experiments. At cathodic potentials more negative than –1.10 V (SCE), a visible deposition of zinc occured on the steel. At applied potentials more positive than –1.10 V (SCE), no bulk deposition of zinc was observed. The membrane had the same open circuit potential of –0.550 V (SCE), as the potential measured before the deposition. To avoid bulk deposition of zinc on steel, our permeation experiments were performed at potentials more positive than –1.10 V (SCE).

To determine the mechanism of the discharge of hydrogen ions on HY-130 steel, experiments were carried out with the supporting electrolyte in which the cathodic current density and the permeation current density was measured as a function of the applied overpotentials. In these experiments, the alloy membrane on the cathodic side of the cell was polarized potentiostatically. At the beginning of a permeation experiment (performed in the absence of zinc ions in the electrolyte) the cathodic side of the steel membrane was held at a potential of –0.58 V (SCE). Then, the potential was stepped to a more negative value after

the hydrogen permeation current reached a steady state value. After the permeation stabilized at appl potential of about –0.87 V (SCE), the applied potential was switched off, and the decay curve was recor The steady state hydrogen permeation current densities, shown in Figure (5), increased with the appl cathodic potential. Figure (6) shows the dependence of the steady state hydrogen evolution reaction cur and hydrogen permeation current on the overpotential. At low overpotentials, the slopes in Figure $-\frac{\partial\eta}{\partial lgi_c}$ = (240 to 900 mV/decade) and $-\frac{\partial\eta}{\partial lgj_\infty}$ =220 to 900 and are not consistent with the diagnostic crit for coupled discharge recombination mechanism for hydrogen evolution reaction; 2.3x2RT/F (T=298.1 and 2.3x4RT/F(T=298.15K), respectively (22,30). Figure (7) shows the dependence of the steady s permeation current upon the hydrogen cathodic current. Also in Figure (7), a linear dependence obtained between j_∞ and i_c, and is not consistent with the square root dependence of the permeat current, predicted by the coupled discharge-recombination mechanism (22,30). The same relations (a linear dependence between j_∞ and i_c) was observed in several sources on palladium (23–26) and i (27–29) and cannot be explained by the existing mechanism of hydrogen entry into iron (22,30). Accord to this mechanism, the hydrogen enters the metal lattice from the adsorbed state. However, Bagotsk (31) and Frumkin (32) have postulated an alternative mechanism, in which the hydrogen enters a meta protons, i.e. without the intermediate chemisorption stage. The intermediate state through which hydro enters the metal lattice is not identical to the adsorbed intermediate. Bogotskaya (31) and Frumkin (suggest that both reactions (absorption of hydrogen and hydrogen evolution) occur independently. In case the reaction at the cathode surface is as follows:

$$H^+ + M + e \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} MH_{abs}$$

$$H^+ + M + e \overset{k_2}{\rightarrow} MH_{ads} \overset{k_3}{\rightarrow} \frac{1}{2}H_2 + M$$

where k_1, k_{-1}, k_2, and k_3 are the rate constants. Bockris et al. (33) check this model by solving permeation equation:

$$j_\infty = F\left[k_1\left(1 - \frac{C_o}{C_s}\right)e^{-\alpha_1 a\eta} - k_{-1}C_o e^{(1-\alpha_1)a\eta}\right]$$

where a=F/(RT); F is Faraday's constant; C_0 is the hydrogen concentration directly beneath the cath surface; C_s is the concentration of hydrogen in the lattice at hydrogen saturation (the saturation value C_0) and α_1 is the transfer coefficient in reaction 1. Solving this equation for the limiting case where permeation current depends on the diffusivity and the membrane thickness they obtained the follow dependence for the permeation current at high negative potentials where the metal approaches hydro saturation:

$$j_\infty = \frac{FDC_s}{L}$$

Solving for low overpotentials, the authors concluded that the direct entry hydrogen mechanism should sh

$$j_\infty \propto i_c^2$$

dependence for which there is not any existing experimental evidence in literature. Thus, they conclu that the model proposed by the Russian scientists does not predict the observed results and is unable

explain the hydrogen permeation through a membrane. However, assuming that the metal is far from the saturation point [$1 - \frac{C_0}{C_s} \approx 1$] and that the backward reaction constant in Equation (1) is negligible, then Equation (3) becomes

$$j_\infty = Fk_1 e^{-\alpha_1 a\eta} \tag{6}$$

by taking the natural log of Equation (6),

$$\ln j_\infty = \ln (Fk_1) - \alpha_1 a\eta \tag{7}$$

and then

$$-\frac{\partial \eta}{\partial \ln j_\infty} = \frac{RT}{\alpha_1 F} \tag{8}$$

According to Iyer, Pickering and Zamanzadeh (22), the Langmuir hydrogen surface coverage can be written according to Equation (2) in the form:

$$i_c = i_0' e^{-\alpha_2 a\eta} \tag{9}$$

$$\ln i_c = \ln (i_0') - \alpha_2 a\eta \tag{10}$$

and

$$-\frac{\partial \eta}{\partial \ln i_c} = \frac{RT}{\alpha_2 F} \tag{11}$$

Dividing Equation (11) by Equation (8) one can obtain

$$\frac{d \ln j_\infty}{d \ln i_c} = \frac{\alpha_1}{\alpha_2} \tag{12}$$

By integrating and rearranging, Equation (12) gives

$$j_\infty = K i_c^{\frac{\alpha_1}{\alpha_2}} \tag{13}$$

where K is an integrating constant. If α_1/α_2=1, the hydrogen permeation current vs hydrogen cathodic current dependence becomes linear and describes the results obtained by Hoare et al (23), by Schudiner et al. (24), by Early et al. (25), by Heath (26), by Raczynski (27), by Zakroczymski et al. (28) and by Evseev (29). Our results also show that direct hydrogen proton entry is possible and predicts $j_\infty \propto i_c$. Notice that Equation (6) does not seem to be a valid limiting case for the permeation equation, since it shows that the hydrogen permeation current does not depend on the diffusivity and the thickness. However, there has been speculation that in some cases, the hydrogen permeation does not depend on the membrane thickness and diffusivity. For cathodic current densities less than 800 μA/cm^2, Bowker and Piercy (34) reported that the same values for the steady state permeation current were obtained on a palladium membrane with three different thicknesses, namely, 0.15, 0.25 and 0.55 mm. They also found that at low cathodic currents the same permeation currents could be obtain on tin plated mild steel (L=0.35mm) on 410 stainless steel (L=0.5 mm), and Fe (L=0.25 and L=0.43 mm). Hoare and Shuldiner (23), using cathodic current densities

up to 3.0 mA/cm^2, also observed that the hydrogen permeation rate is independent of the Pd membr thickness (for L=0.025: L=0.050; L=0.075 and L=0.100 mm). It is important to note that in every c where this phenomena was observed, the relation $j_\infty \propto i_c$ was experimentally obtained. We may offer following explanation for the observed phenomena. The second term in Equation (3) may be neglec when either k_{-1} is very small or the overpotential is very large. Because it has been found in the literat that $j_\infty \propto \sqrt{i_c}$ is valid at high overpotentials, the results obtained in this study can be explained assuming a small backward reaction rate constant, k_{-1} in Equation (3). Neglecting the backward react due to small k_{-1} means that the reaction in Equation (1) is not in equilibrium and that the rate of hydro diffusion through the membrane is comparable with the forward rate of the reaction in Equation (1). T may occur only when the hydrogen atom diffusion rate is faster than the absorption rate. In such a c the absorbed hydrogen immediately diffuses from the anodic side of the membrane which requires metal to have a high diffusivity. Therefore, the permeation was found to be independent of the membr thickness and hydrogen diffusivity only on palladium and iron (high diffusivity metals) and their allo This phenomena was not observed on nickel and its alloys which have low diffusivity. At high curr densities, since the membrane does not have the ability to transfer the adsorbed hydrogen immediately, hydrogen permeation rate depends on the thickness and diffusivity of the membrane.

In Figure (6), the dependence of the steady state hydrogen evolution reaction current and hydro permeation current on overpotential is not linear as predicted by Equation (6) and Equation (9). Fig (6) also shows that at high overvoltages, the cathodic current is approaching a limiting value which n be a mass transfer limiting current. The following explanation may explain the observed results. Equat (9) was derived assuming the sytem had a large mass transfer rate or was at low current densities so t the hydrogen surface concentrations [C(x=0)] are close to the bulk concentrations [C*]. By including mass transfer factor, Equation (9) becomes:

$$i_c = i_0'(1-\theta_s)\frac{C(x=0)}{C^*}e^{-a\alpha_c\eta} \quad (10)$$

According to Bard and Faulkner (35)

$$\frac{C(x=0)}{C^*} = 1 - \frac{i_c}{i_l} \quad (11)$$

where i_l is the limiting current density. Inserting Equation (15) into Equation (14) and rearranging, can obtain:

$$\frac{i_c i_l}{i_l - i_c} = i_0'(1-\theta_s)e^{-a\alpha_2\eta} \quad (12)$$

taking the logarithm of Equation (16), we have

$$\log\left(\frac{i_c i_l}{i_l - i_c}\right) = \log\left(i_0'(1-\theta_s)\right) - \frac{a\alpha_2\eta}{2.303} \quad (13)$$

A linear relationship was obtained in Figure (8), where $\log\left(\frac{i_c i_l}{i_l - i_c}\right)$ and $log\left(\frac{j_\infty j_l}{j_l - j_\infty}\right)$ are plotted a function of η consistent with derived Equation (17). By fitting and extrapolating the experimental cur

the hydrogen limiting current was determined to be $i_l = 600\mu A/cm^2$. Including the mass transfer factor in the permeation equation, Equation (7) becomes:

$$\log\left(\frac{j_\infty j_l}{j_l - j_\infty}\right) = \ln(Fk_1) - \frac{\alpha_1 a\eta}{2.303} \tag{18}$$

The permeation limiting value j_l, was estimated by fitting the experimental data and is equal 27 μA/cm^2. Using the intercepts and slopes in Fig.8, the transfer coefficient α_1 and α_2, rate constant k_1 and i'_o were calculated to be: $\alpha_1=\alpha_2=0.39$, $k_1=1.79\text{x}10^{-13}$mol/(cm^2 s), and $i'_o=5.34\text{x}10^{-7}$A/cm^2. The equation with mass transfer correction factor corresponds to Equation (13) which results in:

$$\frac{j_\infty j_l}{j_l - j_\infty} = K\left(\frac{i_c i_l}{i_l - i_c}\right)^{\frac{\alpha_1}{\alpha_2}} \tag{19}$$

Hydrogen Permeation Studies on Cathodically Polarized HY-130 Steel in the Presence of Zinc Ions. The permeation experiments in the presence of zinc were repeated in the presence of a supporting electrolyte (1M Na_2SO_4, 0.5 M H_2SO_4) in which $2\text{x}10^{-3}$ M Zn^{+2} was added. In the absence of zinc ions, the experiments were started at potential of –0.650 V (SCE) and increased in steps up to an applied potential of – 0.870 V (SCE). In Figure (9), the permeation current densities decrease sharply compared with those in Figure (5). The results from the permeation experiments are summarized in Figure (10), where the cathodic current density and the steady state permeation current density are plotted as a function of the overpotential. Both the cathodic hydrogen evolution current density and the steady state hydrogen permeation current density decreased in the presence of underpotential deposited zinc on HY-130 steel, compared with the same dependence in Figure (6), obtained in the absence of zinc. According to our analysis, a linear dependence of the steady state permeation current on the hydrogen cathodic current in Figure (11) indicates a hydrogen proton direct entry mechanism.

In Figure (12), $\log\left(\frac{i_c i_l}{i_l - i_c}\right)$ and $\log\left(\frac{j_\infty j_l}{j_l - j_\infty}\right)$ are plotted as a function of η. By fitting and extrapolating the experimental curve, the limiting current i_l was found to have a value of 145μA/cm^2. Using the same procedure, j_l was estimated to be 2.35 μA/cm^2 . Using the intercepts and slopes in Figure (12), the transfer coefficients α_1 and α_2, the rate constant k_1 and the exchange current density i'_o were calculated to be: $\alpha_1=\alpha_2=0.39$, $k_1=4.60\text{x}10^{-14}$mol/(cm^2 s), and $i'_o=3.21\text{x}10^{-7}$A/cm^2. Values of i'_o and k_1 in the presence of zinc were reduced by 40% and 74% respectively compared with the same values obtained in the absence of zinc ions in the electrolyte. Figure (13) shows a plot of $\log\left(\frac{j_\infty j_l}{j_l - j_\infty}\right)$ vs $\log\left(\frac{i_c i_l}{i_l - i_c}\right)$ in the presence and absence of zinc, which shows a linear relationship with a slope of 1, consistent with Equation (19).

The hydrogen entry efficiency, defined in % as $\frac{j_\infty}{i_c}$x100, is plotted *vs* overpotential in Figure (14). In the presence of underpotential deposited zinc the hydrohen entry efficiency decreased by a factor of 3.

CONCLUSION

The polarization experiments show that deposited zinc effectively inhibits the discharge of hydrogen up to 58% compared with the values obtained on bare HY-130 steel. The hydrogen permeation studies performed in the presence of zinc ions in the electrolyte show that the underpotential deposition of a monolayer of zinc decreased the degree of hydrogen ingress into HY-130 steel. In the presence of a monolayer coverage of zinc on the substrate, the hydrogen entry efficiency was decreased by a factor of

three. The hydrogen proton entry mechanism was found and the mass transfer term was introduced the model to interpret the experimental data. The hydrogen entry rate constant was reduced 74% in presence of zinc.

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LIST OF SYMBOLS

a = F/RT, a constant, V^{-1}.

b = L/(FD), a constant, mol $(A\ cm)^{-1}$.

$C_{Zn^{+2}}$ = zinc concentration, mol cm^{-3}.

C_o= hydrogen concentration beneath the cathode surface, mol/cm^3.

C_s= saturation value of C_o, mol/cm^3.

C*= hydrogen bulk concentration, mol/cm^3.

D = hydrogen diffusion coefficient, $cm^2\ s^{-1}$.

E_{app} = applied potential, V.

E^{eq} = equilibrium potential for the h.e.r, V.

E_c = cathodic potential, V.

F = Faraday constant, 96,487 C/eq.

i = current density, A/cm^2.

i_c = cathodic current density, A/cm^2.

$i_{h.e.r.}$= hydrogen evolution reaction current density, A/cm^2.

i_l= mass transfer limiting current density of i_c, A/cm^2.

i_o = exchange current density, A/cm^2.

$i_o' = \frac{i_o}{1-\theta_e}$, A/cm^2.

j_l= mass transfer limiting current density of j_∞, A/cm^2.

j_t = transition hydrogen permeation current density, A/cm^2

j_o = initial hydrogen permeation current density, A/cm^2.

j_∞ = steady state hydrogen permeation current density, A/cm^2.

k_1= absorption constant, $mol(cm^2 s)$

k_{-1}= adsorption constant, cm/s.

L= membrane thickness, cm.

Q= amount of charge C/cm^2.

t= time, s.

R = gas constant, 8.3143 $J(mol\ K)^{-1}$.

t = time, s.

T = temperature, K.

v = scan rate, mV/s.

Greek Symbols

α_1, α_2 = transfer coefficients, dimensionless.

θ_e = equilibrium hydrogen surface coverage, dimensionless.

θ_H = hydrogen surface coverage, dimensionless.

η = overpotential, $[E_{app} - E^{eq}]$, (V).

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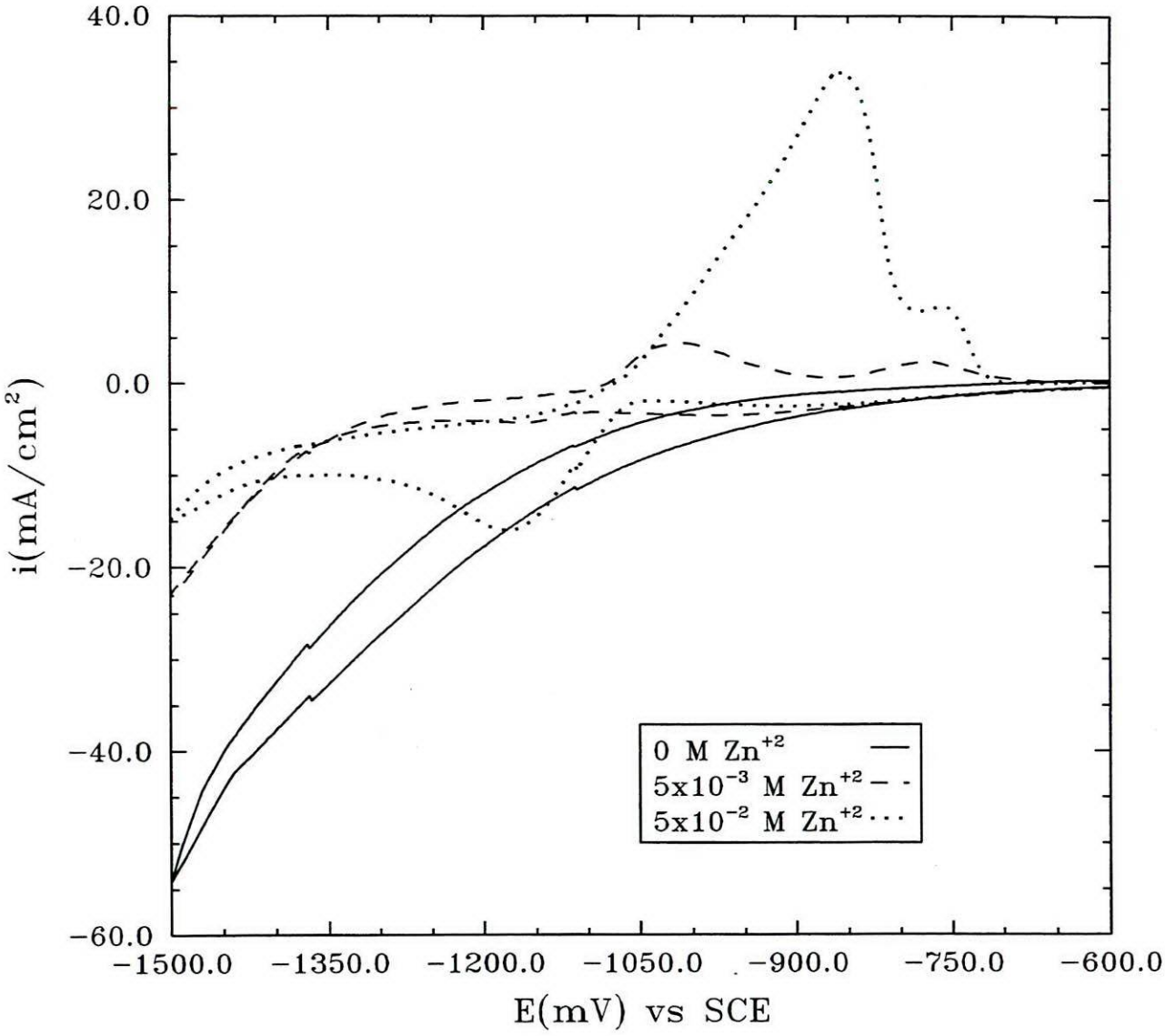

Fig.1 Cyclic voltammetry curves obtained on HY-130 in the absence and presence of Zn^{+2},sweep rate,v=500mV/s.

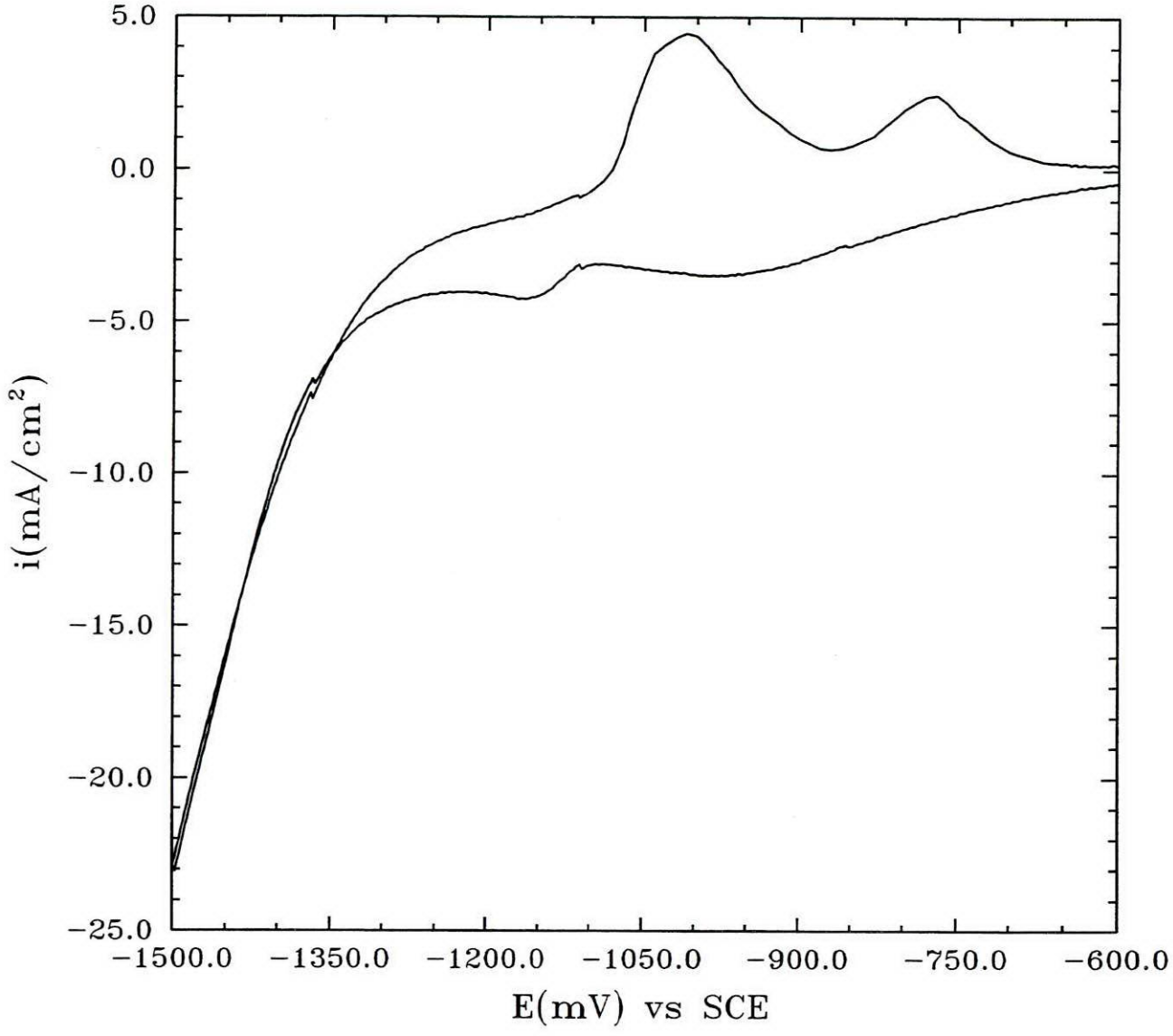

Fig.2 Cyclic voltammetry curves obtained on HY−130 in the presence of $5x10^{-3}$ Zn^{+2},sweep rate=500mv/s.

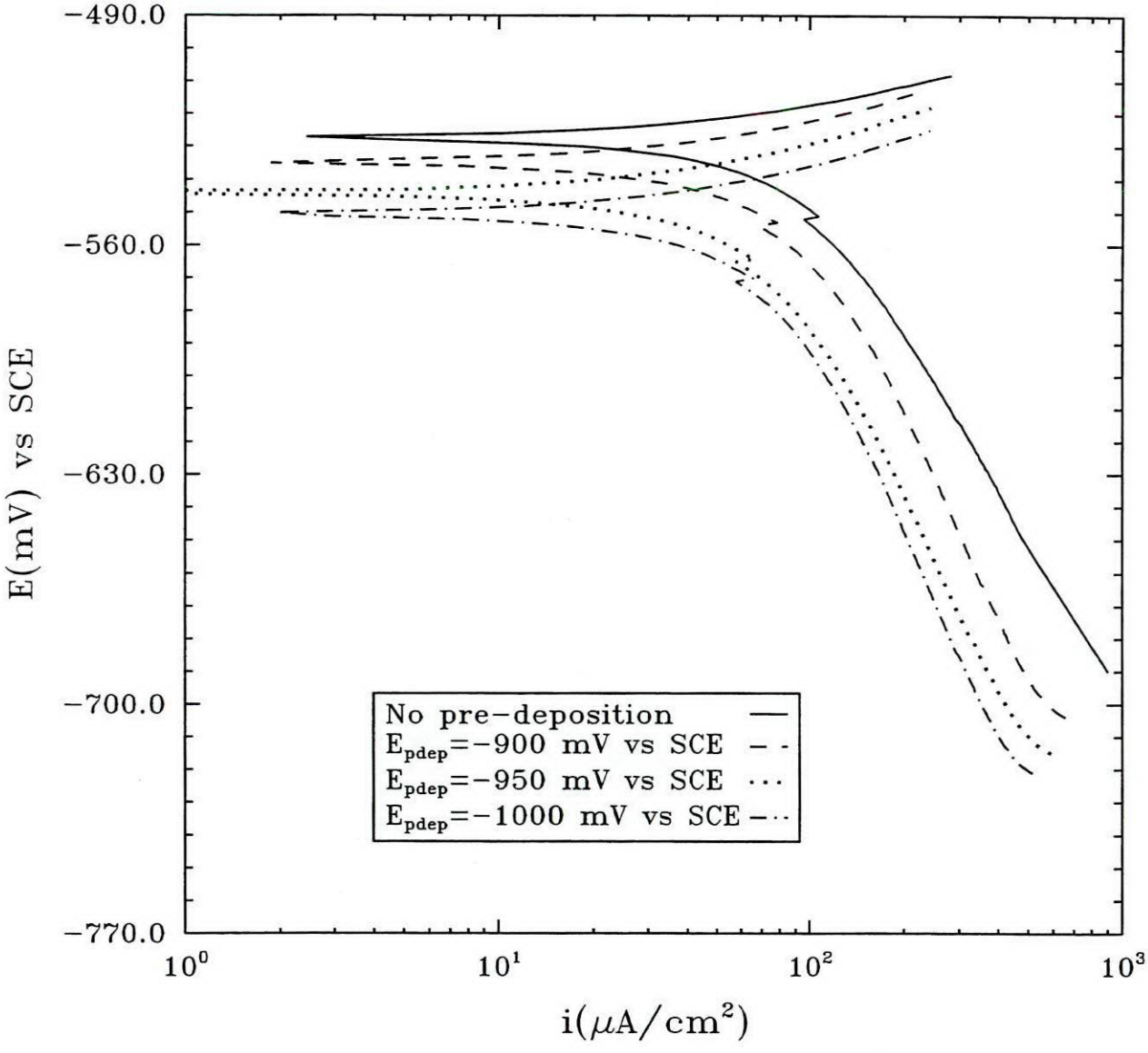

Fig.3 Tafel curves on HY−130 with and without the predeposition of zinc. The predeposition time=5 min. v=1mV/s.

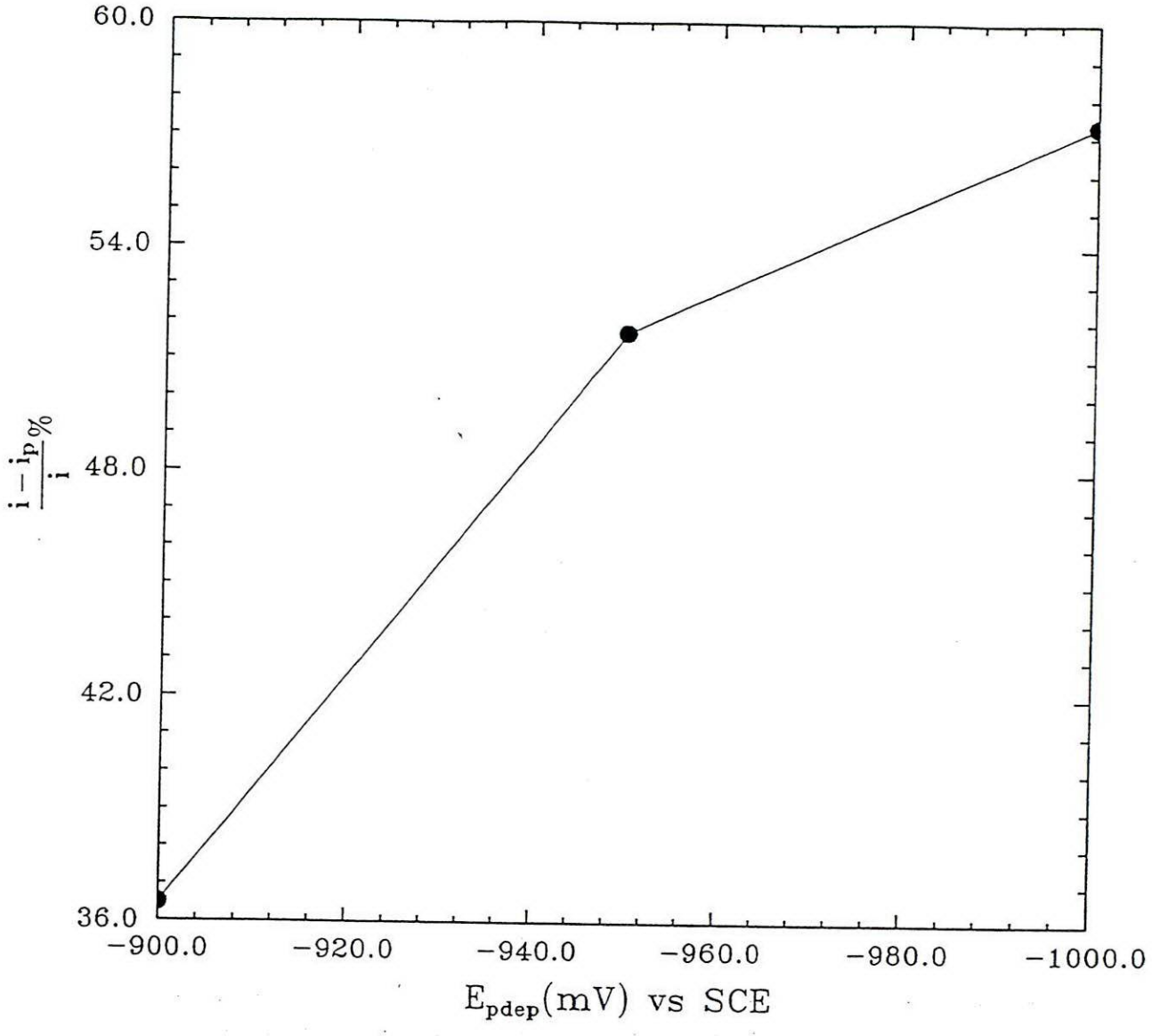

Fig.4 Dependence of hydrogen evolution current on HY−130 at E=−0.65V (SCE) as a function of the applied potential.

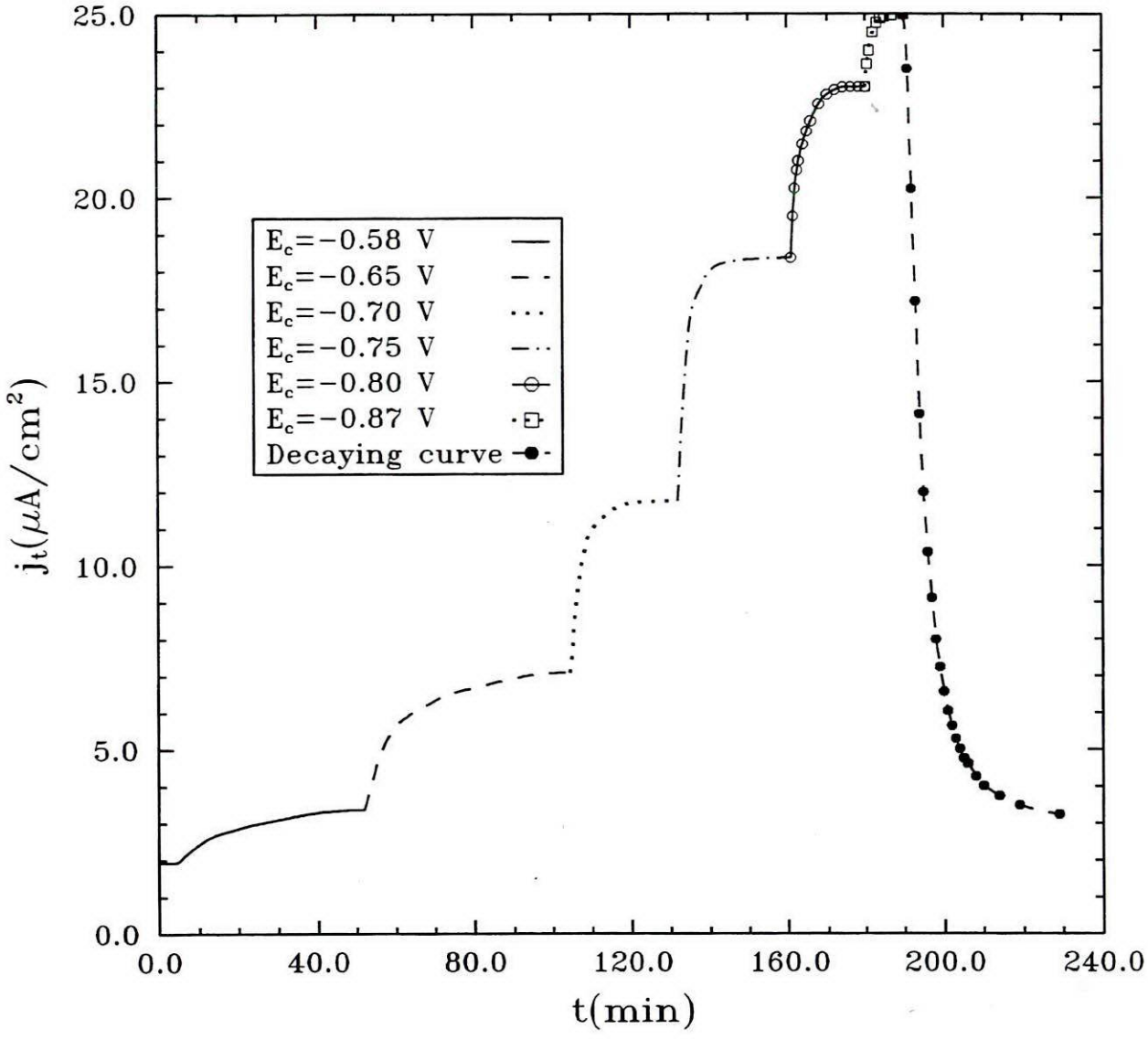

Fig.5 The atomic hydrogen permeation transients through a HY−130 membrane in the absence of zinc.

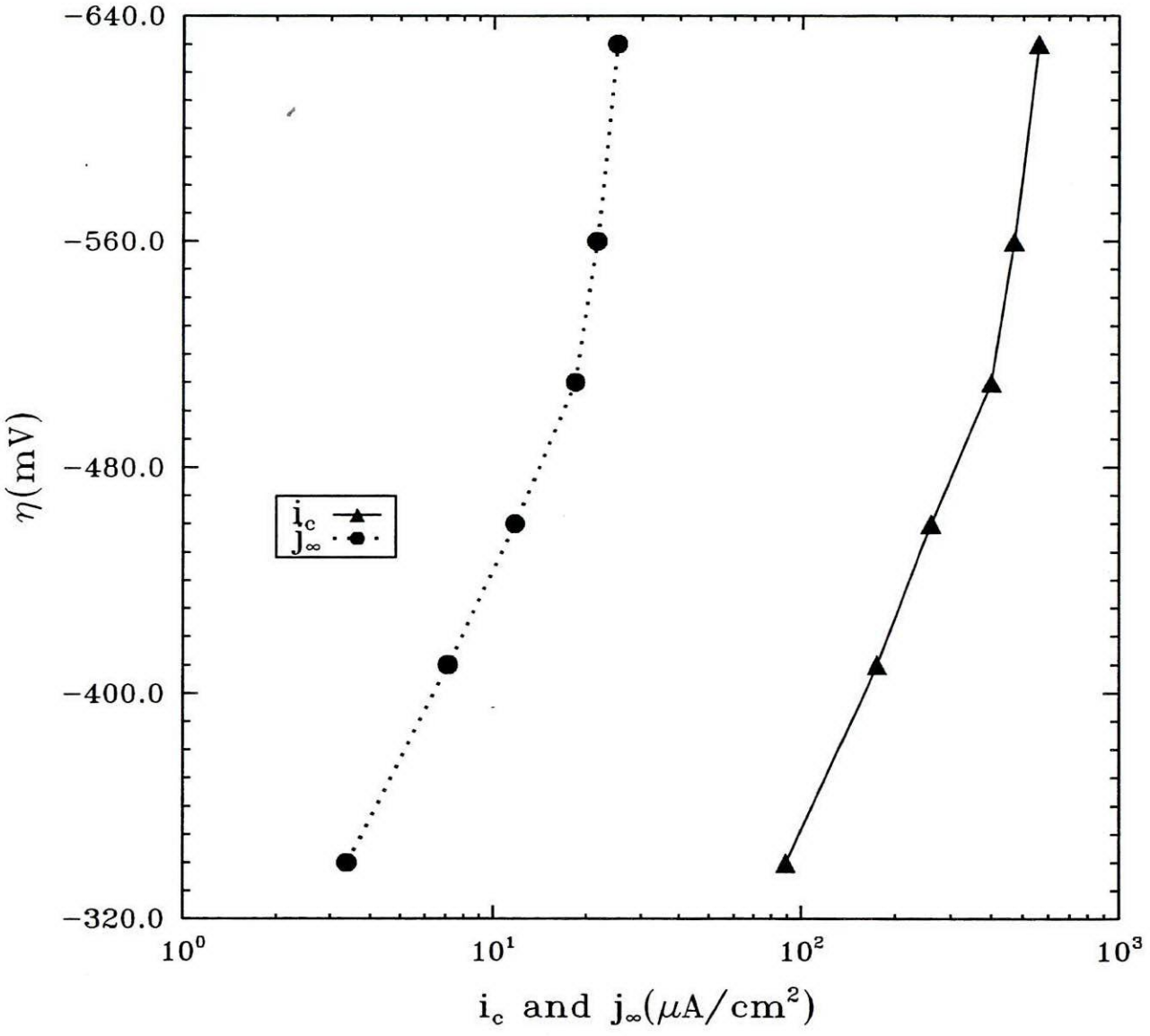

Fig.6 Dependence of cathodic current density and permeation current density on overpotential in the absence of zinc.

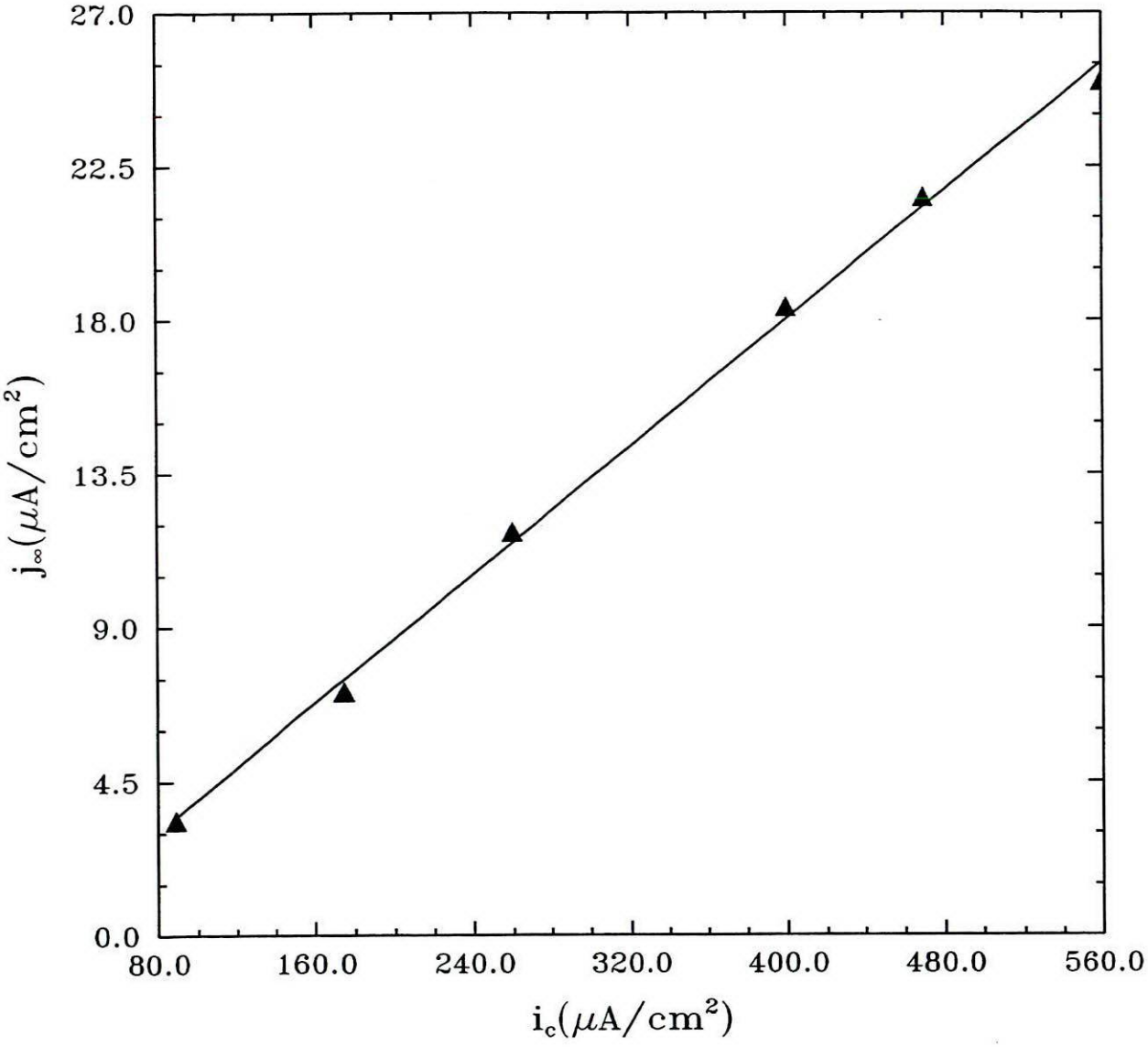

Fig.7 Hydrogen permeation current density as a function of cathodic current density in the absence of zinc ions.

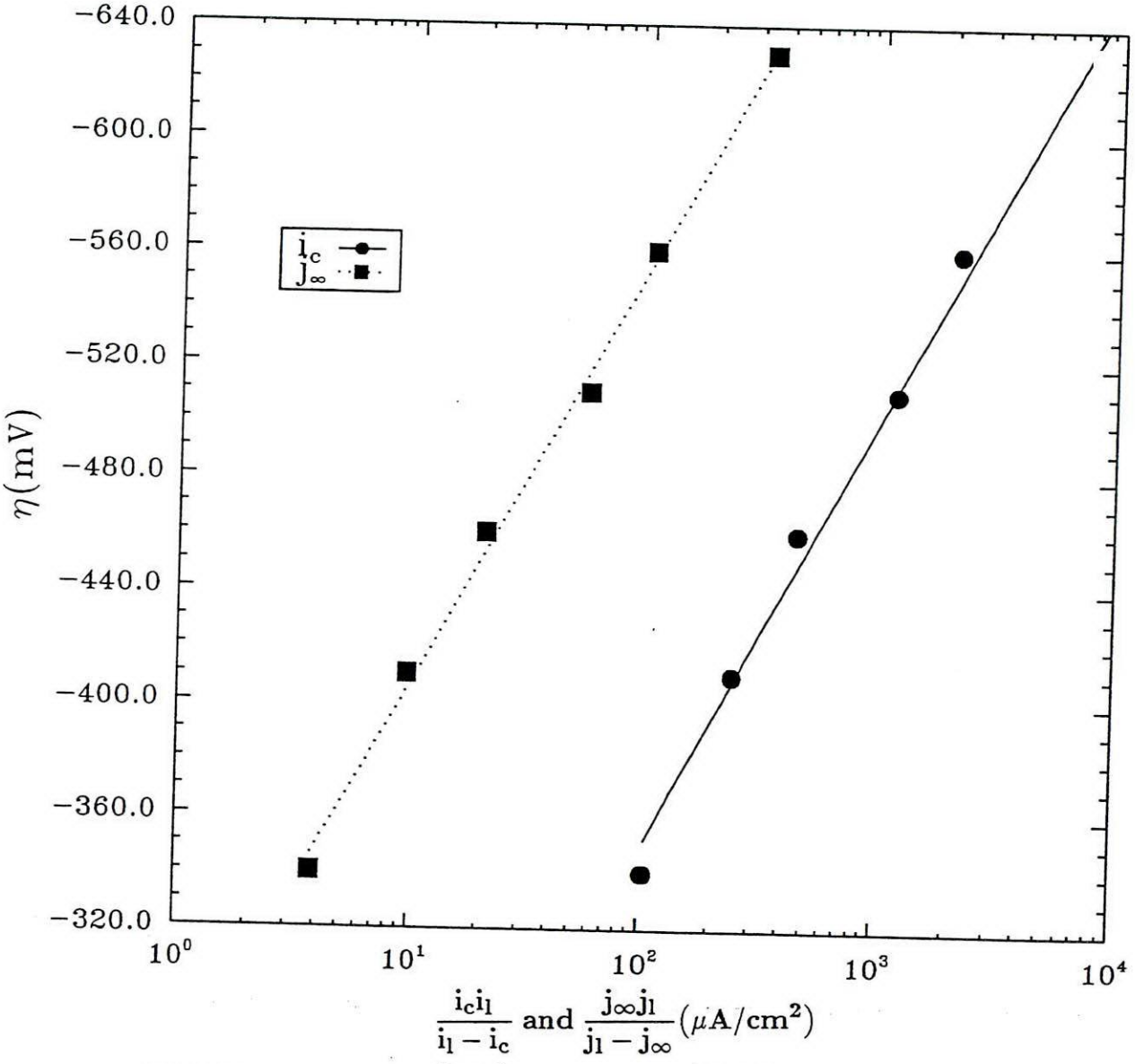

Fig.8 Plots of η vs log $\left(\frac{i_c i_l}{i_l - i_c}\right)$ and η vs log $\left(\frac{j_\infty j_l}{j_l - j_\infty}\right)$ in the absence of zinc.

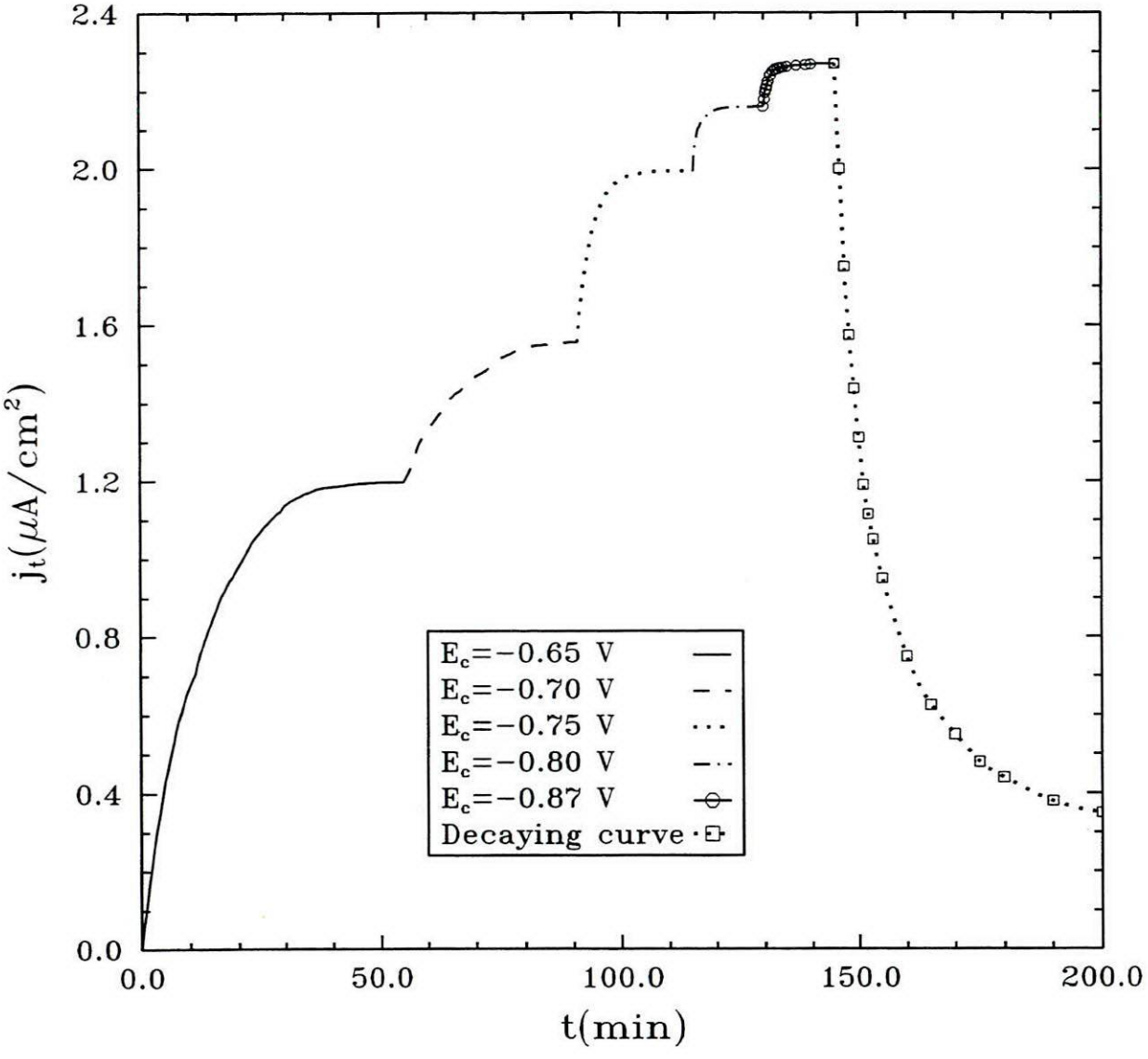

Fig.9 The atomic hydrogen permeation transients through a HY−130 membrane in the presence of zinc.

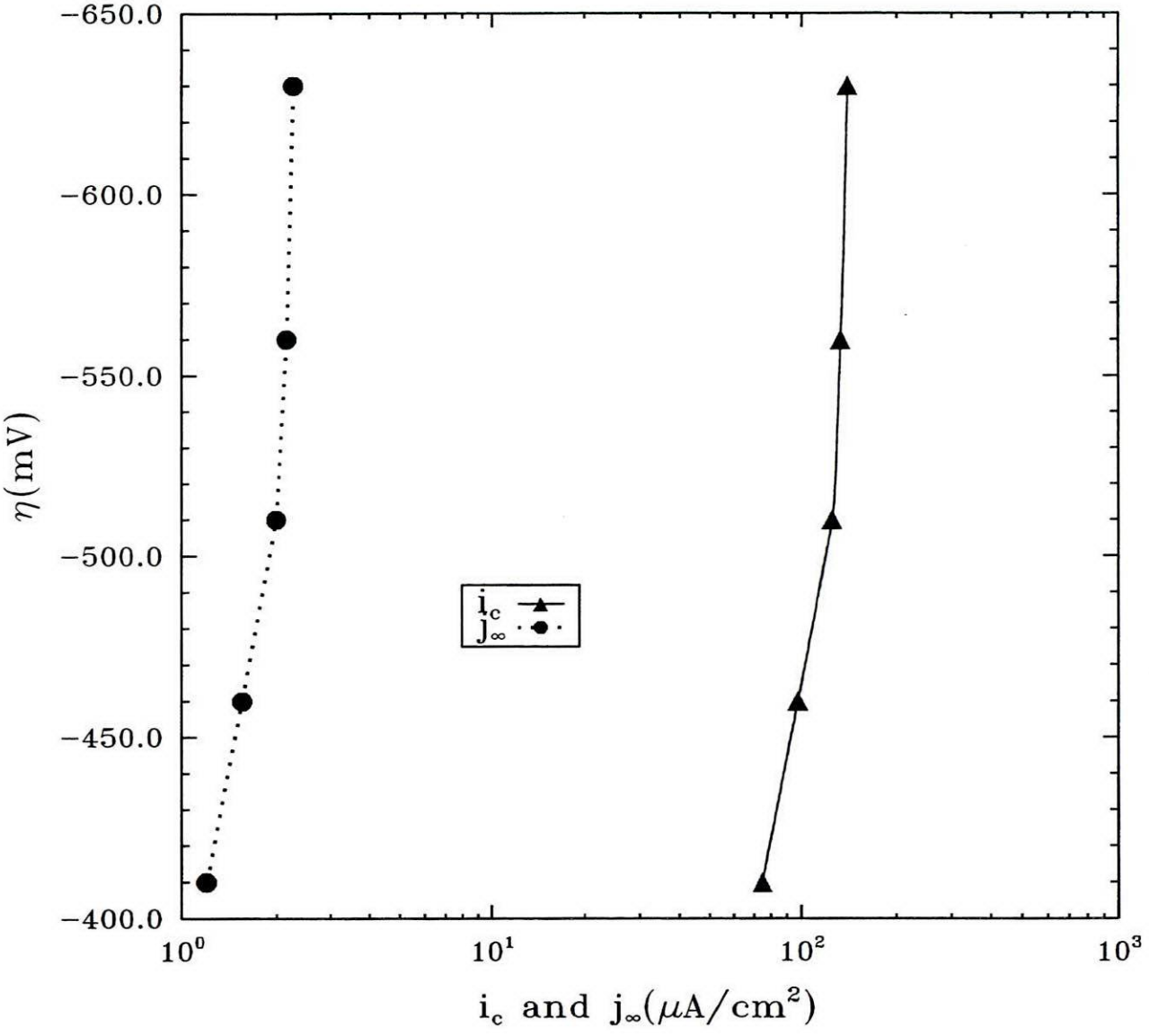

Fig.10 Dependence of cathodic current density and permeation current density on overpotential in the presence of zinc

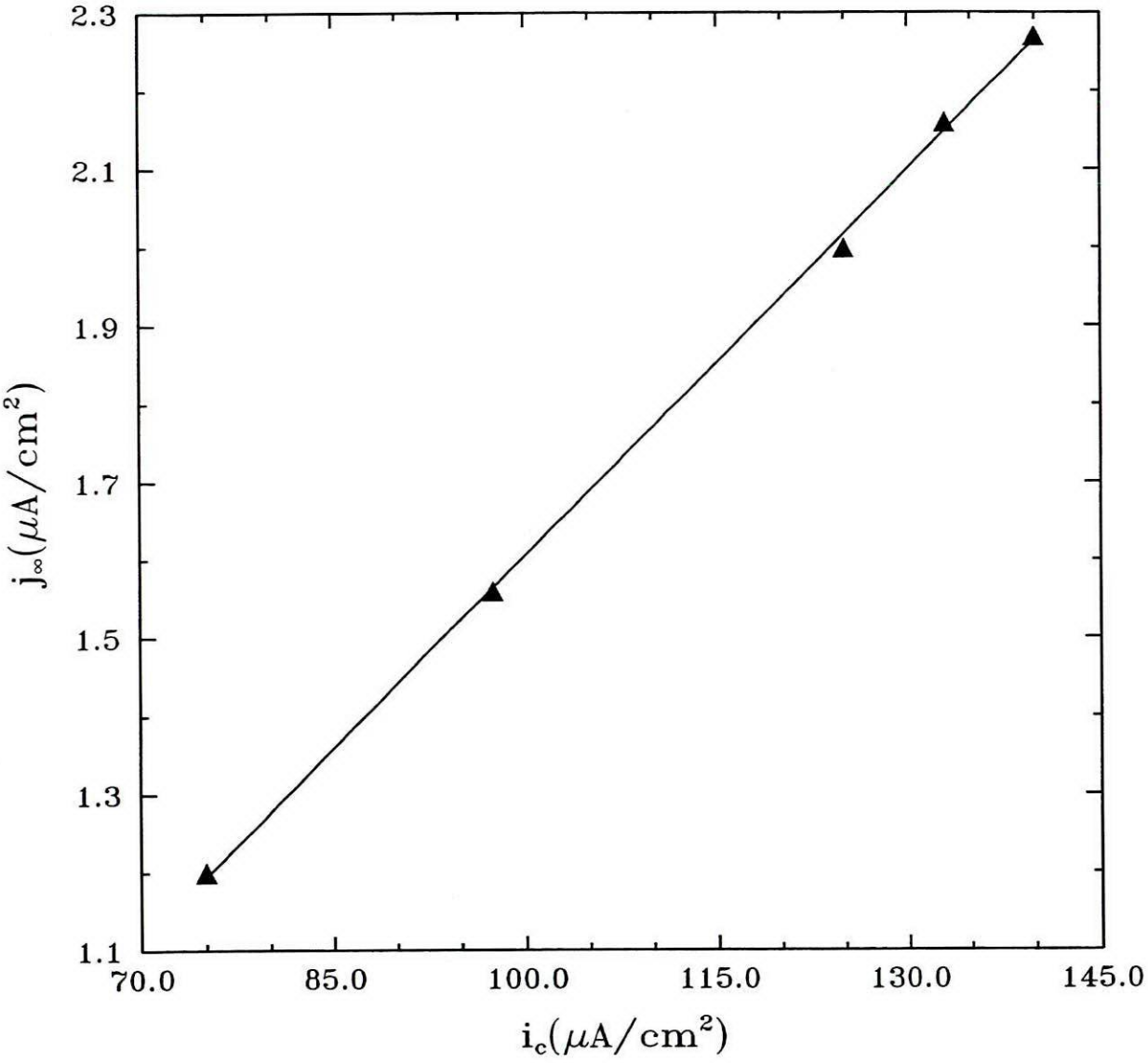

Fig.11 Plot of hydrogen permeation current density vs cathodic current density in the presence of zinc.

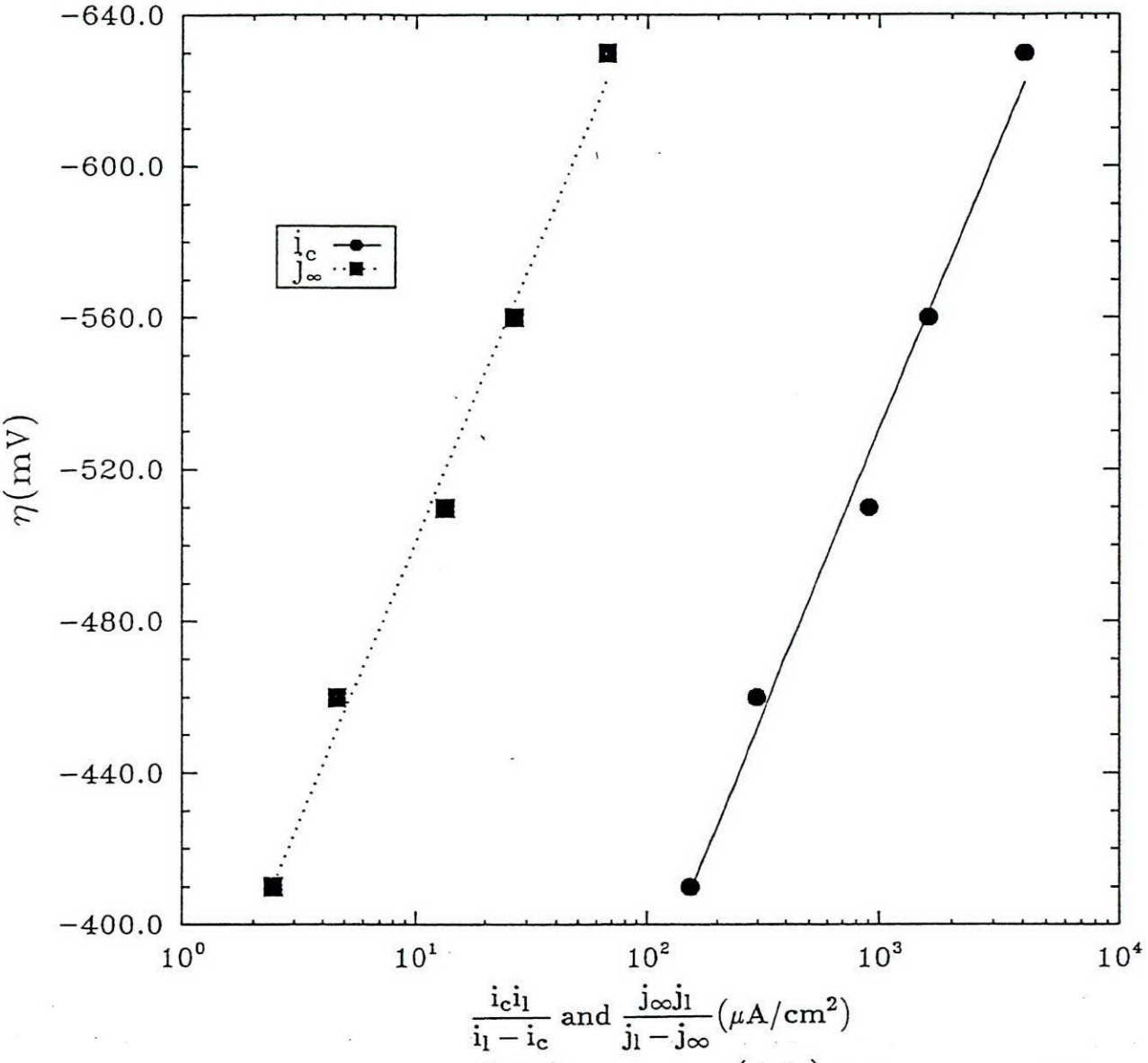

Fig.12 Plots of η vs log $\left(\frac{i_c i_l}{i_l - i_c}\right)$ and η vs log $\left(\frac{j_\infty j_l}{j_l - j_\infty}\right)$ in the presence of zinc.

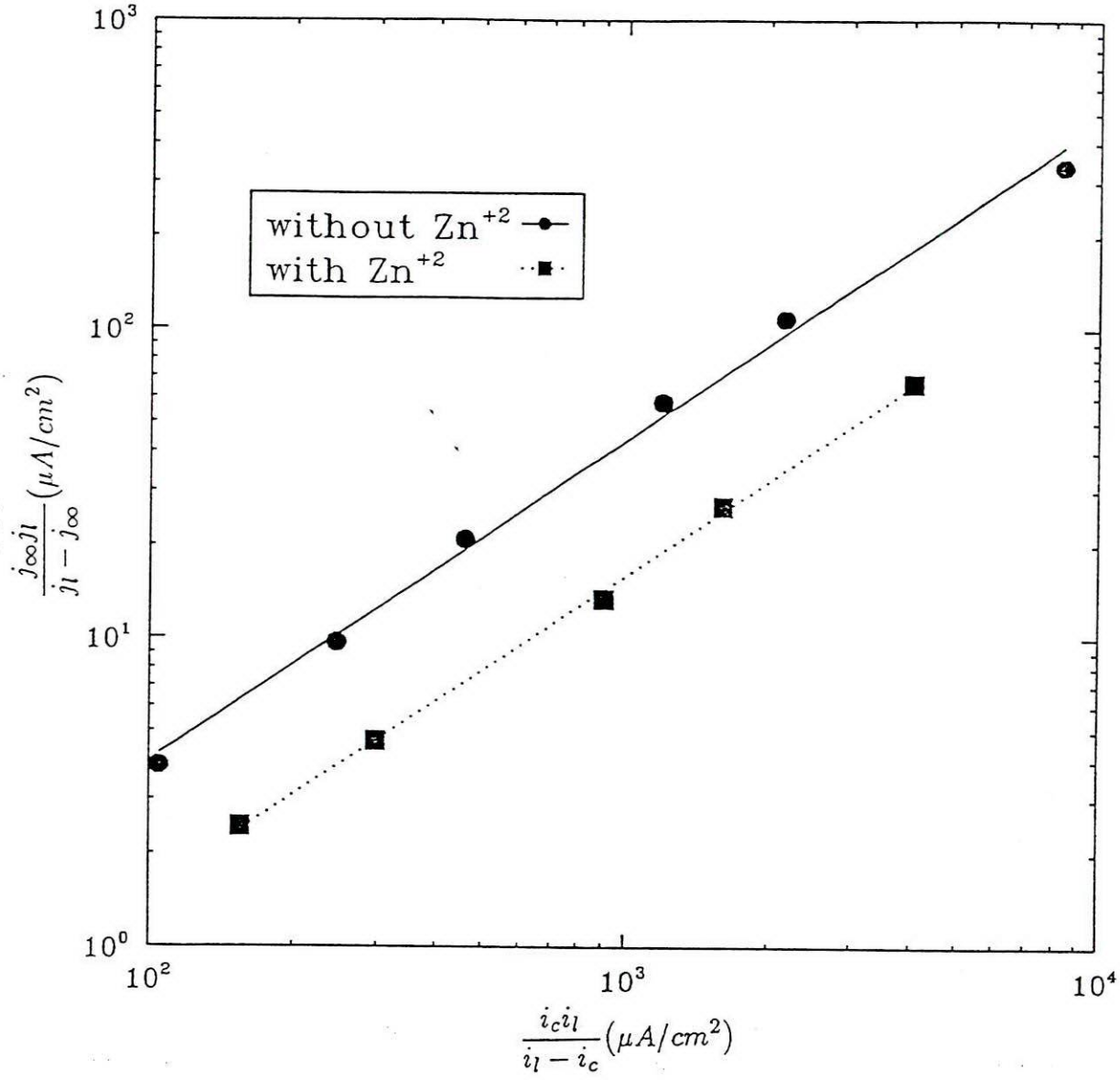

Fig.13 Plots of log $\left(\frac{j_\infty j_l}{j_l - j_\infty}\right)$ vs log $\left(\frac{i_c i_l}{i_l - i_c}\right)$ in the absence and presence of zinc.

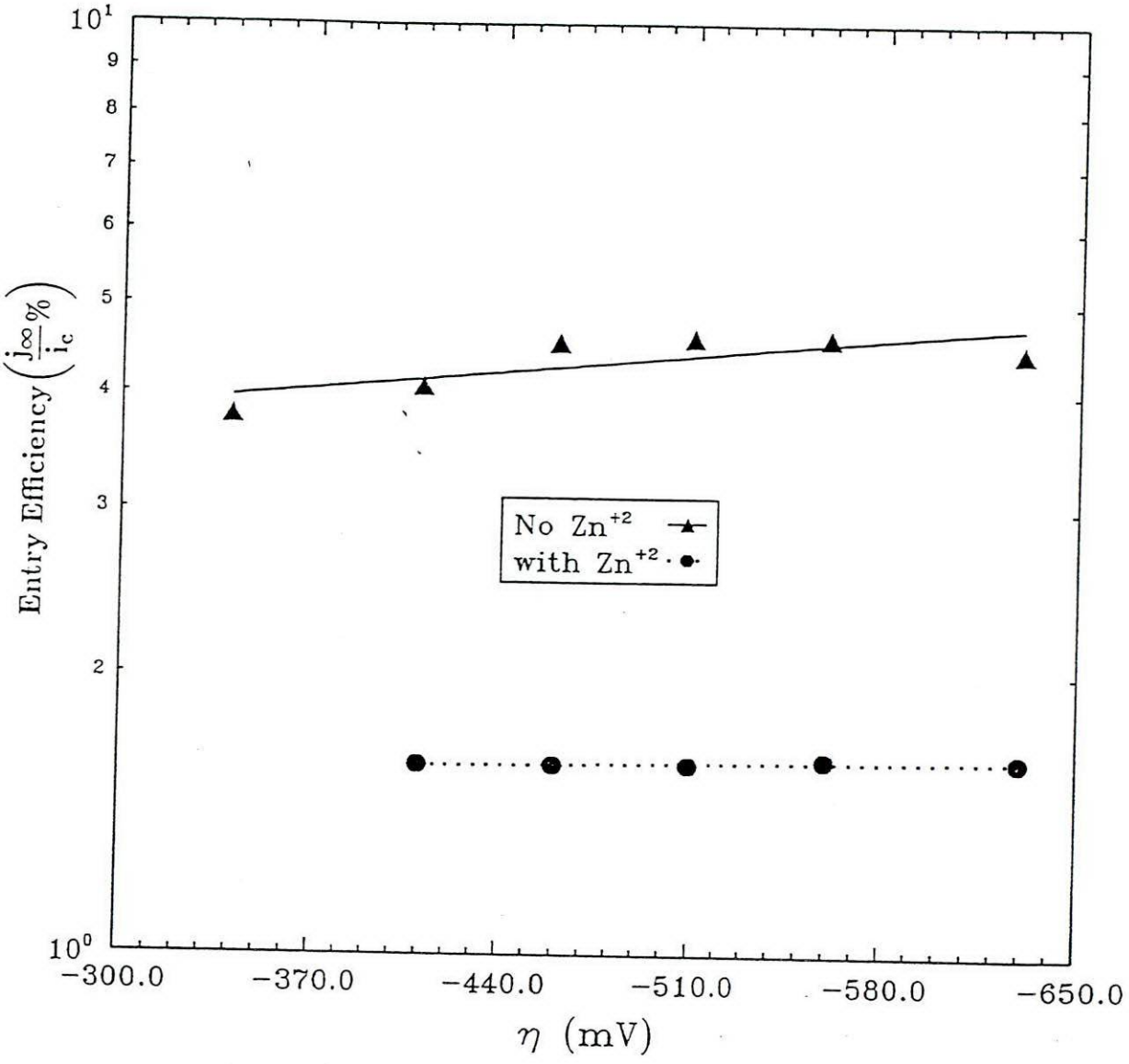

Fig.14 Dependence of the hydrogen entry efficiency as a function of applied cathodic overpotential.

ELECTRODEPOSITION OF IRON-NICKEL ALLOYS IN THE PRESENCE OF ORGANIC ADDITIVES-SOLUTION CHEMISTRY OF Fe-Ni PLATING BATH

S. N. Popova, B. N. Popov Ken Ming Yin and R. E. White
Department of Chemical Engineering
University of South Carolina,
Columbia, SC, 29208

ABSTRACT

The solution chemistry was studied by determining the Fe-Ni plating bath equilibrium concentrations at various pH levels. It was found that $Ni(OH)_2$ precipitates preferentially instead of $Fe(OH)_2$. A small change in pH at the electrode surface had dramatic effects on alloy composition and surface morphology. The plating bath concentrations vs pH plot illustrates the chemical equilibrium conditions and also serves as a guide for solution behaviors of the electroactive species in an Fe-Ni codeposition process.

INTRODUCTION

Ni-Fe deposition is classified as an anomalous codeposition (1–10). At most operating conditions, the less noble species Fe has much higher deposition rate than Ni. According to Dahms (1) and Dahms and Croll (2), anomalous codeposition appears to be closely related to the local pH rise at the surface. According to the stability constants of $Ni(OH)_2$ and $Fe(OH)_2$, the preferential precipitation of $Fe(OH)_2$ cannot be justified as suggested by Dahms and Croll. The objective of this work is to study the pH dependence and the solution chemistry of Fe-Ni plating bath and to determine the best deposition conditions when galvanostatic pulse plating is used to deposit Fe-Ni alloy from sulphate electrolytes containing organic additives.

EXPERIMENTAL

Two types of plating solutions were used. A basic plating solution contained nickel sulphate (0.5M), iron sulphate (0.05M) and sodium sulphate (0.5 M). The second type of plating solution contained ingredients from the basic bath + different concentrations of organic additives. The bath pH's were adjusted to 3 by using 20 % H_2SO_4 and experiments were carried out at room temperature for all baths. Copper discs with exposed area of 0.458 cm^2 were used as working electrodes; the anode used was a large platinum gauze and a SCE served as the reference electrode. Before each experiment, the copper disc was polished by using 400 and 600 grit sand papers and then by using 0.3 and 0.05 μm aluminum powder. The electrode was then cleaned with acetone and 10% H_2SO_4 solution before plating. Pulse current was applied by the Potentiostat/galvanostat Model 273 (EG&G PAR). The applied pulse current and associated potential responses were monitored by an

oscilloscope (Textronix 2430A digital oscilloscope). The peak cathodic potential (at the end of T_{on}) and the peak anodic potential (at the end of T_{off}) were recorded as E_p and E_r, respectively. The pulse period (T_{on}) and relaxation time were set at 100 ms each, and i_p varied. The duty cycle of 0.5 was found to be most useful in the experiments where i_p varied.

RESULTS AND DISCUSSION

Solution Chemistry of Fe-Ni Plating Bath. The solution chemistry was studied by determining the Fe-Ni plating bath equilibrium concentrations at various pH levels. The concentration of all electroactive species in the bath were calculated by using various element balances, equilibrium conditions, and electroneutrality conditions for a specified pH. In order to obtain the whole spectrum as a function of pH, suitable amounts of NaOH and H_2SO_4 were utilized in the computation. The equations were solved by using the Newton-Raphson iterative method. Evaluated solution equilibrium concentrations as a function of pH are presented in Figure (1). In Figure (1), three regions are considered. In the first region all electroactive species are completely dissolved. In the second region, $Ni(OH)_2$ precipitates at a higher pH, while no $Fe(OH)_2$ precipitation occurs. In the third region both $Ni(OH)_2$ and $Fe(OH)_2$ precipitation occur at high pH levels. The total materials are the sum of 1000 g of H_2O +147.35 g [0.5 M] $NiSO_4$ + 13.89 g [0.05 M] $FeSO_4$ + 125 g [0.5 M] Na_2SO_4. As shown in Figure (1), at equilibrium, for pH<6.6, there was no precipitation.

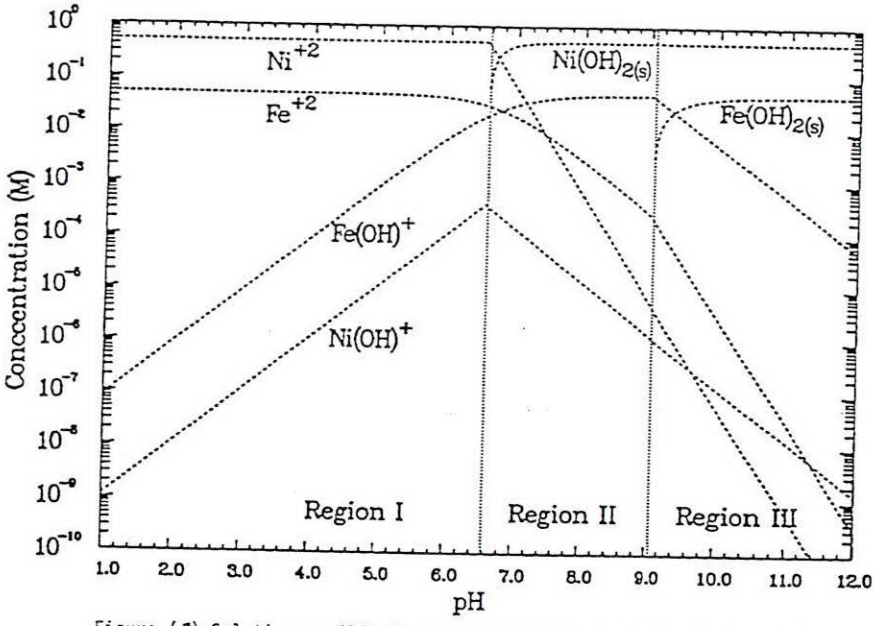

Figure (1) Solution equilibrium concentrations in Fe-Ni plating bath as a function of pH.

Also, $Ni(OH)_2$ precipitates preferentially instead of $Fe(OH)_2$. Because of the difference in metal hydroxide ion stability constants [$K_{spNi(OH)_2} = 6.3\text{x}10^{-16}$ mol/L^3; $K_{spFe(OH)_2} = 3.16\text{x}10^{-14}$ mol/L^3], $Ni(OH)_2$ precipitation occurs at a pH two units smaller than $Fe(OH)_2$. These results are not consistent with Dahms and Croll theory (1,2). They suggested that the preferential adsorption of $Fe(OH)_2$ rather than $Ni(OH)_2$ occurs on the electrode at high pH values. The adsorbed $Fe(OH)_2$ inhibits the discharge rate of nickel but does not interfere with iron deposition. Besides the fact that Ni^{+2} ions are present in the electrolyte in much higher concentration than Fe^{+2}, according to Figure (1), the $Fe(OH)^+$ concentration is two orders of magnitude larger than the $Ni(OH)^+$ concentration. From the shape of the equilibrium curves in Figure 910, it can be concluded that any metal hydroxide will precipitate completely due to a small change in pH. Thus, a small change in pH at the electrode surface should have dramatic effects on alloy composition and surface morphology. Although Figure (1) illustrates equilibrium conditions, it also serves as a guide for solution behavior of the electroactive species in an Fe-Ni codeposition process.

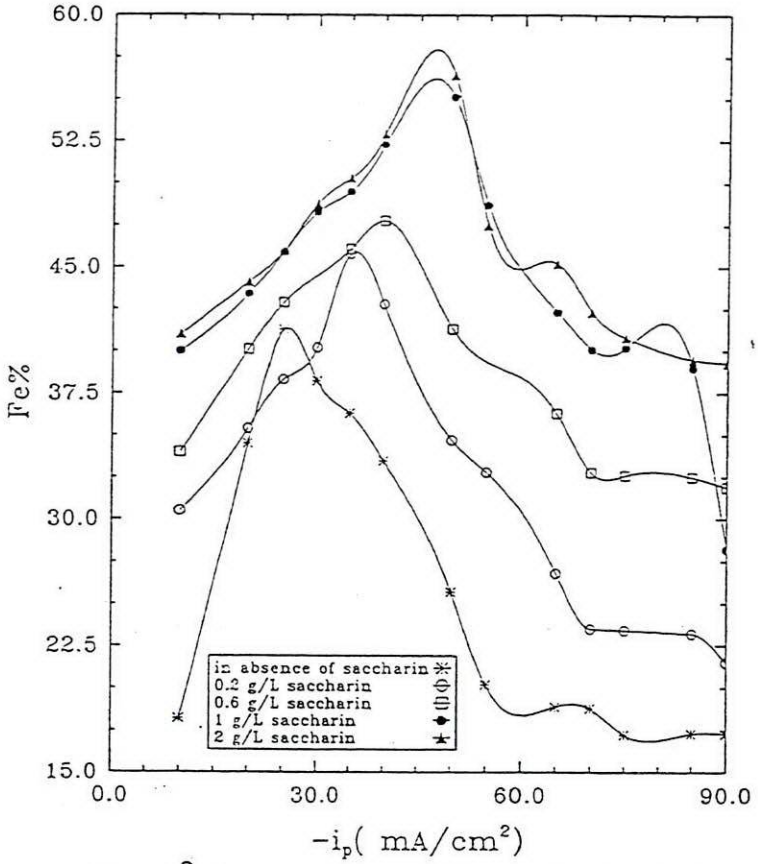

Figure (2). Iron compositions profiles as a function of pulse peak current and saccarin concentrations. The deposition was carried out from electrolytes containing 0.5 M $NiSO_4$+ 0.2M Na_2SO_4+0.05M $FeSO_4$.

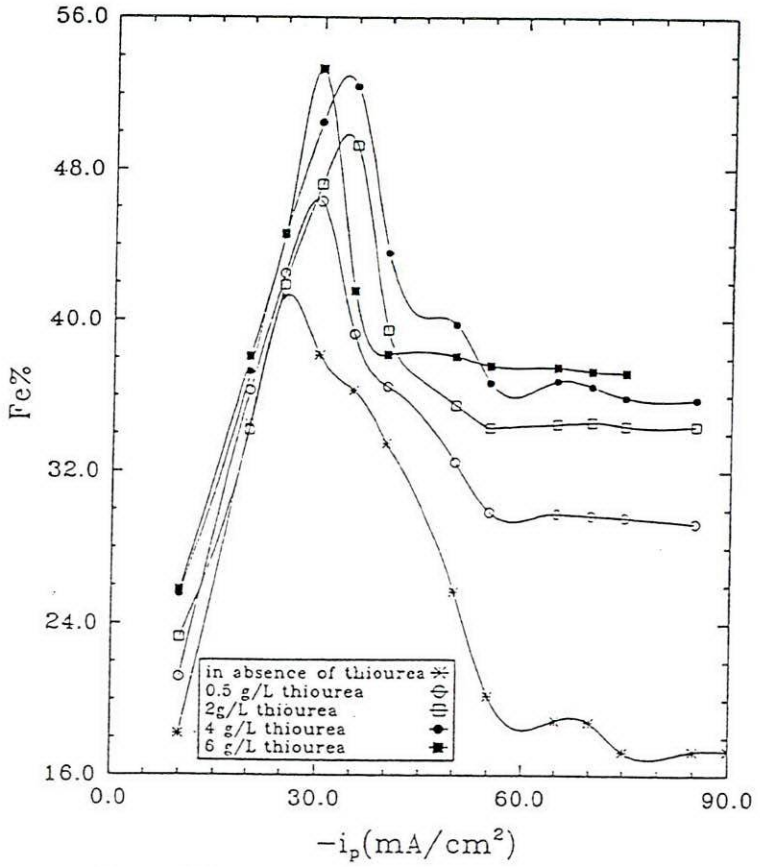

Figure (3) Iron composition profiles as a function of pulse peak current and thiourea concentrations. The deposition was carried out from electrolytes containing 0.5M $NiSO_4$+0.2M Na_2SO_4 + 0.05M $FeSO_4$.

Galvanostatic Pulse Plating. The electrodeposition of Fe-Ni alloys was studied galvanostatically in the presence of sulfate electrolytes and organic additives. Sulfate electrolytes have good conductivity and are not aggressive or toxic. In addition, sulfate ions are not reduced at the cathode and are not oxidized at the anode. Additives have been used in order to buffer the solution or to decrease the deposit stress and to produce smoother deposits. Figures (2), (3) and (4) show the iron atomic percentage as a function of peak currents in the presence of different concentrations of saccharine+adipic acid, thiourea and 2 butyn-1,4 diol, respectively. The pulse plating was carried out from electrolytes containing: 0.5M $NiSO_4$ + 0.05M $FeSO_4$ + 0.5M Na_2SO_4. In the absence of organic additives, by increasing the peak current density from 10 to 30 mA/cm^2, the iron content in the alloy increases from 17% to 41.5 %. As shown in Figure (2), for high peak currents, the Fe content in the alloy decreases, indicating that the iron deposition rate at these peak currents levels off.

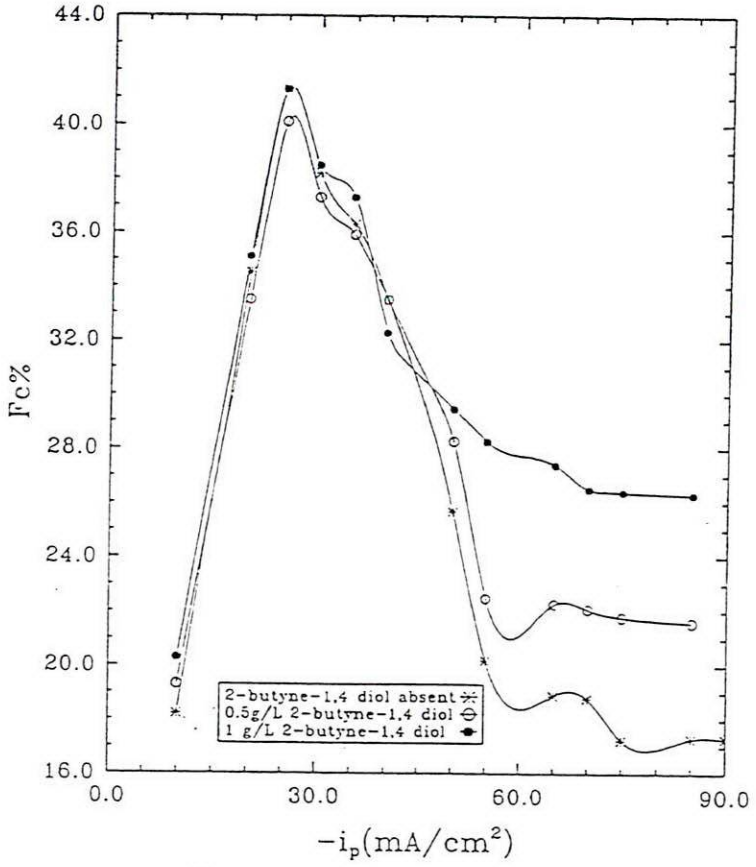

Figure (4) Iron composition profiles as a function of pulse peak current and 2 butyn-1,4 diol concentrations. The deposition was carried out from electrolytes containing 0.5M $NiSO_4$+0.2M Na_2SO_4 + 0.05M $FeSO_4$.

The presence of organic additives in the plating bath decreases the total current density, enhancing the uniformity of the alloy. According to Figures (2), (3) and (4), in the presence of organic additives, the iron atomic percentage increases, while the nickel atomic percentage decreases, as shown in Figures (5), (6) and (7).

One of the functions of the additives in this study was to maintain lower pH at the interface. In the presence of organic additives, less nickel is deposited and the iron content in the alloy increases. The observed phenomena does not correspond with the prediction of the Dams and Croll theory (1). According to this theory it is expected that by decreasing the pH at the interface, the nickel content will increase. The results can be explained by taking into account the surface reactions occurring on the cathode. Because of the surface adsorption phenomena certain assumptions can be made about Fe-Ni deposition: (1) The discharge rates of $FeOH^+$ and $NiOH^+$ are proportional to their respective surface coverage fractions. (2) The discharge rates of Ni^{+2} and Fe^{+2} are proportional to the surface fractions not covered

by the organic additives. (3) According to Langmuir isotherm, the adsorption fraction of all species on the cathode surface is related to its respective interfacial concentration, assuming that the uncovered surface is negligible compared to the covered surface.

According to this study, the increased pH does not favor the Fe deposition. The iron content in Figure (2), (the curve obtained in the absence of organic additives) shows that at high peak currents (where an increase of pH at the interface is expected), there is a decrease of Fe content in the alloy. The results obtained from galvanostatic plating are consistent with the solution chemistry computation and the pH dependence as discussed in the previous section. When the interfacial pH increases, $Ni(OH)_2$ precipitates before $Fe(OH)_2$.

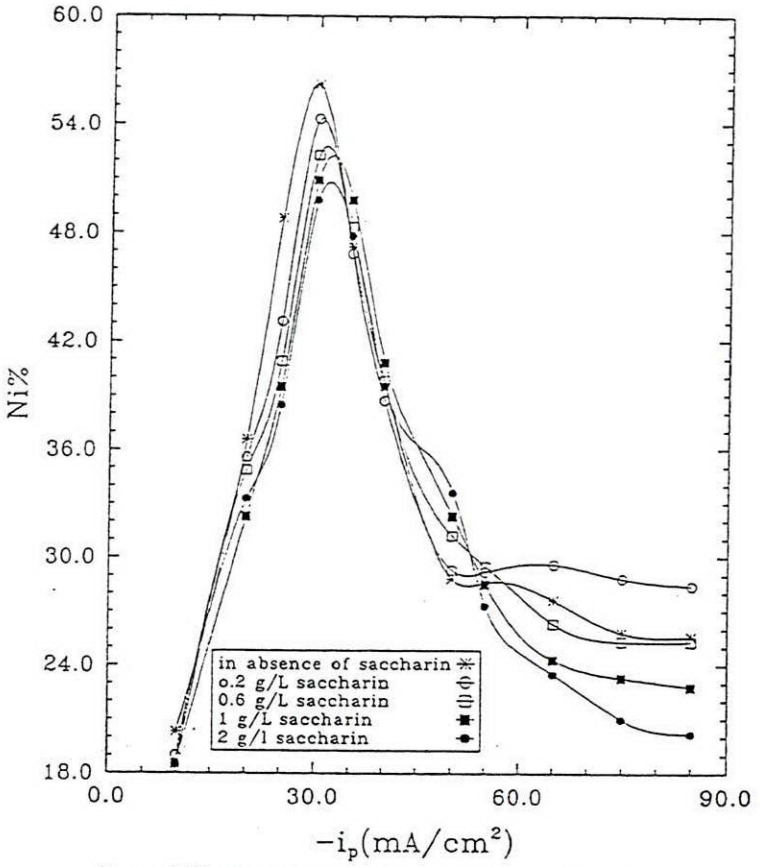

Figure (5) Nickel composition profiles as a function of pulse peak current and saccharin concentrations. The deposition was carried out from electrolytes containing 0.5M $NiSO_4$+0.2M Na_2SO_4 + 0.05M $FeSO_4$.

Due to the electrode surface coverage with organic additives, one can expect the interfacial concentrations of the reactants to increase even at high applied peak currents. The concentration depletion is alleviated because of the increased surface resistance due to surface adsorption of organic compounds. Thus, in the presence of organic compounds, the concentration polarization is reduced. Since the electrode overpotential is increased, the mass transfer limitation of reactants is avoided and the electrochemical reactions are confined to the kinetically controlled region. Since the iron limiting current is extended towards high peak currents in the presence of organic additives, it is expected that the iron content in the alloy to increase in the presence of adipic acid-saccharin, thiourea and 2buty-1,4 diol. This

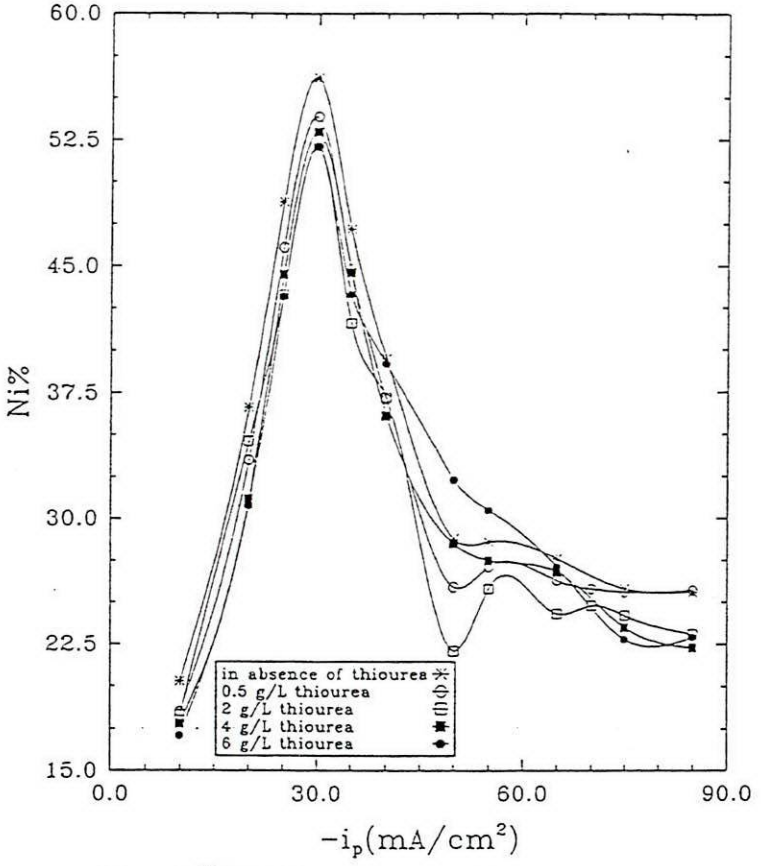

Figure (6) Nickel composition profiles as a function of pulse peak current and thiourea concentrations. The deposition was carried out from electrolytes containing 0.5M $NiSO_4$+0.2M Na_2SO_4 + 0.05M $FeSO_4$

phenomena was observed in Figures (2), (3) and (4). Also, the coverage of all electroactive species Ni^{+2}, $NiOH^{+}$, $FeOH^{+}$, Fe^{+2} ad H^{+} is proportional to their interfacial concentrations. In the absence of organic compounds, the surface coverage is dominated by $Fe(OH)^{+}$, because the $Fe(OH)^{+}$ is at a much higher concentration in the solution than $Ni(OH)^{+}$. In the presence of organic compounds, the additive surface coverage increases with the applied peak currents, while $\theta_{Ni(OH)^{+}}$ and $\theta_{Fe(OH)^{+}}$ are reduced. The interfacial concentrations of $Ni(OH)^{+}$ and $Fe(OH)^{+}$ are depleted significantly in the presence of organic compounds and consequently are reduced at higher overpotentials (applied peak currents).

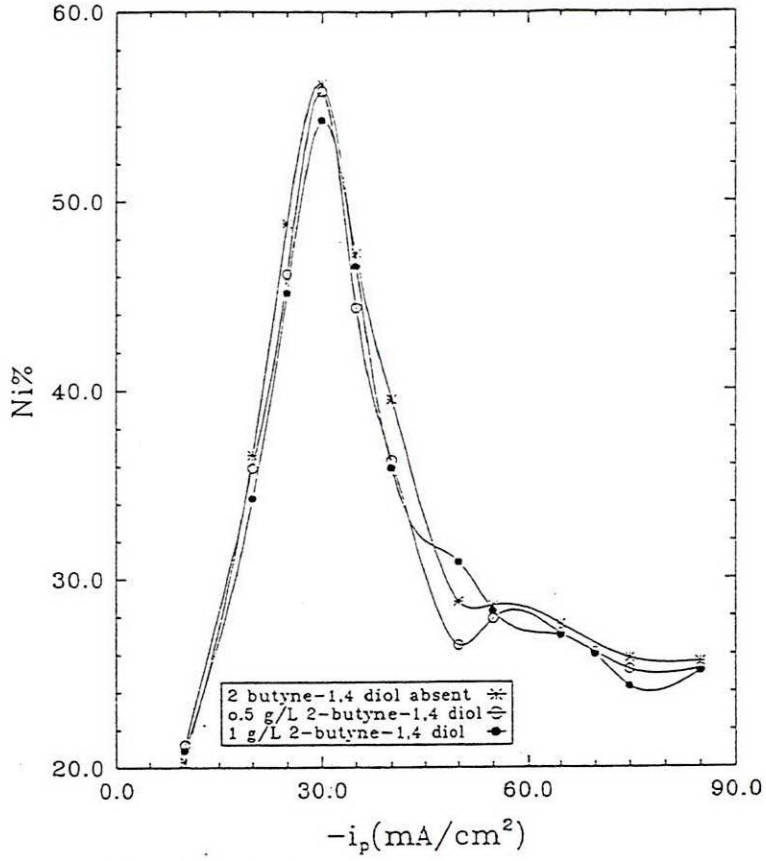

Figure (7) Nickel composition profiles as a function of pulse peak current and 2 butyn-1,4 diol concentrations. The deposition was carried out from electrolytes containing 0.5M $NiSO_4$+0.2M Na_2SO_4 + 0.05M $FeSO_4$

EDS of the Coating One of the functions of the additives used in this study was to maintain lower pH. In the presence of organic additives a decrease of the total current density was observed which enhances the uniformity of the alloy. Also, less nickel is deposited, while the iron content in the alloy increases. Figure (8) represents a comparison of EDS spectrum obtained at the edge and at the center of the plates deposited at high peak currents.

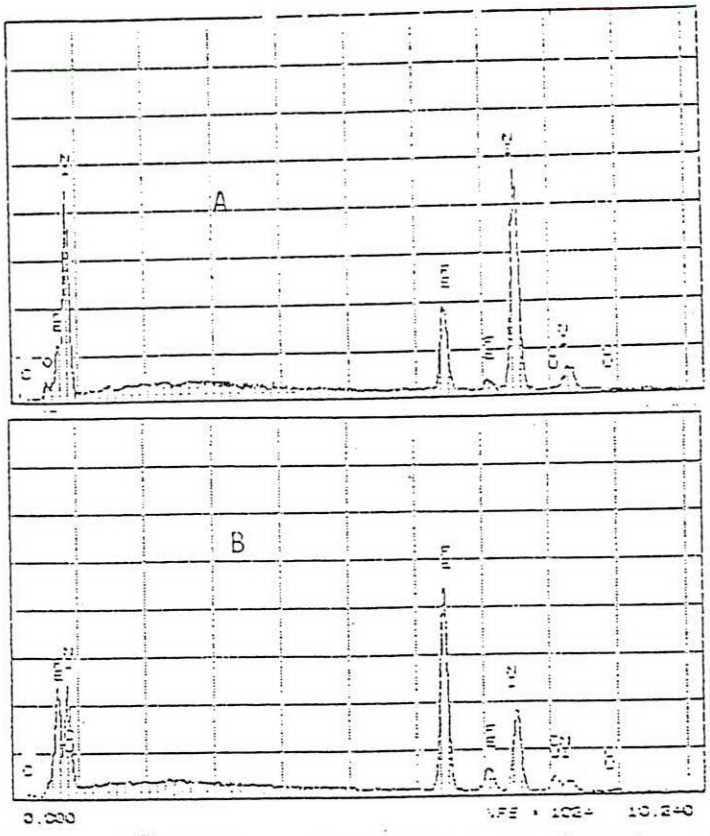

Figure (8) EDS spectrum taken at the edge of the plate (A) and at the center of the plate.

The higher current density on the edge results in a high hydrogen evolution reaction rate. As a consequence higher rise of pH at the edges occurs which induces a porous precipitation of nickel and iron hydroxides. An average of 0.25 to 0.35 of Fe mole fraction was observed at the edges of the electrode compared with the values of 0.45 to 0.6 mole fractions of Fe observed at the center of the of the plate. These results were not consistent with Dahms and Croll's mechanism (1,2). According to these authors a much higher Fe content would be expected on the edges, where higher current density and higher h.e.r. occur. However, as found in this study, the increased pH did not favor the Fe deposition rate. The results

reported here are, however, consistent with the solution chemistry equilibrium behavior and solution chemistry of Fe-Ni plating bath.

Acknowledgment

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CONTINUOUS ELECTROLYTIC TREATMENT OF COMPLEX CYANIDE WASTES WITH A PLATING BARREL

C.-D. Zhou and D.-T. Chin
Department of Chemical Engineering
Clarkson University
Potsdam, New York 13699-5705

ABSTRACT

A continuous electrolytic process consisting of a plating barrel cathode and a packed-bed anode was used to recover metals and to destroy cyanide in waste silver, copper and cadmium cyanide solutions. The experiments were carried out with and without the addition of NaCl to the feed solutions. The effluent concentrations of total cyanide, free cyanide and metal ions were examined for various cell currents, solution temperatures, solution feed rates, solution recirculation rates, barrel rotational speeds, and barrel loadings. The total cyanide concentration was reduced from 520 ppm to less than 10 ppm and metal concentrations from 225 - 486 ppm to less than 1 ppm.

INTRODUCTION

The sources of metal and cyanide wastes and their characteristics are listed in several literature[1,2]. Because of toxicity, these wastes must be adequately treated before being allowed to discharge from the process plant. In a previous paper[3], the present authors described a batch electrolytic process to recover copper and destroy cyanide using a plating barrel cathode and a packed-bed anode. The total cyanide concentration was reduced from 580 ppm to less than 10 ppm. The process was more cost effective than conventional alkaline chlorination method for the treatment of waste cyanide solutions. It also had a cost advantage over a commercial carbon fiber electrolytic process because of a lower capital investment.

For dilute solutions, such as plating rinse water, electrolytic recovery of metal and destruction of cyanide is difficult because of mass transfer limitation and low reaction rate per unit electrode area. A number of electrolytic cells have been designed with the electrodes that either enhance mass transfer rate or have a large surface area. Some of these designs are: porous electrode[4], concentric cylinder[4], rotating cylinder[5], packed-bed[6-9], fluidized-bed[9-11], and carbon fiber[12]. The porous electrode, packed-bed and carbon fibre provide a large surface area; whereas the concentric and rotating cylinders have a high mass transfer rate. The fluidized-bed offers a large surface area and a high mass transfer rate; however, it has a high electric resistivity because electrode particles lose contact with their current collector during the fluidization movement. The tumbling bed, such as a plating barrel, is a good choice for the treatment of dilute waste solutions. The particles in the tumbling bed possess a large surface area, and the tumbling motion of electrode particles improves mass transfer without losing electric contact with the current collector. Several patents[13-15] described the use of tumbling beds to treat waste water. Oehr[16] used a plating barrel to destroy cyanide. Tison[17-19] used a tumbling bed to recover copper from a dilute copper sulfate solution. He found that the tumbling bed had a more uniform current and metal distribution than the packed-bed.

In this study, a continuous electrolytic process using a plating barrel cathode and a packed-bed anode to simultaneously recover metals and destroy cyanide in waste plating solutions was examined. Silver cyanide, copper cyanide, and cadmium cyanide solutions were used in the experiments. The effect of temperature, cell current, solution feed rate, NaCl concentration, barrel rotational speed, barrel loading, and solution recirculation rate on the effluent cyanide and metal concentrations and energy consumption was studied.

EXPERIMENTAL

Test Solutions

Experiments were carried out with a continuous flow cell to treat silver cyanide, copper cyanide, and cadmium cyanide solutions. The copper cyanide and cadmium cyanide experiments were carried out with the addition of NaCl.

For the silver cyanide test, a solution containing 0.0045M AgCN, 0.0155M NaCN and 0.005M Na_2CO_3 at 25°C and 65°C was used. The total cyanide, free cyanide, and silver concentration in the solution was equivalent to 520 ppm, 286 ppm and 486 ppm, respectively.

For the copper cyanide test, a solution containing 0.005M CuCN, 0.015M NaCN and 0.1M NaOH was used. The solution composition corresponded to a concentration of 520 ppm of total cyanide, 112 ppm of free cyanide and 318 ppm of copper. The test was carried out without NaCl as well as with 0.2, 0.4 and 0.6 M NaCl at 25°C and 65°C.

For the cadmium cyanide test, a solution containing 0.002 M CdO, 0.02 M NaCN, 0.1 M NaOH and 0 - 0.6 M NaCl at 25°C and 65°C was used. The concentrations of total cyanide, free cyanide and cadmium were 520 ppm, 380 ppm, and 225 ppm, respectively.

Cell Setup

The continuous flow cell used in the experiment is schematically shown in Figure 1. The system consisted of an electrochemical cell having a packed-bed anode and a plating barrel cathode of 6.4 cm inside diameter by 10 cm in length (Model Snap Lock™, Singleton Company, Cleveland, Ohio), a solution feed tank, an effluent solution tank, and two metering pumps. These components were connected together by polyethylene and Tygon tubes.

The electrochemical cell was made of Plexiglas sheets of 1.25 cm in thickness; it had a dimension of 18 cm in length, 15 cm in width, and 25 cm in height. The cell was divided into a cathode and an anode compartment as shown in Figure 1. The plating barrel loaded with metal particles was placed in the cathode compartment. A copper cylinder of 0.6 cm in diameter by 1.2 cm in length was used as the dangler contact in the barrel. The packed-bed anode was located below the plating barrel to serve as a partition between the cathode and anode compartments. It had a dimension of 13 cm in length, 10 cm in width, and 9 cm in height, and was loaded with 500 g of active carbon pellets of 0.2 cm in diameter by 0.5 cm in thickness. A piece of graphite felt of 1.25 cm in thickness inserted through the anode compartment was used as the anode current collector. The solution temperature in the cell was controlled by a quartz heater and a temperature controller (Model 2157, Cole-Parmer, Chicago, IL).

Two 5-gallon polyethylene tanks were used as the feed and effluent solution tanks. A metering pump (Model A161-61S, Walchem Co, Holliston, MA) with a flow range of 0.02 to 2.1 ml/s was used to pump the test solution from the feed tank to the plating barrel. The solution flowed from the plating barrel through the packed-bed anode to the anode compartment and overflowed to the effluent tank as shown in Figure 1. A second metering pump (Masterflex L/S, Cole-Parmer, Chicago, IL) with a flow range of 0.05 to 4.7 ml/s was used to recirculate the solution from the anode compartment to the top of plating barrel. A DC power supply (Model 6274B, Hewlett-Packard, Albany, NY) was used for the electrolysis; a digital multimeter (Model 178, Keithley Co, Cleveland, Ohio) was used to measure the anode-to-cathode cell voltage.

For the copper cyanide and silver cyanide tests, copper chips with a diameter of 0.1 cm - 0.3 cm were used in the plating barrel to recover metals. For the cadmium cyanide test, steel rings of an inside diameter of 0.7 cm, an outside diameter of 1.4 cm, and a thickness of 0.1 cm were used as the cathode material. The cyanide ion released by the electrodeposition of complex metal cyanide ion at the barrel cathode was

transported by the solution flow to the packed-bed anode where it was oxidized to nontoxic N_2 gas and HCO_3^- ion.

Experimental Procedures

For each run, a known amount of metal particles was placed in the plating barrel, which was then immersed in the cell filled with the test solution at a constant temperature. The solution feed pump and recirculation pump were turned on and the plating barrel began to rotate at a constant speed. A constant current from the DC power supply was applied to the cell. The cell voltage and solution pH were monitored during the electrolysis.

The effluent concentration was analyzed by taking 50 ml of a solution sample every one to two hours from the effluent overflow port until the steady-state was reached. Free cyanide concentration was measured with a cyanide ion selective electrode and a double junction Ag/AgCl reference electrode. Afterwards, the sample was acidified in a distillation device[20] (with 50 ml of 6 M H_2SO_4 for the copper cyanide and cadmium cyanide sample or with 50 ml of 1 M HNO_3 for the silver cyanide sample). The gaseous HCN liberated was absorbed in a glass flask containing 100 ml of 1.25 M NaOH solution. The total cyanide absorbed in the NaOH solution was determined with the cyanide ion selective electrode. The sample left in the distillation flask was used to determine the metal ion concentration with a silver, copper, or cadmium ion selective electrode. For the copper and cadmium cyanide solutions containing NaCl, a small amount of $AgNO_3$ was added to precipitate Cl^- before the copper or cadmium ion selective electrode was used to analyze the metal concentration.

A run was terminated when the effluent total cyanide, free cyanide and metal concentrations were no longer changed with the time. Depending upon the solution feed rates and cell currents, it took approximately 8 to 16 hours to reach the steady state.

RESULTS AND DISCUSSION

A mathematical model based on a continuous stirred tank reactor[21,22] was made to analyze the effluent concentrations of metal, free cyanide and total cyanide ions for the continuous electrolysis of a waste cyanide solution. Several dimensionless variables were identified from the analysis:

Dimensionless Cell Current

$$I^* = \frac{I}{n_a F} \frac{1}{Q\, C_{TCN,inlet}} \qquad (1)$$

Dimensionless Effluent Metal Ion Concentration

$$C^*_M = \frac{C_M}{C_{M,inlet}} = f(\eta_c\ ,\ I^*) \qquad (2)$$

Dimensionless Effluent Free Cyanide Concentration

$$C^*_{CN} = \frac{C_{CN}}{C_{TCN,\,inlet}} = f(\eta_c\ ,\ \eta_a\ ,\ I^*) \qquad (3)$$

Dimensionless Effluent Total Cyanide Concentration

$$C^*_{TCN} = \frac{C_{TCN}}{C_{TCN,\,inlet}} = f(\eta_a\ ,\ I^*) \qquad (4)$$

where, I is the cell current (A); n_a is the number of electrons transferred for the oxidation of cyanide (2 eq/mol); F is Faraday's constant (96500 C/eq); Q is the solution feed rate (l/s); $C_{M,inlet}$ and $C_{TCN,inlet}$ are the inlet concentrations of metal and total cyanide (mol/l), respectively; C_M is the effluent metal concentration (mol/l); C_{CN} is the effluent free cyanide concentration (mol/l);

C_{TCN} is the effluent total cyanide concentration (mol/l); η_c is the cathodic current efficiency; and η_a is the anodic current efficiency. The values of η_c and η_a are calculated from the following equations:

$$\eta_c = \frac{(C_{M,inlet} - C_M) Q n_c F}{I} \qquad (5)$$

$$\eta_a = \frac{(C_{TCN,inlet} - C_{TCN}) Q n_a F}{I} \qquad (6)$$

where, n_c is the number of electrons transferred in the cathodic electrodeposition reaction (1 eq/mol for silver and copper cyanide solutions and 2 eq/mol for cadmium cyanide solution). The energy consumption per kilogram of total cyanide destroyed is:

$$Energy\left(\frac{kWh}{kg\ CN}\right) = \frac{E_{cell} I}{3600(C_{TCN,inlet} - C_{TCN}) QM} \qquad (7)$$

where, E_{cell} is the anode-to-cathode cell voltage (V); and M is the molecular weight of cyanide (26 g/mol).

The dimensionless metal concentration depends only on the cathodic current efficiency and dimensionless cell current; whereas the dimensionless free cyanide concentration depends on the dimensionless current and anodic and cathodic current efficiencies. The anodic and cathodic current efficiencies, η_a and η_c, vary with the operating conditions, such as cell current, solution temperature, feed rate, NaCl concentration, barrel rotational speed, barrel loading, and solution recirculation rate. These variables need to be determined with experimental investigations.

Figure 2 shows the dimensionless effluent total cyanide, free cyanide, and copper concentrations as well as energy consumption vs. dimensionless cell current curves for the treatment of a copper cyanide solution free of NaCl at 25°C, a barrel rotational speed of 15 rpm, a barrel immersion level of 50% of barrel diameter, and a barrel loading of 50% of barrel volume. The results indicate that the effluent dimensionless concentrations of total cyanide, free cyanide, and copper initially decreased with increasing cell current and then levelled off at high current. The energy consumption per kilogram of total cyanide destroyed increased linearly with increasing cell current.

Continuous Treatment of Silver , Copper , and Cadmium Cyanide Solutions

The continuous treatment of silver cyanide solution was carried out at 25°C and 65°C without adding NaCl in the feed solution. The plating barrel cathode was loaded with 520 g of copper chips (corresponding to a 50% of barrel volume) and was set at a barrel rotational speed of 15 rpm, a barrel immersion level of 50% of barrel diameter and a solution recirculation rate of 4 ml/s. Two solution feed rates of 0.025 ml/s and 0.05 ml/s and two cell currents of 1.5 A and 3 A were used; these values corresponded to the dimensionless cell currents of 7.8, 15.5, and 31.1.

The tests for the copper cyanide solution were carried out with the addition of 0 - 0.6M NaCl at two cell temperatures of 25°C and 65°C and a 50% barrel immersion level. Three barrel rotational speeds of 3 rpm, 8 rpm and 15 rpm, and three barrel loadings of 25%, 50% and 75% of barrel volume were used. The solution recirculation rates were: 0 ml/s, 3 ml/s, and 4 ml/s. The tests were carried out at the dimensionless cell currents of 7.8, 15.5, and 31.1.

The continuous treatment of cadmium cyanide solution were carried out at a 50% barrel loading and a 50% barrel immersion level. The tests were carried out with the addition of 0 - 0.6M NaCl to the feed solution at two cell temperatures of 25°C and 65°C. Three barrel rotational speeds of 3 rpm, 8 rpm, and 15 rpm and three solution recirculation rates of 0 ml/s, 2

ml/s and 4 ml/s were examined. The dimensionless cell currents were: 7.8, 15.5, and 31.1.

The results indicate that the cyanide current efficiency decreased with increasing dimensionless current. The energy consumption per kilogram of total cyanide destroyed increased with increasing dimensionless current. Figures 3 and 4 show the dimensionless effluent total cyanide and metal concentrations vs. dimensionless cell current for silver cyanide, copper cyanide, and cadmium cyanide solutions at 25°C and 65°C. Figure 5 shows the energy consumption per kilogram of total cyanide destroyed vs. dimensionless current for the three cyanide solutions at 65°C. These results reveal that the effluent concentrations of total cyanide and metal decreased with increasing cell current and solution temperature. The energy consumption per kilogram of total cyanide destroyed increased with increasing cell current. At the same operating conditions, the effluent total cyanide concentration and the energy consumption followed the order of cadmium cyanide < silver cyanide < copper cyanide. This order agrees with the fact that copper cyanide complex has the smallest dissociation constant and cadmium cyanide has the highest dissociation constant among the three cyanide solutions[23].

Effect of NaCl on Cyanide Destruction

To exam the effect of NaCl concentration on the electrolytic treatment of complex cyanides, NaCl was added to the feed solutions of copper cyanide and cadmium cyanide to the NaCl concentration of 0.2 M, 0.4 M, and 0.6 M, and the results were compared to the runs without the addition of NaCl. The experiments were carried out at the cell currents of 1.5 A and 3 A with the solution feed rates of 0.025 ml/s and 0.05 ml/s; the corresponding dimensionless cell currents were: 7.8, 15.5, and 31.1. The solution temperature was 25°C and solution recirculation rate was 4 ml/s. The barrel rotational speed was kept at 15 rpm. Figure 6 and 7 respectively show the dimensionless effluent total cyanide and metal concentrations vs. dimensionless cell current for the copper cyanide solution with four different NaCl concentrations. The results indicate that the effluent total cyanide and metal concentrations decreased with increasing NaCl concentration and cell current. At a dimensionless cell current of 7.8, the dimensionless effluent total cyanide concentration decreased from 0.047 without NaCl to 0.01 with 0.6M NaCl. The addition of NaCl improved the cyanide oxidation because ClO^- was generated at the anode and it subsequently reacted with cyanide to CNO^-, HCO_3^- and N_2. Figure 8 shows the energy consumption per kilogram of total cyanide destroyed vs. NaCl concentration at three dimensionless currents for cadmium cyanide and copper cyanide solutions. The energy consumption per kilogram of total cyanide destroyed decreased with increasing NaCl concentration and with decreasing cell current. The decrease in energy consumption with the addition of NaCl was due to the improvement in the rate of cyanide oxidation and solution conductivity. The energy consumption for cadmium cyanide was smaller than that of copper cyanide because of the higher dissociation constants for cadmium cyanide complexes.

Effect of Barrel Rotational Speed, Barrel Loading, and Solution Recirculation Rate

The effect of barrel rotational speed, barrel loading, and solution recirculation rate was not as large as the effect of cell temperature, cell current and NaCl concentration. The optimal barrel settings were found to be at a barrel rotational speed of 15 rpm, and a barrel loading of 50% of barrel volume.

Figure 9 shows the effluent dimensionless total cyanide concentration and energy consumption per kilogram of total cyanide destroyed vs. barrel rotational speed for cadmium cyanide and copper cyanide solutions. The effect of barrel rotational speed on energy consumption was small; however, the effluent total cyanide and metal concentrations decreased with increasing barrel rotational speed. This is because the mass transfer rate was large at high barrel rotational speed.

Figure 10 shows the effluent dimensionless total cyanide concentration and energy consumption vs. barrel loading for copper cyanide solution. The effect of barrel loading on energy consumption was small; however, the effluent total cyanide concentration was smallest at a 50% barrel loading. The improvement from a 25% to a 50% barrel loading was due to an increase in cathode surface area for metal deposition reaction. The cyanide oxidation reaction at the anode was also improved because more free cyanide ions were released due to the increased rate of copper deposition reaction at the cathode. Further increasing in loading from a 50% to a 75% of barrel volume resulted in a lower mass transfer rate and less uniform current distribution in the plating barrel cathode. This caused an increase in the effluent total cyanide concentration as shown in Figure 10. The performance of a 50% barrel loading was better than that of a 75% barrel loading for the present waste treatment.

Figure 11 shows the effluent dimensionless total cyanide concentration and energy consumption vs. the ratio of recirculation to feed rates for the treatment of cadmium cyanide and copper cyanide solutions. The results indicate that the effect of solution recirculation rate on energy consumption was small; however, the effluent total cyanide concentration decreased with increasing solution recirculation rate because of an improvement in mass transfer at high recirculation rates.

CONCLUSIONS

A study has been made of using a plating barrel cathode and a packed-bed anode to continuously treat silver, copper, and cadmium cyanide solutions. The total cyanide concentration was reduced from 520 ppm to less than 10 ppm, and metal concentration was reduced from 225 - 486 ppm to less than 1 ppm. The effect of operating conditions, such as cell current, solution temperature, solution feed rate, solution recirculation rate, NaCl concentration, barrel speed, and barrel loading on the effluent total cyanide and metal concentrations and energy consumption was examined. The effluent total cyanide and metal concentrations decreased with: i) increasing cell temperature; ii) increasing cell current; iii) increasing NaCl concentration; iv) increasing barrel rotational speed; and v) increasing solution recirculation rate. The energy consumption decreased with decreasing cell current and with increasing cell temperature. At the same operating conditions, the energy consumption per kilogram of total cyanide destroyed followed the order of cadmium cyanide < silver cyanide < copper cyanide. The optimal barrel loading was 50% of barrel volume.

ACKNOWLEDGEMENT

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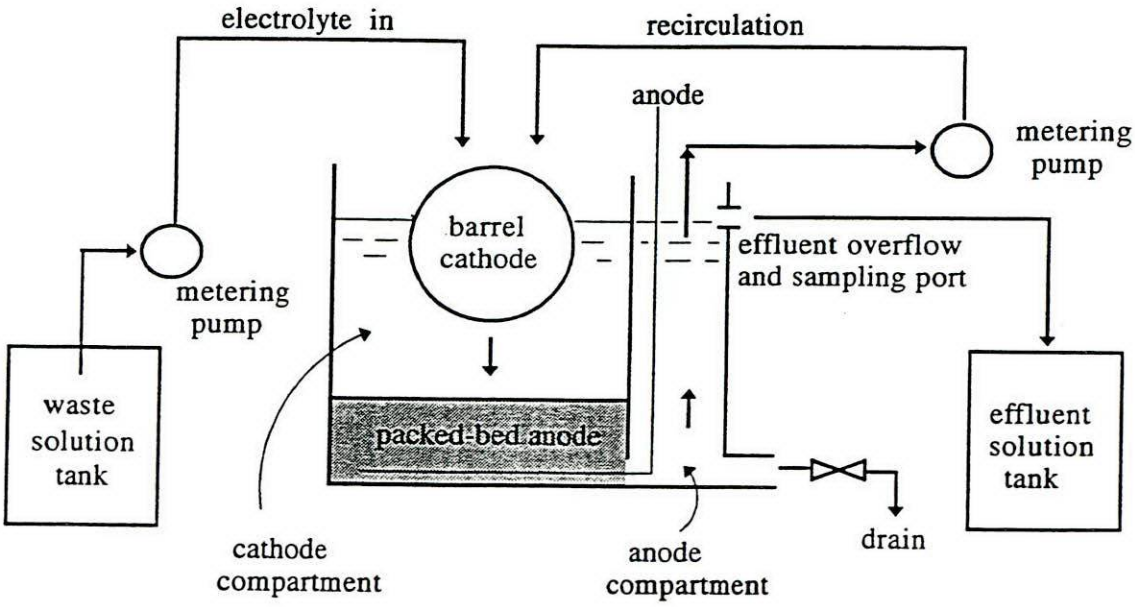

Figure 1: Schematics of cell setup

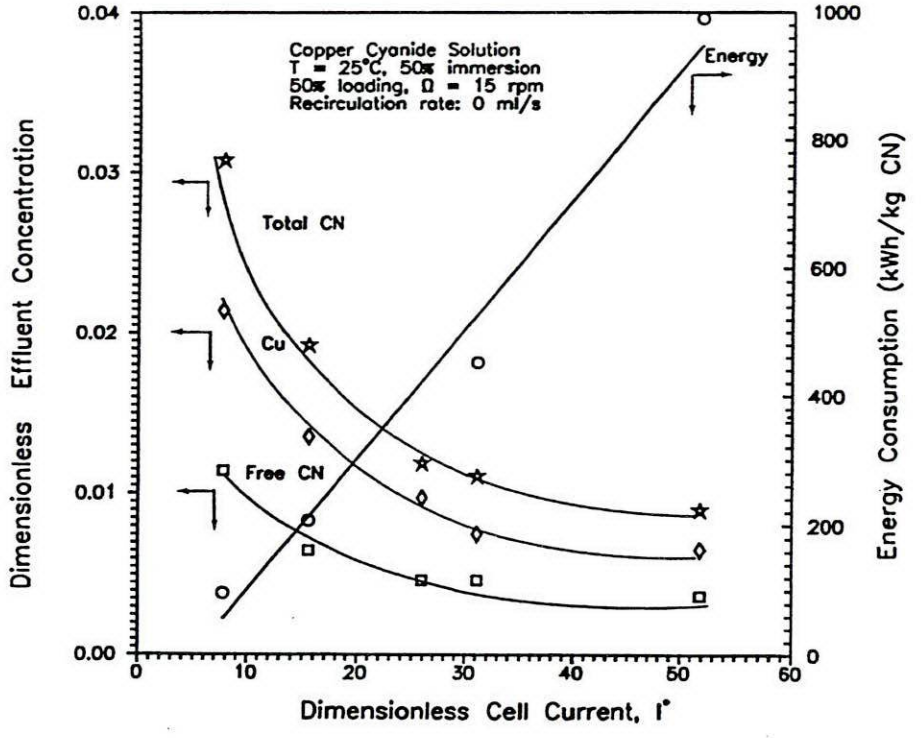

Figure 2: Dimensionless effluent total cyanide, free cyanide, copper concentrations and energy consumption per kilogram of total cyanide destroyed as functions of the dimensionless cell current for the treatment of copper cyanide solution.

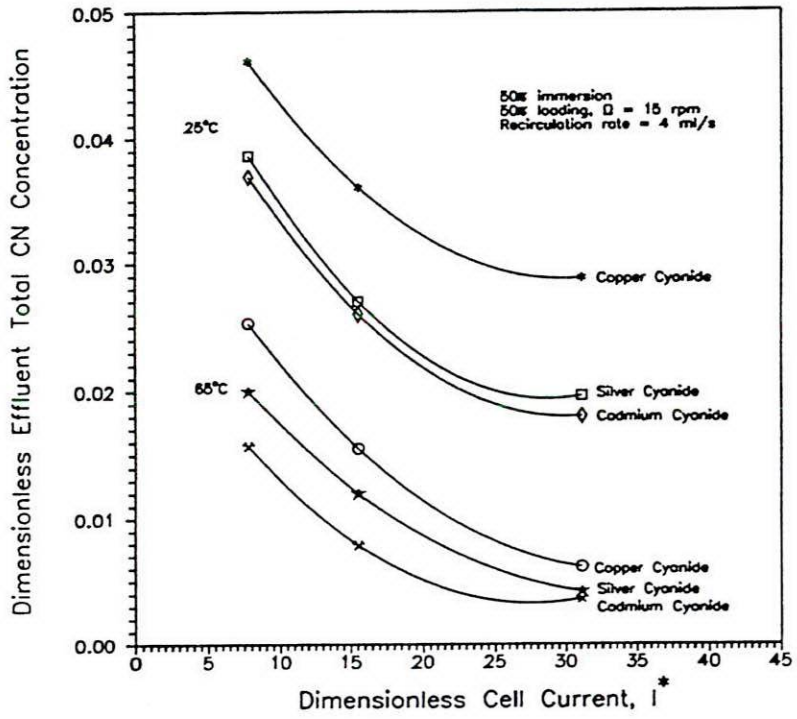

Figure 3: Dimensionless effluent total cyanide concentration vs. dimensionless cell current for the treatment of silver, copper, and cadmium cyanide solutions at 25°C and 65°C.

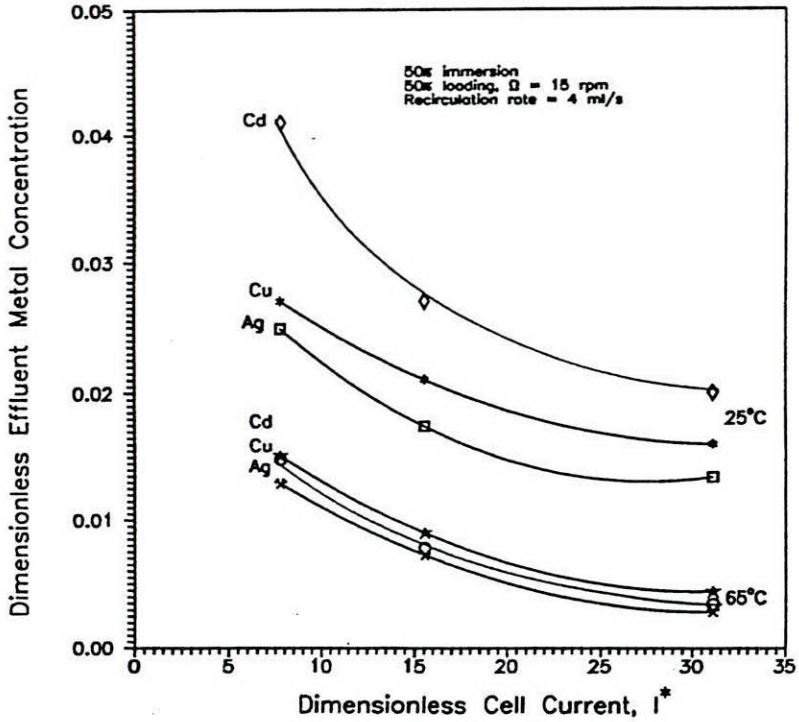

Figure 4: Dimensionless metal concentration vs. dimenionless cell current for the treatment of silver, copper, and cadmium cyanide solutions at 25°C and 65°C.

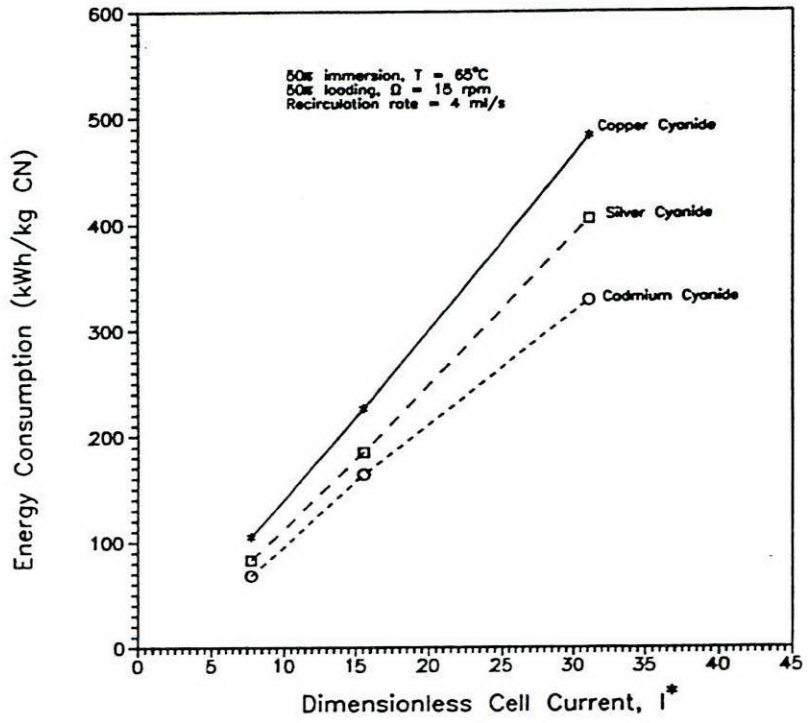

Figure 5: Energy consumption per kilogram of total cyanide destroyed vs. dimensionless cell current for the treatment of silver, copper, and cadmium cyanide solutions at 65°C.

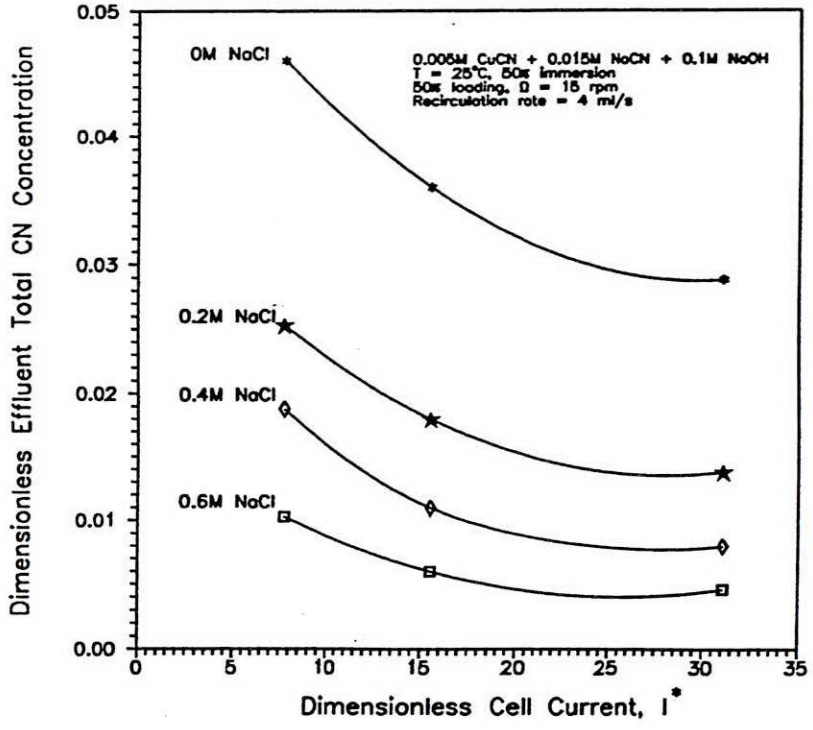

Figure 6: Dimensionless effluent total cyanide concentration vs. dimensionless cell current for the treatment of copper cyanide solution with four different NaCl concentrations.

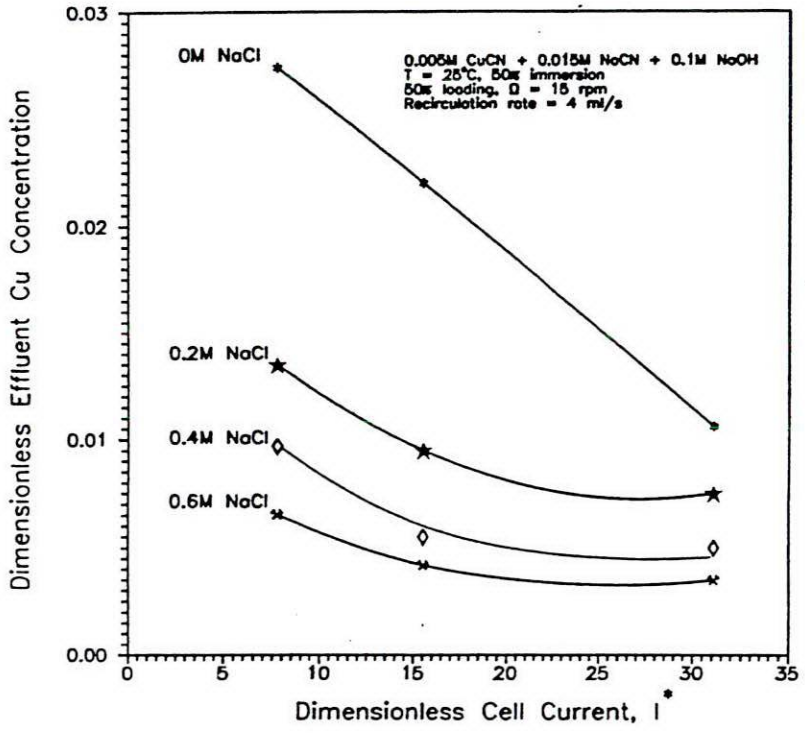

Figure 7: Dimensionless effluent copper concentration vs. dimensionless cell current for the treatment of copper cyanide solution with four different NaCl concentrations.

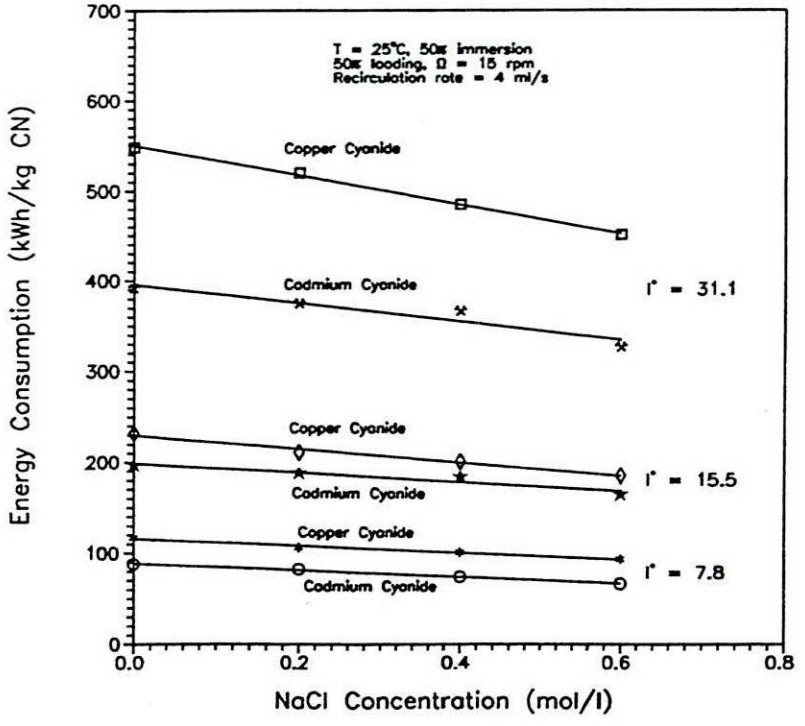

Figure 8: Energy consumption per kilogram of total cyanide destroyed vs. NaCl concentration for the treatment of copper and cadmium cyanide solutions.

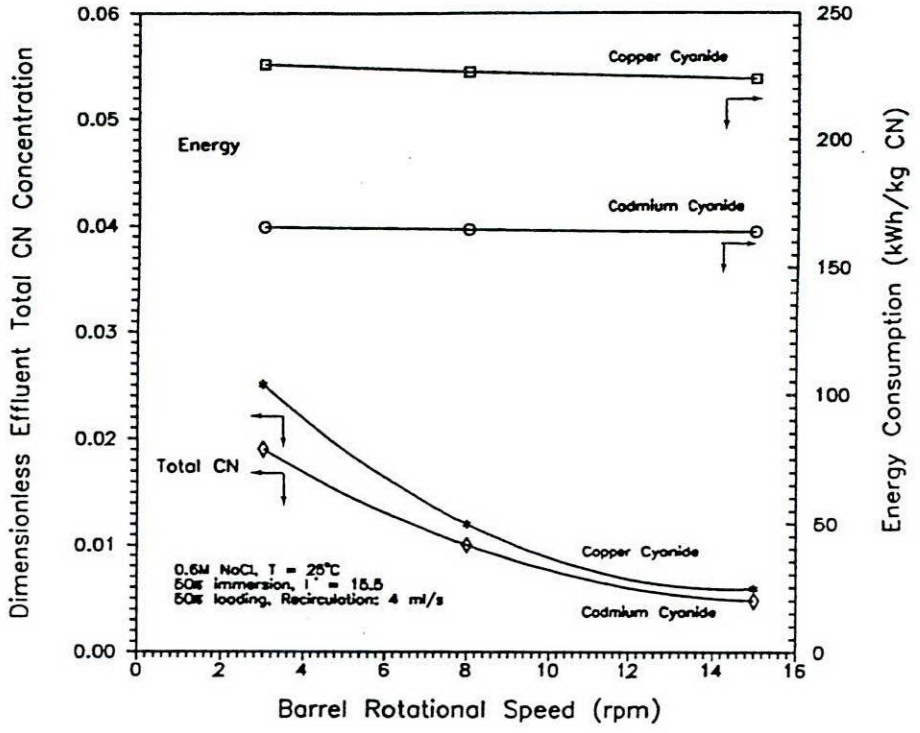

Figure 9: Dimensionless effluent total cyanide concentration and energy consumption vs. barrel rotational speed for the treatment of copper and cadmium cyanide solutions.

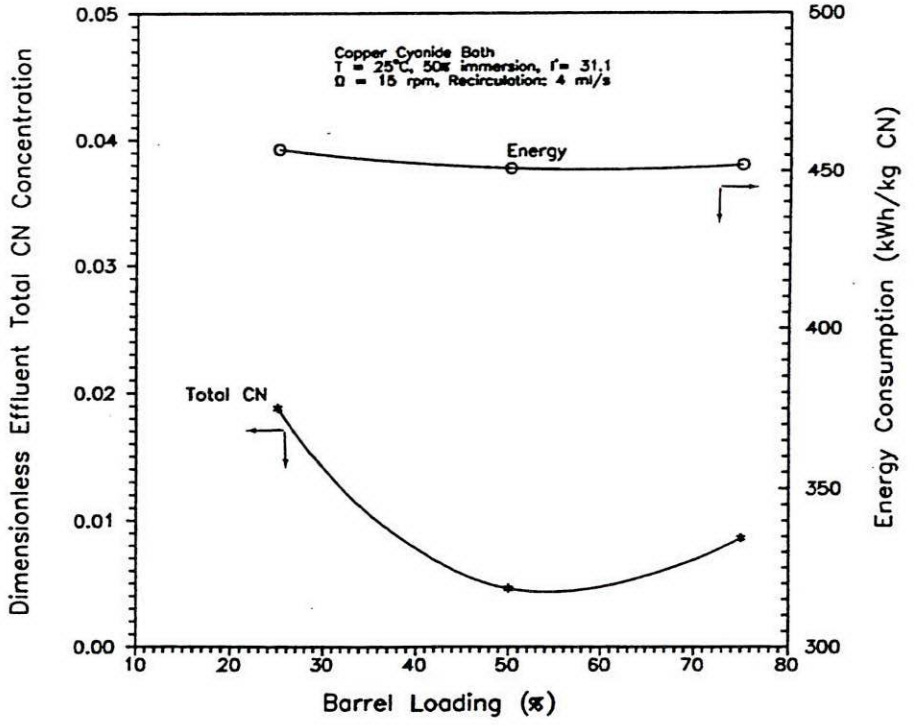

Figure 10: Dimensionless effluent total cyanide concentration and energy consumption vs. barrel loading for the treatment of copper cyanide solution.

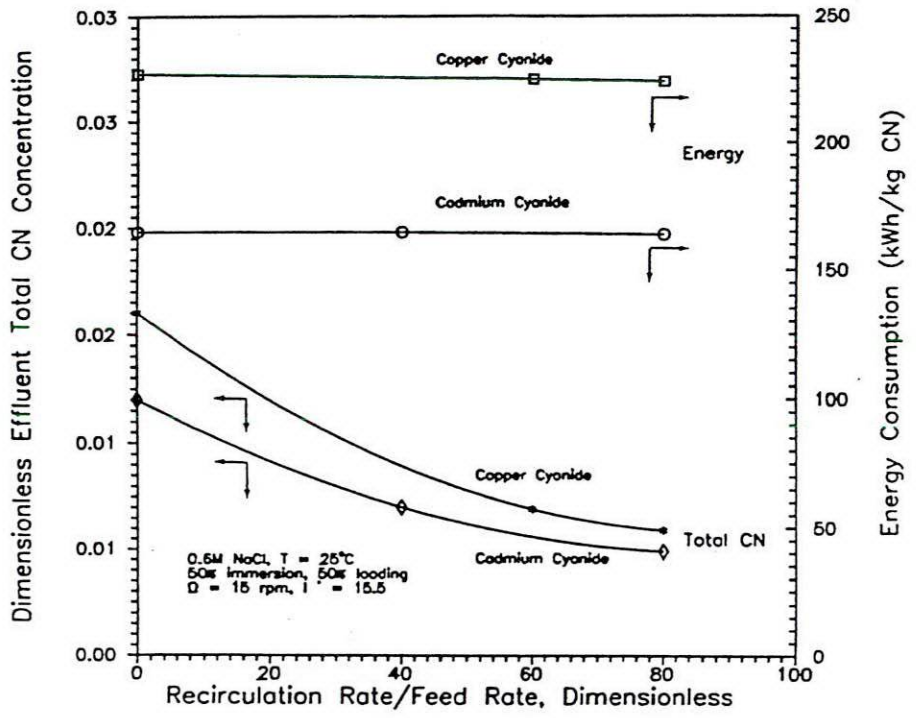

Figure 11: Dimensionless effluent total cyanide concentration and energy consumption vs. ratio of recirculation to feed rate for the treatment of copper and cadmium cyanide solutions.

The Effect Of The Interaction Between Particles And Matrix Metal In Composite Coating On Its Electrocatalytic Function

by He-Tong Guo, Qi-Xian Qin and Wei Wang
Department of Applied Chemitry, Tianjin Univerity, Tianjin, 300072 China

XRD analysis has proved that ZrO_2 particles in Ni–ZrO_2 composite coating can alter the preferred orientation of crystal plane of nickel matrix. This is unfavorabl to the hydrogen evolution reaction in acid solution on the Ni–ZrO_2 coating served as an electrode. XPS and UPS detections have shown that there exists orbital interaction between zirconium and nickel in the composite coating. So it results in the enhancement of electrocatalytic activity for hydrogen evolution reaction on the Ni–ZrO_2 coating. The particles and matrix metal in Ni–ZrO_2 coating are not simply in a form of mechanical mixture.

Composite coatings have gained very wide application in a great many of fields[1]. In general the particles and matrix metal in the coating were considered to be in a form of simple mechanical mixture, and some good characteristics of them were explained by this point of view as well[2]. However, the view of simple mechanical mix-up has been far from solving satisfactorily their excellent performance, along with the occurence of verious composite coatings with some new special functions (e.g. coatings with photoelectric effect, coatings with electrocatalytic activity etc.). We shall approach the interaction between particles and matrix metal in the coating by the electrocatalytic effect of Ni–ZrO_2 composite coating in the hydrogen evolution process.

Experimental

Ni–ZrO_2 composite coatings were prepared by adding ZrO_2 particles to the common nickel plating bath and agitating the bath to that ZrO_2 particles are fully suspended in it. The Nickel plating bath composition was as follows.

$NiSO_4 \cdot 6H_2O$	200g/L
$NiCl_2 \cdot 6H_2O$	50g/L
H_3BO_3	40g/L
pH	2.8

With the variations in current density and ZrO_2 content of the bath the composite coatings with different content of particles could be obtained. The texture of composite coatings were studied with XRD spetra by means of D/max–YA type x-ray diffraction spetrograph. For understanding of the state of electons in zirconium and nickel VG ESCA LAB-5 Electron Spectrometer was used to obtain XPS and UPS. The ac impedance of pure nickel or Ni–ZrO_2(17.8wt%) cathode (platinium as anode) in 0.1mol/L H_2SO_4 + 0.5mol/L Na_2SO_4 solution was measured by a Solartron 1250 frequency response analyser.

Rsults and Discussion

1. XRD Analysis

The codeposition of ZrO_2(particle size 0.6l μm) with nickel has been carried out

to form Ni-ZrO_2(8.2wt%) deposit. The relative intensity of XRD peaks of all crystal planes of nickel matrix in the composite coating differs obviously from pure nickel deposit (see Table 1), that is, the preferred orientation of (200) plane of pure nickel deposit (differing from nickel powder) is converted into (220) plane of composite coating, and the preferred orientation degree of (220) plane decreases with decrease in ZrO_2 content in the deposit (see Table 2).

Table 1
Relative intensity of XRD peaks of planes parallel to coating surface

specimen	planes(hkl)				
	(111)	(200)	(220)	(311)	(222)
pure nickel coating	26.4	100	34.6	71.1	27.0
Ni-ZrO_2 coating	50.8	26.5	100	38.7	15.8
standard Ni powder	100	42	21	20	7

Table 2
Effect of ZrO_2(0.6 μm) content in the deposits on preferred orientation degree of planes

ZrO_2 content(wt%)	planes(hkl)		
	(111)	(200)	(220)
2.0	53.5	33.9	89.7
5.8	59.5	23.9	95.7
8.2	50.8	26.5	100.0

Note: All vallues in this table are relative to the XRD peak value of (220) plane of Ni in Ni-ZrO_2(8.2wt%) deposit which is regarded as 100.

Some properties of deposits could be somewhat of difference due to the distinction of its texture, e.g., Horiuti et al[3] proved that the recombination rate of hydrogen atoms (2Had → H_2) varies obviously from one plane of nickel electrode to another in following order, (111) ≪(100) ≪(110). As the recombination step is rate determining step for hydrogen evoluton process in acid solutions[4] and this mechanism is still valid for replacement nickel electrode with Ni-ZrO_2 deposit (which was proved by our experiments), texture of electrode can affect the rate of these cathode reactions. Thinking about (200) and (100) planes to be the same family, and (220) and (110) planes also, it is concluded that Ni-ZrO_2 deposit as electrode for hydrogen evolution process can evidently reduce its reaction rate compared with nickel electrode in a same condition of polarization, owing to the change of crystalline texture.

2. XPS Detection

XPS response for zirconium 3d level electron in the Ni-ZrO_2 (17.8wt%, particle size 2.3 μm) coating differs obviously from that in the pure ZrO_2 powder (Fig.1). In order to observe the change of corresponding XPS peaks for zirconium in the composite coating and pure ZrO_2 powder, the curve b in Fig.1 was resolved with the computer simulation on the bases of zirconium peak shape, position and the difference in binding energy between peaks. The result shows that XPS response for zirconium in the composite coating is composed of two groups of peaks similar to that of pure ZrO_2 powder (see Table 3).

When we analyze corresponding $3d_{5/2}$ orbital binding energy for zirconium peaks of two groups in Table 3, it can be found that the binding energy (180.3

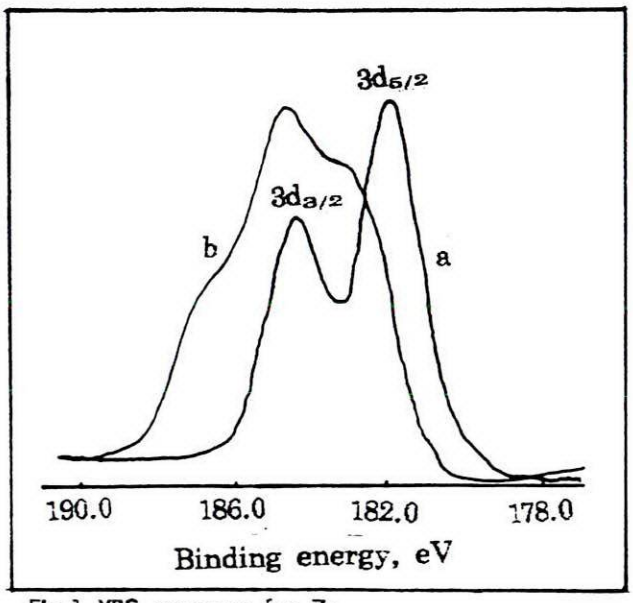

Fig.1—XPS response for Zr
a—pure ZrO_2 powder, b—Ni–ZrO_2 coating.

Table 3
Result of Resolution of XPS Response for Zirconium in the Composite Coating

groups	binding energy of peaks, eV	
	$3d_{5/2}$	$3d_{3/2}$
1	180.3	182.9
2	181.8	184.6

eV) for zirconium $3d_{5/2}$ of first group in composite coating is 1.9 eV lower than that in pure zirconium powder (182.2 eV). Because the negative shift in binding energy of an electron suggests that the oxidation number of corresponding atom decreases, it is held that this group of Zr peaks arises from zirconium ion with lower valence. We may predict it should be Zr^{3+} ion according to the approximate relationship between chemical shift and oxidation number, as the binding energy for $3d_{5/2}$ electron peak in zirconium metal is 178.5 eV. The binding energy for Zr $3d_{5/2}$ peak of second group in the composite coating is only 0.4 eV lower than that in pure Zr powder. The peak of this group which is close to that of pure ZrO_2 powder can be considered to arise basically from Zr^{4+} ion.

Result mentioned above shows that Zr^{4+} on the deposit surface are partially reduced to Zr^{3+} while ZrO_2 particles get into deposit from bath in the codeposition precess, that is, the zirconium valences on ZrO_2 surface in composite coating are +3, +4 and some intermediate valences between +3 and +4.

3. UPS Detection

It can be seen from UPS response for d band of nickel in nickel deposit (Fig.2) and Ni-ZrO_2 composite coating (Fig.3) that the ionization energy for d band of Ni in the two coatings are 1.0 eV and 1.6 eV respectively. The fact that the ionization energy for d band of Ni in composite coating is greater by 0.6 eV than that in Ni deposit indicates more difficulty in ionization of Ni atom in the Ni-ZrO_2

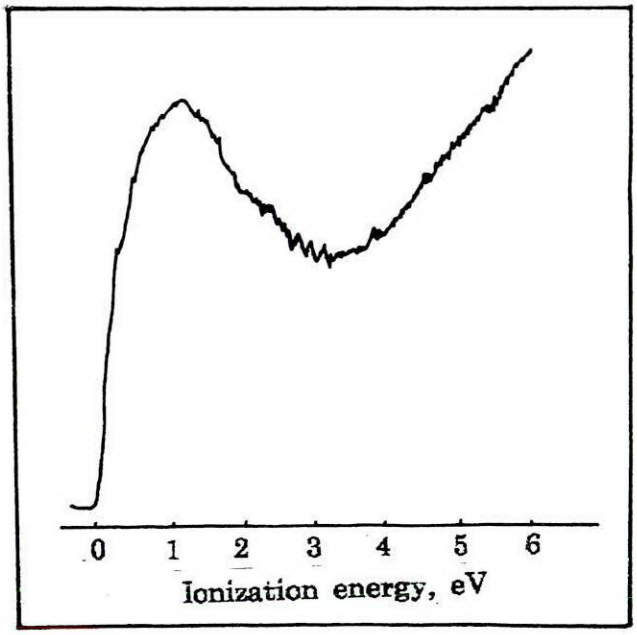

Fig.2—UPS spectrum for d band of Ni in Ni deposit

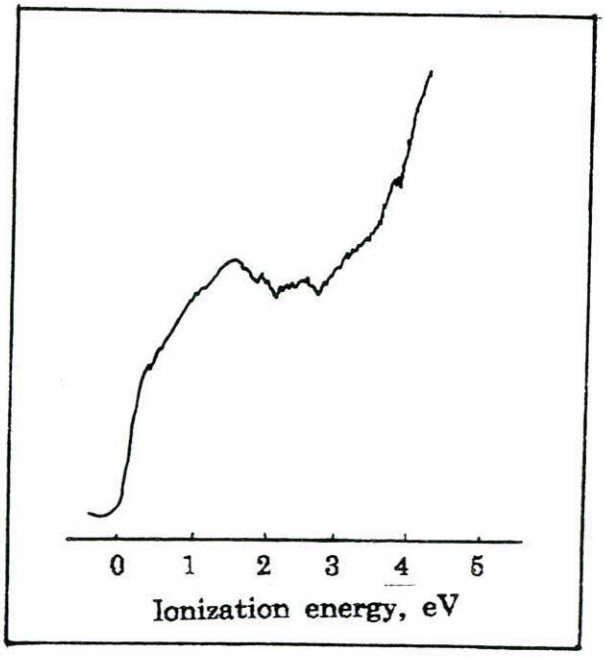

Fig.3—UPS Spectrum for d band of Ni in Ni–ZrO_2 deposit

coating as compared with Ni deposit, and the emission intensity for d electron in Ni decreases markedly in this composite coating too. This result shows indirectly also that nickel in the composite coating is entirely possible of bonding with particle.

4. Catalytic Activity of Deposits for Hydrogen Evolution Reaction

It was proved by means of XPS and UPS measurements mentioned above that valence state and d electron energy in composite coating have evidently changed. This indicatis that orbital interaction exists between nickel and zirconium in the ZrO_2 particles which have entered into coating. This orbital interaction has an important effect on the properties of coating. For example, when the hydrogen evolution reaction is carried out with Ni–ZrO_2 coating as an electrode, that catalytic activity of this electrode is evidently higher than that of pure nickel deposit just because this orbital interaction acts on them. The former studies have shown that catalytic activity of transition metals is closely related to the condition of filling up with electrons on its d orbital. The more the d orbital is filled with elections, the higher the catalytic activity of electrode[5,6]. Because the degree of filling for d orbital of nickel in Ni–ZrO_2 coating is greater than in pure nickel deposit, which leads to the decrease in adsorption heat of hydrogen atoms on the nickel and hydrogen atoms adsorbed on nickel can more easily be desorbed thereby, the catalytic activity for hydrogen evolution reaction of this composite coating should be higher.

After finding out charge transfer resistance R_r from the impedance plane plots for pure nickel and Ni–ZrO_2 electrodes[7], the exchange current density, i^o, at small overpotential and at temperature 293K for hydrogen evolution reaction on them can be calculated from

$$i^o = 0.01262(1/R_rS)\ (A/cm^2)$$

Substituting measured value R_r and real surface area S of deposits which can be determined by the capacitance measurement into above formula, we could find $i^o = 5.19\times10^{-6}A/cm^2$ for pure nickel electrode and $i^o = 2.15\times10^{-5}$ A/cm^2 for Ni–ZrO_2 composite electrode. The latter is 4.1 times larger than the former. If the effect of texture change of nickel in Ni–ZrO_2 coating on the decrease of the rate of hydrogen evolution were eliminated, the raise of catalytic activity for hydrogen evolution due to orbital interaction between nickel and ZrO_2 would be still more than above value.

Conclusions

The particles and matric metal in composite coating are not simply in a form of mechanical mixture. At the appearance of ZrO_2 in the composite coating

the preferred orientation of crystal planes of nickel can be turned from plane (200) to (220) on which the progress of hydrogen evolution reaction is unfavourable. The orbital interaction between ZrO_2 and nickel causes the filling up with elections on d orbital to be higher and the hydrogen atoms adsorbed on the composite coating to be easily desorbed, so it is favourable that the hydrogen evolution reaction may occur. That the catalytic activity of Ni-ZrO_2 composite coating is evidently higher than that of pure nickel deposit is just as a result of the interaction between matrix metal and particles.

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Dual-bath Plating of Composition Modulated Alloys (CMA) based on a newly developed Computer Controlled Plating System

PETER T. TANG*, PETER LEISNER, PER MØLLER

Centre of Advanced Electroplating (CAG), The Technical University of Denmark, building 425, 2800 Lyngby, Denmark

CHRISTIAN B. NIELSEN

Physics Department, The Technical University of Denmark

DAVID MA NABIRAHNI

A Fulbright Chemistry Professor on leave from Pace University, Bedford Road, Pleasantville, NY 10570

Abstract

Composition Modulated Alloys (CMA) are attracting ever increasing interests, as new and fascinating applications are reported. Until recently, producing these multilayered coatings have been difficult, particularly for larger samples.

This presentation will explain the design, use and purpose of a computer controlled plating system for producing large scale CMA-coatings. Employing a dual-bath technique, multilayered materials with more than 1000 alternating layers have been manufactured and investigated. The thickness of each layer ranges from 25 nm to several microns.

The characterisation results, as obtained with SEM and applications for multilayered systems such as Cu/Ni and Cu/Co, as well as the possibilities and limitation of the plating system will be discussed.

Introduction

Unique properties of multilayer composites consisting of two electroplated metals have been reported several times in the last 15 years. In 1984 Tench and White[1] reported a significant rise in tensile strength when alternating layers of copper (400 nm or less) and nickel were electrodeposited from a nickel bath containing small amounts of copper (single-bath technique).

There are two basic ways to produce a metal multilayer by electrodeposition:

- The single-bath technique in which a pure metal, and an alloy of the first metal and another metal, is plated successively by changing the current density, by controlling diffusion or potential or by a combination of these possibilities.
- The dual-bath technique involves two different electrolytes, which usually are standard plating baths. The composite is created by moving the substrate back and forth between the two baths - plating thin well-defined coatings of alternating metals.

This paper will concentrate on the dual-bath technique, the advantages and disadvantages in general and on the automated system build for this investigation.

CMA Applications

When thin layers of two alternating metals are electrodeposited on a substrate, the structure tends to get extreme properties when the wavelength (layer thickness) gets below approximately 1 μm. Tensile strength, ductility and other mechanical properties have been reported by a number of researchers. Other, perhaps even more interesting, properties such as magnetic, optical, physical and chemical properties are known to change as well. Composition modulated alloys (CMA) can be looked upon as new materials, because the two alternating metals in the structure are constantly blocking the formation of the individual structure that each of the two metals would approach if allowed[3].

Some of most promising results indicate several interesting applications:

1. The use of structures with high tensile strength in micro-mechanics.
2. Storage devices using a perpendicular orientation of the magnetisation vector[4] to create true vertical recording (for hard discs etc.).
3. Optical devices such as laser mirrors or mirrors for long wavelength neutrons[5].

This investigation will concentrate on a method to *produce* CMA structures, and not as much on the different applications.

Plating System

Plating CMA structures manually, or semi-manually, makes it extremely difficult to get reproduceable multilayers in which the thickness of each layer is well defined and every layer has a good adhesion to the layer just before.

Design of the Plating System

Dealing with automated systems, it is important to ensure that every move can be controlled, and that it is possible to leave the system unattended for several hours.

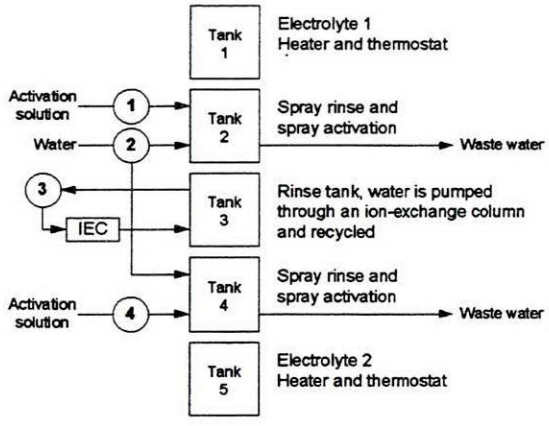

Figure 1: Simplified drawing of the automated dual-plating system used in this investigation.

Finally, when designing the system, problems such as activation, rinse, contamination of plating baths, distance to anodes and maximum system flexibility has to be considered.

The automatic plating system consists of five tanks, two plating tanks - one in each end of the line - and three tanks for rinse and activation. The four pumps are connected through electronic valves. Pump ① pumps activation solution through a valve to tank 2, pump ② deliver water for spray rinsing to tanks 2 or 4, pump ③ recycles the rinse water in tank 3 across an ion-exchange column (IEC) and pump ④ sends activation solution through a valve to tank 4 (see figure 1).

The plating tanks (1 and 5) and the rinsing tank (3) has air agitation and the electrolytes in tanks 1 and 5 are both equipped with heater and thermostat.

All movement of the arm holding the sample is powered by compressed air and controlled by a set of computer controlled valves and sensors.

Selecting Electrolytes

In principle the metals that can be combined in multilayers using this system are only limited to the metals that can be plated from aqueous solutions. Although one has to keep in mind that the adhesion between the alternation layers should be reasonably good - f.ex. combining copper and hard chromium can not be recommended since the adhesion when copper is plated on chromium is rather low.

When two metals have been selected, a suitable electrolyte for each of them will have to be provided. Since each layer is relatively thin, it is important that the electrolyte used has an excellent levelling effect, so that the surface of the CMA remains smooth, and so that the two metals involved are not mixed within each other, but keeps perfectly secluded allowing the extraordinary CMA structure to be formed. Typical electrolytes would be any electrolyte producing a smooth surface with a well-defined structure.

Finally an activation system for each metal will have to be selected. Activation is usually necessary to avoid passivation of a surface, or parts of a surface, during rinse and transportation. Some electrolytes, especially the ones containing organic additives, can leave a thin

layer on top of the metal that prevents further plating unless it is removed. Typical activation systems are organic or inorganic acids or solutions containing strong complexing agents. Additives to reduce surface tension (tensides) can also be used with some success.

An example of what can happen if one of the electrolytes produces rough deposits* can be studied in figure 2.

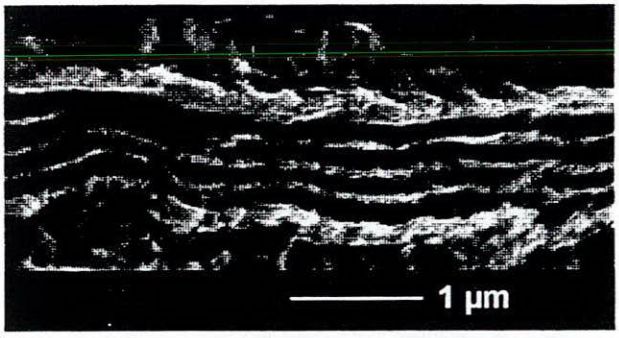

Figure 2: CMA structure (Exp 2165, cobalt/copper) with one thick and three thin cobalt layers each followed by a thick copper layer. The system is not confined to producing layers of identical thickness.

Programming the System

For the plating system a small computer program has been developed to ensure perfect timing, ease of use, real-time monitoring and flexibility.

For each experiment a small sequence of orders has to be typed. The system accepts a few different words and their combinations, but there is no limit to the number of lines in a sequence.

Using table 1 as an example, the general idea of the computer program becomes obvious. After a few lines just stating the name of the experiment, the metal in the electrolytes etc., the line `UNIT = 100` appear. The unit set here is the basic time unit used throughout the experiment. The unit controls the time used to execute each line of the program in 1/100 of a second. In table 1 the unit is set to 100, this means that a line as `PAUSE 120` makes the program wait for 120 units (in this case 120 seconds). The machine will execute an order, f.ex. `ARM UP`, and then wait the remaining time until 1 unit has passed. This ensures perfect timing during all steps of the plating process.

```
PROGRAM =CMA4
TANK(1) =NICKEL
TANK(3) =RINSE
TANK(5) =COPPER
VALVE(1)=
VALVE(2)=
VALVE(3)=WATER
VALVE(4)=ACID
UNIT    =100

REPEAT 50
  MOVE 4
  ARM DOWN
  VALVE 3,1
  VALVE 3,0
  VALVE 4,1
  PAUSE 1
  VALVE 4,0
  VALVE 3,1
  VALVE 3,0
  ARM UP
  MOVE 3
  ARM DOWN
  ARM UP
  MOVE 1
  ARM DOWN
  PAUSE 120
  ARM UP
  MOVE 4
  ARM DOWN
  VALVE 3,1
  VALVE 3,0
  VALVE 4,1
  PAUSE 1
  VALVE 4,0
  VALVE 3,1
  VALVE 3,0
  ARM UP
  MOVE 3
  ARM DOWN
  PAUSE 120
  ARM UP
END REPEAT

END PROGRAM
```

Table 1: Program example. This was used to produce the CMA structure seen in figures 4 and 5. Note that tank 2, and valves 1 and 2 are not used.

The system also has the possibility to make loops (`REPEAT 50 ... END REPEAT`) and to open (`VALVE 3,1`) or close (`VALVE 3,0`) the four valves in the system and of course to move the arm holding the substrate (`MOVE 3`) to any of the 5 tanks, or up and down (`ARM UP/DOWN`).

* The cobalt bath contained no additives, but it is otherwise close in composition to the the nickel bath described in table 3.

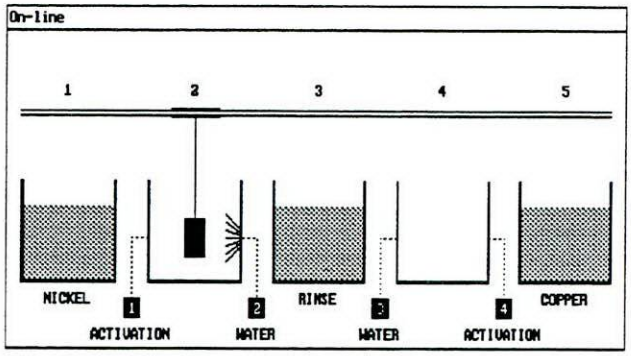

Figure 3: Screen dump showing the status of the system, along with a schematic representation of system components (real-time monitoring).

Limitation of the System

The two basic ways to generate CMA structures, the single-bath and the dual-bath methods, both have their advantages and disadvantages.

	Single-bath	Dual-bath
Diffusion dependence	High	Low
Number of metal combinations	Medium	High
Minimum layer thickness	About 1 nm	About 25 nm
Waste water generation	Low	High
Flexibility of sample geometry	Low	Medium
Process speed incl. plating time	Medium	Low
Process control complexity	High	Medium
Mass-production potential	Low	Medium

Table 2: Advantages and disadvantages of the two different ways to produce CMA structures.

The most important difference between the two methods mentioned above is that plating from a single bath system usually gives a pure metal layer (of the most noble metal in the electrolyte) and an alloyed layer containing both of the two metals in the solution - although the amount of the noble metal can be as low as 3 atomic per cent[6].

It is equally important to note, that in spite of the production advantages (see table 2) the dual-bath method is incapable of plating layers much thinner than approximately 25 nm.

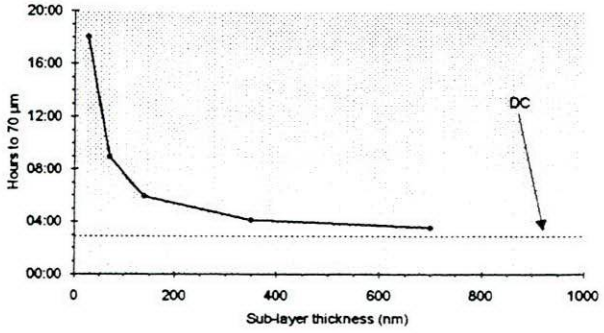

Figure 4: Time needed to produce a CMA structure of 70 µm versus the thickness of each individual sub-layer. The dotted line is the time needed to plate 70 µm of one metal at the same current density (2 A/dm^2).

This is because the time needed for producing a reasonably thick CMA structure increases exponentially when the thickness of the layers is reduced.

The main reason for this huge rise in time consumption when layer thickness goes below 50 nm, is that the time used for transportation, rinsing and activation is constant and only depends on the *number* of layers, not on the thickness (see figure 4).

Experimental

In order to test the new dual plating system, and for this investigation, nickel/copper CMA structures have been produced with different combinations of layer thickness and number.

Bath Chemistry

For the present investigation the following compositions of electrolytes and activation solutions were selected.

Nickel bath

The nickel plating bath was a standard semi-bright Watts electrolyte. This bath was used because of the

reasonably smooth finish of the nickel. The temperature in the bath was keeps at 50°C and the pH-value adjusted to approximately 4.0.

Semi-bright Nickel	Concentration (g/l)
$NiSO_4 \cdot 6\ H_2O$	300
H_3BO_3	40
$NiCl_2 \cdot 6\ H_2O$	40
Formaldehyde (37%)	0.8
Duplalux™ 538	0.2
OXY™ 62A surfactant	0.2

Table 3: Composition of the semi-bright (commercial bath) nickel electrolyte used in tank 1 (see also table 1).

Copper Bath

For the copper electrolyte a typical acidic copper bath based on sulphuric acid was selected. This electrolyte also contained additives to get a smooth deposit and to reduce surface tension. Because the concentration of copper is relatively low compared to the concentration of sulphuric acid, good conductivity and high throwing power can be expected.

Bright Copper	Concentration (g/l)
Cu (added as $CuSO_4$)	20
H_2SO_4	200
Schering™ Ansatslösung 210	10
Glanz A	0.3
Glanz B	0.5
NaCl	0.12

Table 3: Composition of the copper electrolyte used in tank 5 (see table 1). The additives improves the levelling effect significantly.

The bath has a pH-value below 1 and was used at room temperature.

Activation Solution

For activation after plating and rinse, a solution of 20 g/l citric acid was used for both copper and nickel surfaces.

Calculating Thickness

In the example from table 1, the semi-bright nickel bath was in tank 1 and the bright copper bath in tank 5. When the arm of the machine was in any of the two tanks it would wait for 120 unit (120 seconds). The rectifiers connected to the two tanks where both set to 4 A. The plateable area was exactly 2 dm^2, one square dm on each side of the panel, giving a total current density of 2 A/dm^2.

Each time the panel goes into one of the two plating baths, it remains there for 121 seconds (that is including 1 second while moving up and down). At a constant current of 4 A, $2.51 \cdot 10^{-3}$ moles of metal will be reduced.

For copper, having a molar weight of 63.55 g/mole each layer weighs 0.1595 g while nickel layers are only 0.1474 g (M_{Ni} = 58.71 g/mole). With a density for solid copper of 8.92 g/cm^3, 0.1595 g of copper on a 2 dm^2 area amounts to an average of 894 nm, while nickel (density = 8.90 g/cm^3) layers are expected to be 828 nm.

The total weight gain was measured to **15.64 g**. This should be compared to the weight of 50 layers of copper (50 times 0.1595 g) plus 50 layers of nickel (0.1474 g each) giving a total of **15.3450 g**. This small difference between the calculated and measured weight origins from one or several of the possible sources of error that an experiment like this always has.

1. Rectifiers are slightly inaccurate, giving more or less than the expected charge.
2. The density of plated metals is a little different than the density for pure metals.
3. Metal has been dissolved during activation.
4. Some charge has been used to reduce oxide layer formed between activation and plating.
5. The current efficiency could be less than the assumed 100 per cent, especially when plating at high current densities.

and finally - but *most* important:

6. During the preparation of the samples for SEM, the cross-sections are polished and etched. This way all the copper is dissolved, but *also* some of the nickel!

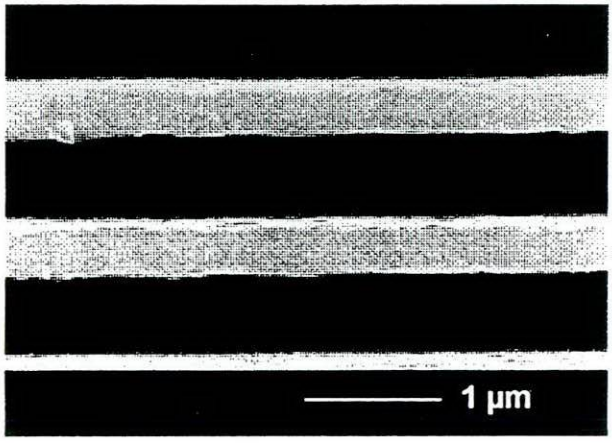

Figure 5: Scanning electron micrograph (Exp 1917) of the copper/nickel CMA produced using the program in table 1. The cross-section has been polished and the copper selectively etched away.

In figure 5 it is possible to measure the thickness of the two layers. The nickel layer (white) is approximately 400 nm and the copper layer (etched away) 670 nm.

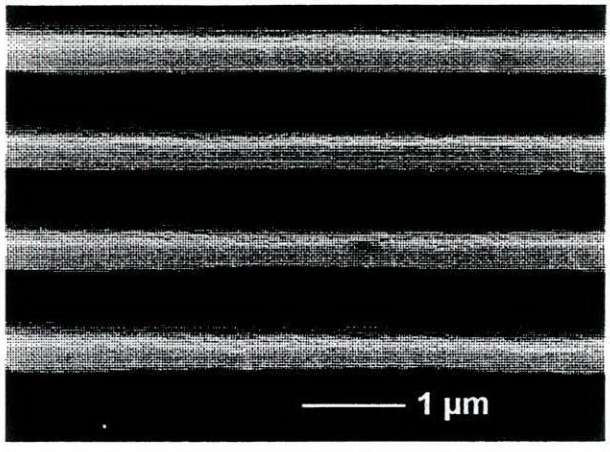

Figure 6: SEM-picture (Exp 1922) of another section of the same sample, but this time the speciment is tilted to get a tree dimensional image (copper layers have etched away selectively).

In figure 6 the nickel layers are about 310 nm while the missing copper layers must have been approximately 760 nm. Looking at other cross-sections of the same panel, nickel layers of 420 nm and copper layers of 640 nm can be found.

The reason for this variation in thickness, depending on which cross-section is used and from where on the panel it has been cut, can be explained by a combination of several well-known problems in the field of electroplating *and* by the way the samples have been prepared (see above and next paragraph).

First of all the current density is not constant across the sample (more metal is deposited on corners than in the centre of the panel), the amount of metal removed during activation (acid) depends on spraying conditions and finally will the layer thicknesses, because of current efficiency, diffusion of metal ions in the electrolytes and distance between anodes and cathode (the substrate) depend strongly on where exactly we make the cross-section.

Galvanic Corrosion

Galvanic corrosion, or ion-exchange deposition, is known to take place when a metal coating is submerged into a solution containing a more noble metal (nickel coated sample in a copper bath). If this happens, already plated nickel atoms will dissolve and at the same time copper ions from the solution will be reduce (deposited). This phenomenon could explain that the copper layers are thicker than calculated, but it is more likely to be because the throwing power of the copper bath is far better than that of nickel (more nickel than copper on corners etc.).

Galvanic corrosion is not believed to have any significant effect on the results from this investigation, because the sample always has a cathodic potential[2]. Even during the 1/10 of a second it takes the compressed air to push the sample into the electrolytes.

When all this has been said, it is equally important to note that the thickness of each layer in each cross-section (secluded area) is very consistent and that layers appear smooth and without pores.

Preparing Samples for SEM

A piece of 1 cm2 was cut from the panel using a SiC disk on a Struers Ultramicrotome™ equipment. To prevent the edges of the cross-section to be destroyed during grinding and polishing, the edges were cast in wax at about 100°C.

In the first grinding 800 grid SiC paper was used, in the second 1200 grid SiC paper was used. The polishing was performed on a Struers DP-Dur™ with 3 μm diamond paste and later with 1 μm paste.

To be able to see the two metals as the different layers they are, in to get the 3-dimentional view from figure 6, the samples were etched in a mixture of water (12.5% by volume), concentrated acidic acid (25%) and concentrated nitric acid (62.5%) for about 2-10 seconds.

Immediately after etching the each sample was rinsed in water and alcohol. Finally the wax was removed with acetone, giving the possibility to get a tilted view of the cross-section and the surface (last layer plated) of the structure.

Summary

As new interesting applications for composition modulated alloys (CMA) continue to arise, it is vital to be able to produce these materials in large amounts in order to get the most out of this possibility.

With the automated system described in this investigation, it is possible to produce well-defined multilayered structures using the dual-bath method. The possible thickness of each layer range from 25 nm to several micrometers. The structures of nickel and copper are uniform in thickness and texture, and appear to be without errors such as pores, cracks etc.

It is possible to predict and calculate the average thickness of each layer. With 100 alternating layers of copper and nickel, each around 800 nm thick, the calculated weight was only 2% from the measured weight after plating in one experiment and even lower in others.

The first preliminary tests of the CMA structures have in bending tests* indicated some improvements as far as ductility and the propagation of cracks is concerned.

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* The bending tests were performed by Dr. Tohru Watanabe at Tokyo Metropolitan University, Japan.

Paper Not Available In Time For Publication

ctrochemical Regeneration of Chromating Solutions (AESF Research Project 89)

Sergei Kruglikov, Alexander Anufriev, and Julia S. Svirshevskaya,
Mendeleyev University of Chemical Technology, Moscow, Russia

trochemical regeneration of chromate-based solutions used for the treatment nc-plated and brass parts has been studied. Two-chamber cell with cationic brane contained spent chromating solution in the anode compartment and 3– rcent sulfuric acid in the cathode compartment. Lead, platinum and titanium ed with ruthenium-titanium oxide were used as anodes. Complete regenera- ncluded removal of zinc or copper from the spent solution, pH adjustment and ation of trivalent chromium to a hexavalent state. High anodic current efficiency obtained with lead anodes, which are stable in chromate-sulfate solutions only. oval of metal cations from spent solutions can be performed effectively with stable anodes.

copies of this paper please contact:

Sergei Kruglikov
Mendeleyev Univ. of Chemical Technology
Miusskaya Place
9 Moscow, Russia 125190
709 52004204

BRUSH PLATING, A HISTORY

Bob Brookshire
Brushtronics

As far as I know, no one knows for sure just when anything was first started or who came up with the original idea. Many things, just like Topsy, just grew. A process such as Brush Plating evolved and has been making advancements ever since.

At one time in my life I was very anxious to get patents on the various "new ideas" that I came up with. Much to my dismay many of them were shot down and the gentleman that did the most was Benjamin Franklin. It was mind boggling to me the things that he did and thought of doing. We got to gold plate the State capitol dome in Sacramento, Ca. when I was able to point out to the men in charge that the ball on the very top was electroplated in 1862 and was still in good shape. The man was Edmond G. (Pat) Brown, who at the time was governor of the state. The job was let out in 1980 a mere 20 years after the first sales call. It just goes to show you some things do not happen over night. Then they sent it out for three bids. I was told no one else wanted to do the job. Now back to the ball. We touched it up with our modern state of the art Brush plater with all sorts of switches, counters, dials, calculators and computers. And as we were doing it I was thinking of what the conditions were for them then. Back in 1860 what was their state of the art? One thing, gold was $12.00 an ounce and I'll bet they did not have that many suppliers to choose from as we do now.

I feel sure that brush plating is as old as electroplating its self. Many a time I've gone into a place to introduce Brush plating to the platers and more likely that not, an old palter will call me aside and tell me that he has been fixing parts something like that for years. Sometimes it would turn my stomach to see them take an old dirty shop rag, wrap it around a wire, dip it into a tank and slop plating solution around a part that was held up against the cathode rod. Sometimes only a color of metal would plate.

So to say who invented it, as far as I can see, can not be done. The first people to sell a commercial Brush type plating was either Raymer, Dalics. Raymer in the U.S. and Dalic in Europe. It never ceases to fascinate me that parts of any size, shape, or in any location can be plated. With any metal that can be electroplated out onto any conductive surface.

Many people ask,"Just how does it work?" and I am often tempted to say "Just fine". It works very well. But of course they mean the process in general, or at least that is what I think that they mean. Sometimes I feel like I tell them how to build a watch and all they want is to know the time. My favorite way to explain a tough job for Brush plating is "A hand full of nuts and bolts". This would take for ever and might not be done to meet mil specs. In 1960, there were, to my knowledge, 4 companies selling Brush plating

or Brush plating type systems. At the start of this year there are approximately 50. New ones starting as we speak.

I know that some people would like to have the name changed to various other things It has been Brush plating for fifty years. Calling it by another name certainly will not change it.

Some of the names it has been called as: "swab plating", tankless plating", selective plating". A French magazine had an article that called it "tampon plating", and there are many more.

The thing that put Brush plating on the map and made it into a meaning-full process was when the United States Navy started using it for extremely critical parts and put limiting specifications and definite requirements. Federal Specifications, and the major Contractors gave Brush Plating recognition by also creating specifications.

One of the pioneers in the beginning of the growth on Brush Plating is Mildred Patterson at the Alameda Naval Air Station. I have spent more than half of my life Brush plating and during that time I have seen a fantastic industry grow. Millions upon millions of dollars are saved using the Brush plate process. I have also seen quite a few characters come and go. And the most fascinating one to me was Marv Rubinstein. I did not agree with a lot of the ways he did things but he certainly did more than his share to advance the Brush plate Industry.

We have come a long way since the process was first started by Pete the plater, and I am sure we will go a good deal farther.

I would like to go into just how the process works but there are mores talks today and I want to save some of the good parts for the other speakers. If any of you have any questions or want to talk about Brush plating, corner me after the sessions. The only thing that I know more about than Brush plating is women so if you have any questions on either, look me up at any time.

GOLD PLATING AUTO TRIM IN CANADA

Paul Andaloro GOLD MERIT of Canada
Peter Andaloro GOLD MERIT of Canada

Today's automobile industry is any ever growing part of the world society. This society puts great emphasis on personalization and craftsmanship of their individual vehicle. There have been many ways to personalize or customize that vehicle. Many chose to do as little as pinstripe or as much as a complete body refabrication but the most important asset of any personalization job is the quality of the product. With the need for a societies desire to show wealth and success, there has only been on thing that has stood the test to time. There is no better way to show that one thing then adding it to one of your most prized possessions, your vehicle. It has been used to show power since the beginning of time and is used today as an indicator for a persons success, and that is Gold.

Gold has been used in many applications on automobiles. It has been used for many years to show special edition cars and to show that your vehicle is different from others. In the past this has been limited to a select few, but today it can be assessable to just about every one. The automobile customizing industry has always tried to provide the customer with an efficient way to add detail to his vehicle. This allows the customer to customize his vehicle as his or her taste changes. Gold has been an effective customizing detail for many people in the past but today with the new technology that will allow people to Gold plate items on the vehicle without removal, it also has become affordable to many. With immediate results while the customer waits for his finished product and a reasonably low cost, Brush-Plated Gold has found its place in the auto customizing industry.

The advantage that the Brush Plating System has is that the parts can be processed on the vehicle. This is of extreme importance because many emblems and trim pieces are permanently bonded to the vehicle. Removal would mean destruction of the part. This, however; does not mean the part can only be done on the vehicle. The plating process can be accomplished on or off the vehicle with the same quality Gold deposit. There are a wide range of automotive parts that can be changed from Gold to Chrome. Some of the more common parts are emblems, wheels, and trim molding but anything that is chrome or stainless steel inside or outside the vehicle can be changed to gold. There are uncountable uses for this process on stock or custom applications with quick high quality results.

Performing this service in our region of Canada, it is very important to ensure a durable finish that withstands the elements of weather and time. Key factors that permit this are a well prepare part and a hard wear resistant finish. There are many factors that can

contribute to failure of the plate The first most common problem is usually the improper care of the finish. Many owners of gold packages tend to treat the gold as paint. This means, as the car is washed and compounded, no precaution is taken to preserve the gold finish. Abrasive compounds and excessive scrubbing can damage or sometimes even remove the finish. I recommend cleaning al gold finishes with soap and water and buffing to a shine with a soft cloth. Secondly, power buffers and automatic car washes using power brushes can put excessive scrubbing pressure on the gold finish which again can damage the finish by generating a scrubbing effect with the dirt or road debris. We always recommend keeping the gold package clean to prevent premature deterioration of the gold from road salt scratches and car washing abrasion. Lastly, parts that have begun to deteriorate may give you problems in finished appearance and adhesion of the gold to the nickel substrate. Old parts that have failing chrome usually are an indication of many other problems. You want to watch for stress fractures that will appear in a finished part and any pitting that will affect the finished product. Gold will not hide imperfections in the base metal. Adhesion of the gold can be applied to any chrome plated or stainless steel parts. Many people ask how we can plate on plastic, but actually we are plating on a metalized plastic part. This means, a plastic base has a copper, nickel and chrome deposit on it. This allows us to draw current through the part and perform our process to the item. If it is a completely plastic part, we would not be able to draw current and in turn, our process could not be done. When beginning on an item, we recommend doing a continuity test to the part This will tell you two things, either current can be drawn through the part or not. If the current cannot be drawn, it is possible a clear coat is on the surface. We would suggest finding an area on the part that cannot be seen and try scratching through the surface with a probe and retest the continuity. If you then achieve current flow, you must strip the clear coat with a solvent. If you still get no current flow, the part cannot be gold finished. If current can be drawn, usually the part can be finished in a quality gold finish.

Our standard process for gold plating over chrome is considered a three step process. Using a electroplater in a reverse or deplate current flow, we use a hand held anode made of either graphite or stainless steel, and brush the area with an chrome strip solution. This would develop an immediate yellow coloration on the anode wrapping. If no coloration appears, we would first suggest checking to make sure the electroplater is in reverse current. If so, a standard process can not be accomplished and another process must be used. After you have established a standard process can be used, and a yellow color is achieved on the

anode wrap, begin stripping the part in one select area until a nickel substrate appears. Increase that area until the entire part is stripped. We suggest spending a little extra time on the stripping to ensure you will not have to rework or restrip any missed areas. If any chrome remains the gold will not adhere to the surface. Now that you have a completely nickel part, since you have stripped al the chrome, you may now begin your activation step. As you are performing the process we also suggest keeping the solution run off to a minimum amount due to clean up. All the chemicals in this process will not effect the paint, but clean up will be increased if some precautions are not taken. Now we must activate the oxidized nickel. Again using your electroplater in forward polarity or plate position swab the area with another anode saturated with nickel activator. We suggest leaving the activator on the surface to prevent oxidation before gold plating. Now we are ready for gold plating. We will deposit gold on the surface using a third anode until a desired thickness is reached. It is also possible to gold plate stainless steel trim by not stripping and adding in a nickel flash before the gold deposit. This will allow you to gold finish just about any car trim you will encounter.

Gold applied with the Brush-Plating method has been a very valuable tool in the automobile customizing industry It has allowed a way for our company to provide the customer with a cost effective high quality gold finish that will last for years to come. This tool has also found its way into many other custom finish industries. Remember, if the finish is initially chrome or stainless steel it can be finished in place with gold.

AEROSPACE BRUSH PLATING

By

R. L. Brookshire CEF

Scientist
Hughes Aircraft Company
Materials and Process Technology Department
Technology Support Division
Electro-Optical Systems

Brush plating has been used effectively at Hughes Aircraft Company for many years. In the early 70's brush plating was used to apply copper and tin/lead to aluminum heat exchangers for solderability. Later in the 70's a process for nickel and gold plating electrical ground straps on spacecraft was developed and is still used on all spacecraft being built today. As the demand for more cost effective and efficient problem solving has increased, many more exciting applications for selective plating have arisen.

At Hughes the following questions are answered prior to brush plating on hardware:
1. Is the application necessary?
2. Are there unacceptable risks associated with additional processing?
3. Can other processes accomplish the same result?
4. What testing will be required?
5. Is the application cost effective?
6. Are there special customer requirements or restrictions?

These are some of the questions that are asked in determining if the hardware should be brush plated.

The brush plating equipment used at Hughes includes the following:

Two 25 volt, 25 amp machines
One turning head
Three blasting cabinets
Many plating solutions

Three representative case histories are summarized below:

PROBLEM A completed sensor was damaged during the second to last test prior to final acceptance by the customer. The sealing surface on two stainless steel cold fingers were damaged. Both fingers had scratches 0.003 inch deep around the sealing area. The sealing area was 0.5 inch long and 0.125 inch in diameter. The material was a 300 series stainless steel.

Replacing the cold fingers would require the disassembly and retesting of the sensor. The delivery schedule for the sensor was two weeks including ten days for the final acceptance test.

SPECIAL CONCERNS - Cryogenic temperatures, machining stresses, sensor cost

The temperatures extremes were from liquid helium to boiling water - 300°C to 125°C. Testing required thermal shocks of liquid nitrogen to boiling water repeated forty times followed by liquid helium to boiling water repeated 25 times. These tests were conducted on brush plated cold finger samples. The samples were then machined and temperature tested again. There were no failures.

PLATING PROCESS - Required masking was minimal because the sensor was already protected for machining purposes. Care was taken to ensure that the process did not damage the testing equipment or setup:

1. Wipe the area and adjacent areas with acetone and isopropyl alcohol.
2. Apply platers tape to the adjacent area.
3. Electroclean sealing surface.
4. Activate surface.
5. Nickel plate to required dimension.

The actual plating took place in a special laboratory setup where the sensor was to be machined. The areas to be plated were repaired in less than thirty minutes each. The testing and repair to the cold fingers was accomplished within two days.
Cost saving exceeded $500,000.

PROBLEM Electronic housings filled with electro static discharge (ESD) sensitive components required electromagnetic interference (EMI) shielding to meet new requirements. Since mating surfaces were anodized aluminum, the nonconducting surfaces needed to be conductive. The mating surfaces were approximately eight inches by two inches and included an O-ring groove. The plating had to be uniform and smooth on all surfaces. Disassembly would require additional testing and preclude meeting the schedule requirements.

SPECIAL CONCERNS - Electronics already installed in hardware, ESD damage potential to electronics, masking, deep narrow O-ring groove, environmental salt spray requirements.

The plated hardware required EMI shielding in a salt environment. Testing included 168 hour salt spay, electrical grounding/resistance, and adhesion.

PLATING PROCESS - Masking to ensure that exposed electronic components are not affected during processing. Grounding of hardware to prevent ESD damage.
1. Ground hardware.
2. Solvent wipe.
3. Mask adjacent areas to mating surfaces with plater's tape.
4. Remove anodize coating by aluminum oxide blast.
5. Nickel plate.
6. Gold plate.

The aluminum surfaces were blasted with aluminum oxide powder to remove the anodize and then nickel plated. Nickel was plated to 0.0005 inch minimum. Gold was applied over the nickel to a minimum thickness of 0.00005 inch.

The thickness requirements were tested by cross-sectioning of sample pieces and then correlated to amp-hour readings. The sectioning also verified adhesion. The hardware was tape tested.

PROBLEM A large electroless nickel aluminum housing had areas where the plating was peeling. Blisters were discovered in a critical area near a port approximately two

years after the part was electroless nickel plated. The nickel plating was per MIL-C-26074, Class 4, Grade B, (0.0005 inch minimum). The housing was installed and ready for delivery.

Replating the housing would require removal of electronic modules and extensive retesting of the system. An analysis of the housing and blisters was conducted to determine if the blistering problem was isolated to the one area.

SPECIAL CONCERNS - Meeting the surface finish requirements, critical adhesion needed on both nickel and aluminum surfaces.

The area where the nickel was peeling was a sealing surface and required a 16 surface finish.

PLATING PROCESS - All loose nickel had to be removed, the area to be plated included both nickel and aluminum surfaces.

1. Wipe area with acetone and isopropyl alcohol.
2. Apply platers tape to adjacent areas.
3. Blast nickel surfaces to remove loose plating.
4. Activate surfaces.
5. Nickel plate.
6. Hand finish.
7. Repeat 5 and 6 until surface meets finish requirements.

The adhesion testing of brush plated nickel to both electroless nickel and aluminum was critical. Testing for adhesion was limited to tape test on hardware. Coupons were subjected to bake, bend, and cross sectioning. Coupons were electroless nickel plated prior to testing to match the hardware problem.

Other typical brush plating applications are:

1. Plating for solderability
2. Manufacture and repair of printed circuit boards
3. Repair of gold plating
4. Research and Development

CONCLUSION

The future looks promising for brush plating at Hughes. There are many problems that can be solved only by the flexible solutions and the skilled hand of a brush plater.

BRUSH PLATING TECHNOLOGY RESPONDS TO THE ENVIRONMENTAL CONCERNS AFFECTING THE METAL FINISHING INDUSTRY

Jeff Hurrell and Chris Helwig
Brooktronics Engineering Corporation
13161-B Sherman Way
North Hollywood, CA 91605

Abstract

New innovations in brush plating have been developed in response to environmental concerns which affect the metal finishing field. This paper will discuss how brush plating processes and products have provided alternatives to environmentally hazardous materials such as cadmium, hexavalent chromium and cyanide. This paper will also discuss various methods of handling brush plating waste to improve the cost effectiveness of the process.

Introduction

Great concern has been expressed over the pollution problems associated with the metal finishing industry. Regulatory agencies are continually tightening the guidelines for the use and disposal of metal finishing waste products. The results have been higher costs for metal finishing companies and the introduction of safer, more compliant metal finishing products from manufacturers of plating products. Some plating shops have simply closed their doors due to the high cost of compliance with the regulations.

Three compounds used extensively by electroplaters are on the EPA's top ten list for minimization or elimination wherever possible. These compounds are cadmium, chromium and cyanide. This paper will explore the progress which manufacturers of brush plating solutions have made in meeting the challenge of eliminating these compounds.

For years, many have realized the benefits of brush plating to minimize the amount of waste generated. This paper will also provide an overview of treatment processes for brush plating waste. The minimal amounts of waste generated can be treated economically through many various methods.

How the Brush Plating Process is Environmentally Conscious

Brush plating is an electrodepositon process, where metal, pure or alloy, is selectively

deposited on only the specific area which requires electroplating. The process of brush electroplating, when compared to tank plating, has an established set of procedures for metal preparation which are somewhat unique to the process. These procedures have specific advantages when related to safety, ease of use, and quantity of waste generated.

With the nature of brush plating as a selective plating process, the amount of solution required for simple brush plating operations can be as little as a few milliliters to as much as a few gallons fro larger, more difficult parts. Compared to tank plating, where tanks contain several hundred gallons or more of plating solution, brush plating generates minimal waste from spent plating solutions. Rinse water used for brush plating is also significantly less than the quantities used for tanks to rinse tank plated parts.

Another environmental factor for tank platers is the emissions of hazardous fumes from plating tanks. The brush plating process does not pose a significant hazard as compared to the fumes generated from plating tanks. Most brush plating solutions are used at room temperature and, therefore, do not generate the amount of fumes as a heated plating solution. Additionally, brush plating solutions are formulated keeping in mind the human factor inherent with the process. The brush-on application generally dictates close contact of the operator and the plating solutions being used. Therefore, great care is taken not to use chemicals which can be a substantial hazard to the plating technician.

Elimination of Cadmium

Cadmium plating has been used extensively for corrosion protection of steel. Cadmium acts as a sacrificial metal to protect the substrate, usually ferrous alloys, from corrosion. Although cadmium is very effective for the prevention of corrosion, cadmium is poisonous to humans and animals. Cadmium will accumulate in the fatty tissue of humans and animals, causing disease and illness to those exposed. Due to these hazards, many countries have banned the use of cadmium as a corrosion resistant coating.

Alternatives to cadmium must meet certain performance requirements depending on the application. Some of the basic requirements were; comparable corrosion resistance at the same thickness levels used for cadmium, plating solution does not cause hydrogen embrittlement over high strength steel, and deposit will accept a conversion coating to increase corrosion resistance. The most successful plating solution has been a zinc-nickel alloy deposit.

Zinc-nickel alloys have shown great promise for the replacement of cadmium deposits. Many different alloy variations are possible, some exhibiting better results than others. An alloy of zinc-nickel, with approximately 7-10% nickel will exhibit comparable corrosion characteristics as compared to cadmium. A brush plated zinc-nickel can meet the hydrogen embrittlement tests over high strength steel as indicated in QQ-P-416. Additionally, several alloys of zinc-nickel will accept chromate conversion coatings for further corrosion protection.

Elimination of Chromium

Hard chromium has been one of the more difficult plating deposits to replace or eliminate. Hard chromium exhibits many special properties, such as very hard deposits, excellent wear resistance, low coefficient of friction and good corrosion resistance properties. Hard chromium has gained a well deserved reputation as a durable and practical deposit for many applications. This reputation has provided a formidable for challenge for any would-be chromium replacements.

Brush plating has always been limited when it comes to chromium plating for the industrial and decorative markets. Brush plating manufacturers have always avoided the use of hexavalent chromium solutions, which are commonly used in tank plating. Hexavalent chromium solutions are corrosive, very toxic and carcinogenic. Due to the close contact between the operator and the plating solution used for brush plating, brush plating manufacturers have developed safer trivalent chromium solutions. These trivalent solutions, in the past, have only produced thin deposits with a darker color as compared to tank plated hexavalent chromium.

Because metals have unique characteristics, replacing chromium with a deposit exhibiting the exact performance characteristics has been very difficult. The versatility of brush plating allows for the application of many pure metals or alloys which will exhibit similar characteristics. By examining the required performance characteristics of the plated component, many times a brush plated deposit can be used to replace a chromium deposit. For example, a deposit with a low coefficient of friction can reflect the same characteristics as a harder chromium deposit with a higher coefficient of friction. The same principle applies when considering other performance characteristics, such as corrosion resistance or hardness.

In certain instances where all the performance characteristics of hard chromium are required, brush plating manufacturers have worked on the development of a direct hexavalent hard chromium replacement. Brush plated deposits which are hard and corrosion resistant are available. The limitation has been the ability to obtain deposit thicknesses over .001 inches. The latest development in brush plating is an alloy solution (KromeCoat) which produces a hardness of 650 HV and can deposit over .0045 inches of metal.

Hexavalent chromium is also used for conversion coatings and chromic acid anodizing. Brush plating manufacturers are currently testing a boric-sulfuric acid anodize solution for the replacement of chromic acid anodize. Additionally, research is continuing on replacements for chromic acid conversion coatings. Results of these products will be presented in future papers.

Elimination of Cyanide

The use of cyanide in brush plating solutions has been minimal for many years. Yet, the goal to eliminate cyanide has resulted in research to produce solutions without cyanide additives. Brush plating manufacturers produce only gold and silver solutions which contain small amounts of cyanide, most of which is complexed into the solution. Even the small amount of cyanide waste generated in brush plating can be costly and difficult to treat or dispose. Therefore, alternative gold and silver plating solutions are available for cyanide free plating.

Although these solutions are available, the performance of the solution is somewhat limited compared to their cyanide-containing counterparts. Cyanide-free silver has been used in all the same applications as cyanide silver, such as electrical contacts, buss bars, decorative hardware, and switch gear components. The cyanide free silver solution does plate slower, burns at a lower current density and has a maximum deposit thickness of .003 inches. For many users, the benefits of cyanide elimination far outweigh the lower performance characteristics of the cyanide free silver solution.

Cyanide free gold solutions are somewhat more limited than the cyanide-containing counterpart. Cyanide free gold solutions are very unstable and tend to precipitate when the pH level of the solution changes. Tank platers use additives at specific amperehours to maintain the stability of the plating solution, although for brush plating technicians, the solution is difficult to monitor while plating. For this reason, research is continuing to develop a method of maintaining solution stability while plating. The cyanide-free gold solution does deposit slower than cyanide containing gold solutions.

Handling of Spent Brush Plating Solutions

When waste is produced from brush plating processes, it must be handled and disposed within the parameters of federal, state or local regulations. For large generators of waste products, how to dispose spent brush plating solutions is not a difficult task. For the small generator, time must be taken to become familiar with the applicable regulations.

One method of disposal, involves containing waste material in drums for disposal into hazardous waste landfills. Environmentally speaking, this is not the most desirable option. The preferred option is having plating waste recycled by an authorized recycling company. The fees for recycling are also much less than landfill disposal. Because recyclers may require specific storage procedures and may only take certain metals, check with a recycler prior to accumulation of your plating waste for their specific requirements.

Whether recycling or disposing into landfills, excess water contained in plating waste can be evaporated off using an evaporator system. This will reduce the volume of waste and the cost for handling the waste.

Conclusions

For over 35 years, brush plating solution manufacturers have been pioneering new techniques and solutions to meet the needs of the industry. Safety, as well as the environmental aspects of the brush plating process has always been a priority when developing new solutions or processes. Much work has been done to eliminate the need for cadmium, hexavalent chromium and cyanide within the brush plating industry (See Figure 1). Work will continue to improve the alternative processes for more acceptability within the industry. Suppliers have a responsibility to produce products which are environmentally and functionally sound for use by the industry. Additionally, suppliers must work closely with end users providing information on how to use less plating solution and generate less waste.

Figure 1

Current Plating Deposit	Alternative
Hexavalent Hard Chromium	Trivalent Chromium KromeCoat Nickel- Tungsten Cobalt-Tungsten Nickel Sulfamate(Hard) Cobalt
Chromic Acid Anodize	Boric-Sulfuric Acid Anodize
Cadmium	Zinc Zinc-Nickel
Gold (Cyanide)	Cyanide Free Gold
Silver (Cyanide)	Cyanide Free Silver

Automation of Brush Plating
Through Single Anode Metalizing
by W. R. Wachtler

The development of Single Anode Metalizing enables brush plating to be removed from the "operator dependent process" category. It allows for the degree of automation required in any application for cost effective coating. In addition the use of Single Anode Metalizing allows for segregation of discharged materials, frequently allowing for the refurbishment of the spent brush plating solution by the manufacturer significantly reducing the hazardous waste generated. Integrated with precision, temperature compensated measurement and computer control a single anode metalizing brush plating program can be in line, in plant as a production process.

Brush plating was originally developed as a high rate of buildup, portable plating process in France. The development of acceptance of the process itself was based upon its portability, speed of deposit and on the accomplishments of skilled operators with intimate knowledge of the procedures. These practitioners were able to produce acceptable quality coatings, normally, with a minimum of secondary processing requirements. The major applications of the brush plating process developed around the repair of machinery that were no longer to design specification.

New Technologies

The development of brush plating Single Anode Metalizing became a possibility with the development of open mesh platinum coated material for use as an anode. This material did not contaminate. Prior to the advent of open mesh platinum, which was developed for tank plating, the primary material used in brush plating was high density, high purity, metalics free carbon. Because this carbon absorbed chemicals, once used, an anode became dedicated to the solution it had been used in. As an alternative, if the carbon anode were soaked in warm water and abraded to remove the impregnated surface layer then it could be used for another chemical. This was seldom done and the mark of a successful brush plating operation was multiple storage bins for the used carbon anodes of various shapes and for various chemicals.

Once the platinum mesh anode concept was proven to be usable in brush plating, the next area requiring development, if the concept of Single Anode Metalizing was to become a possibility, was the creation of a system that segregated the discharge from the single anode during the process steps. This function was to minimize the hazardous waste generated by the system. A Hazardous Waste Segregation system was developed and tested. The Hazardous Waste Segregation system enabled the segregation of the discharge liquids from the anode system to be directed to separate flow channels depending on the characteristics of each liquid.

The categories of discharged liquids that were determined to encompass the

requirements of the Single Anode Metalizing system are as follows:
- drain safe
- hazardous waste
- reusable buildup material

The third area of development was the set up of a system that routed the correct solution and rinse to the anode at the appropriate time and with a minimum of waste. The Control Valve System requirements were identified. The Control Valve System developed required positive activation, and no leakage. It also had to be able to handle varying flow rates, be chemically inert, fail closed and be capable of remote activation. This Control Valve System is the central concept to the cost effectiveness of the Single Anode Metalizing program that was to be developed.

A container concept for storage of the fluids necessary to be utilized in brush plating was required that was safe and had a secondary containment system for safety and security. Not only did the liquids require storage but each required a system to provide the requisite flow to the Control Valve System and through it to the platinum anode.

Finally, there was the integration of the activities of the four segments above. A System Controller design was developed. The initial System Controller was push button activated with a rotary command switch that coordinated the action of the anode solution Control Valve System, fluid flow rate, rinse water, and Hazardous Waste Segregation Valve.

After completion of the design concepts, the initial Single Anode Metalizing system components were built and the system assembled. When the system worked and provided repeatable, high quality coatings, it was provided to a customer with a job shop for field operation and evaluation. That was in March 1993. As with most prototype systems, however, several areas that required refinement were isolated. The areas requiring upgrading to maximize the system efficiency have since been corrected.
- wrap design needed development from the standard materials to minimize solution retention
- relative motion control had to be available for integration into the System Controller
- The size of the solution valves had to be increased in heavy production appli cations.

With these modifications, the original concept and benefits of the Single Anode Metalizing system were realized.

Current Status

The acceptance of the concept and the customer acceptance of the systems that have been delivered has been excellent. Three systems are operational at this time. Two in heavy industry and one in electronics. In addition there are two on order for single use heavy industry application, three more on order for job shop application and a significant number on quote.

Advanced Research

The fact that the control system has been made computer compatible has opened up some unique capabilities of brush plating. One of the capabilities that Single Anode Metalizing will allow to be accomplished is Computer Assisted Plating. That is, the complete control of a brush plating job by a

PC computer.

Since the variables of a brush plating job are
- Substrate preparation: which is material dependent
- Coating material(s): which is function dependent
- Relative motion: which is solution depen dent
- Voltage: which is solution dependent
- Amperage: which is anode contact area and solution dependent
- Coating thickness: which is part and print dependent
- Ampere Hours: which is area, thickness/ desired dimension and solution dependent
- The Ampere Hour Factor: which is a function of the buildup solution and the amount of Ampere Hours that have been used out of the solution.

We determined that most of these factors were already under the control of the System Controller. It was capable of physical control of all of those factors affecting the variables but needed an operator to effect the decisions and provide the control data to the System Controller. However, if we put the decision making into a computer and allowed it to interrogate the operator with regard to the desired results the computer could run a job without any operator intervention once it completed its initial data acquisition. Feedback information would be required for the computer to be self correcting.

One of the things that allowed for Computer Assisted Plating to be self regulating or self correcting with regard to solution depletion was the use of Temperature Compensated measurement. That is, the measurements of the initial dimension and the finished dimension are made. The finished part dimension is adjusted for the change in temperature of the part and compared to the original dimension of the part prior to coating which is stored in the computer. The actual finished dimension is compared to the dimension that the computer anticipated. This feedback enables the computer to effectively monitor its performance and adjust the amp hour factor to that actually being experienced.

Summary

The development of Single Anode Metalizing promotes the expansion of brush plating into new areas. The system's precise control of the process and the resultant product quality level, allows for Computer Assisted Plating that can provide high quality, controlled thickness coating of substrates repetitiously with a minimum of operator intervention required. It also allows for closer tolerance products with upgraded characteristics and with a minimum of hazardous waste generation. It can provide this at a lower cost than current production methods.

THE EFFECTIVENESS OF BRUSH-PLATING FOR ON-SITE REPAIR

By: Chip Simmons
Brushtronics

In the past, on site repairs of machinery and equipment have been limited to quick temporary fix, due to inadequate technologies for effective long lasting repairs. Many industries rely on what we refer to as conventional repair procedures. Sometimes these repair procedures are a faulty temporary fix which will lead into a complete shut down for a prolonged period of time. This will include dismantling and disassemly of equipment. The procedure also includes shipment of the defective part to a repair facility, down time waiting for the repair, and reassembly time, which could mean weeks of loss of production. When this repair was completed, the effectiveness of the repair; which would include all costs, down time, loss in production, would have been questionable. There is, however; a technology that is not widely known, that will greatly increase the effectiveness of on-site repairs. This industrial grade tool, for many years, was only used by select repair facilities. With the increased knowledge of metal finishing by many industries, this repair tool is becoming a necessity for many in house maintenance shops. This industrial grade tool or process has been known by many names but the most widely used name is Brush-Plating.

Brush-Plating is a portable electroplating process, that uses hand held equipment to selectively deposit a wide range of metals onto a conductive surface. This enables the user to fill, build up, or put a hard wearing surface on many objects in the field. With the mobility of this light weight system, usually weighing less than 40 pounds complete, it can be taken directly to the machinery or equipment that must be repaired. The base equipment, or rectifier, can be set up using standard AC voltage next to the area to be repaired and the hand held tool, or anode, can then be used to apply the metal to the select repair area. The rectifier and hand held anode comes in contact with each other by means of a length of cable. This cable can vary in length to allow the operator of the Brush-Plating system to easily reach the repair area. The mobility of this system also allows the system to be easily transported from facility to facility for repair work. Because of the small physical size of the system, many industry repair facilities had reservations of the quality of the metal deposit, only to be expelled after their first use.

Brush-Plating is basically the same principle as a tank deposit. Both are electro-deposits of metal on a surface using an electrolyte. Let's just say instead of putting the part in the solution we are bringing the solution to the part. This, however, does not mean you can use tank plating solutions for brush plating. The electrolyte for brush

plating is much more concentrated than that of a tank. This allows rapid build up of metal without metal depletion of the electrolyte. With the highly concentrated electrolyte and the constant operator monitoring of the deposit as he or she applies it to the surface. The quality of the deposit usually exceeds that of a tank deposit. The on site quick temporary fix is a thing of the past. A permanent fix can now be accomplished on site. You may think down time of the machinery and/or equipment would be greatly reduced, and it is.

For many years, when operating machinery was damaged due to operator error or part failure on areas that were metal finished, the department could count on days if not weeks of lost productivity. Typically, the machinery would be shut down and disassembled. After disassembly the part would be shipped to the repair facility for metal reworking or plating. This left the client at the mercy of the repair shop to insure quick and satisfactory repairs. Upon completion of the repair, the part then was shipped back for reassembly. This may seem like a large period of time, and it is for a industry that relies on machinery for daily operations. It is imperative that the industrial facilities have a tool that would allow them to repair damaged areas or parts without the great amount of down time and allow them to make a repair that would last without worry of failure. Many facilities tried repairs with epoxies and plastics with poor results. Metal deposits seem to be the only lasting result. Because of this, facilities were forced to either have continuous repair failures, continue to lose production time with disassembly repairs, or come up with an alternative that supplied the best of all options. Today it is possible to have the best of both options with a portable brush plating system. With the availability of the exact tool that an industry needs to keep competitive in an industry, you may question the economics of such a tool.

When discussing economics of a system there are several variables to take into account. The first of which is lost productivity. This can range from complete shut down of a product line to decreased output of a product or service. Immediate repair on site can eliminate days of lost production due to damaged equipment. Secondly is the cost of an off-site repair company to perform the repairs. This would include shipping of parts to and from the repair contractor. Lastly, would be the amount of man hours spent in disassembly for off site repair. Now, if we compare these to the initial cost of a brushplating system, training for your personnel, and man hours spent on the repair, you will usually find the system pays for itself after the first repair. Another factor which plays a role in the choice of brushplating is the ability to repair parts that typically cannot be repaired due to their size. In the past, there may

have not been a choice other than replacement of a damaged item due to the unavailability of repair companies to handle large parts or permanent fixturing of a part in machinery. The brush plating method allows the option of the on-site repair. Now we can address the last set of variables. Should we contract an outside company to perform our task or set up in house repair maintenance? Contracting a professional brush plating company to perform repairs has the advantages of experience in the repair procedure, no need to set up a new department and allocate man hours to the task, and still have expedient results either little or no down-time. This, however, may not be the most efficient way to accomplish your repair. In house repair can provide immediate repair with controlled cost incurred by man hours and equipment. Brush plating used either way can be an effective tool to cut cost, down time, and increase productivity.

There are uncountable numbers of applications that can benefit from this process. Probably the most widely used is the cylinder repair field. This can range from printing press rollers to hydraulic cylinders. It was common practice for many companies to remove damaged cylinders, send out the damaged cylinder to metal finishing shop in which all the plating was removed, good or not, reground and replate the entire part. This sometimes would even exceed the cost of an entirely new part.

Many companies have now switched to a favorable alternative of brush plating repair. With this process they can do immediate repairs to leaking hydraulic cylinders, printing presses with marred or scratched printing surfaces, hard coating of cylinders for wearability, and even rustproofing for longevity. Another favorable application is in the electronics industry. For sometime now, large scale power stations have been forced into disassembly for high power contract such as buss bars. This is no longer true. It is now possible to refinish any contact area large or small without complete removal. Even small contacts on circuit boards can be refinished without complete removal or disassbly. Remember, if it can be reached, it can be refinished with brush plating.

In closing I would like to state, Brushplating can be an effective and valuable tool to any maintenance or repair facility. It allows fast and cost efficient repairs that would not have been possible in the past. On site repair is the future of all effective maintenance departments.

AN INTRODUCTION TO PHYSICAL VAPOR DEPOSITION (PVD) PROCESSES

Donald M. Mattox
Technical Director - SVC

ABSTRACT

Physical Vapor Deposition (PVD) processes are atomistic deposition processes in which material vaporized from a source is transported in the form of a vapor through a vacuum or low pressure gas environment to the substrate where it condenses and film growth takes place. PVD processes mcan be used to deposit films of elemental materials or of compound materials by the reaction of depositing material with the ambient gas environment or with a co-deposited material. The three basic PVD techniques to be described are: vacuum evaporation, which uses thermal evaporation as a source of depositing atoms, sputter deposition, which used physical sputtering as the source of depositing atoms, and ion plating which uses concurrent ion bombardment during deposition to modify the film growth and film properties.

INTRODUCTION

Physical Vapor Deposition (PVD) processes are atomistic deposition processes in which material vaporized from a source is transported in the form of a vapor through a vacuum or low pressure gas environment to the substrate where it condenses. PVD processes may be used to deposit films of compound materials by the reaction of depositing material with the ambient gas environment or with a co-deposited material. The three basic PVD techniques are: vacuum evaporation, which uses thermal evaporation as a source of depositing atoms, sputter deposition, which uses physical sputtering as the source of depositing atoms, and ion plating which uses concurrent ion bombardment during deposition to modify the film growth and properties. A fourth technique which can be considered to be a type of ion plating is Ion Beam Assisted Deposition (IBAD) which uses concurrent bombardment from an "ion gun" in vacuum to modify the film growth and properties. The various PVD techniques are shown in Figure 1. Typically, PVD processes are used to deposit films with thicknesses in the range of a few nanometers* to thousands of nanometers; however they can be used to form multilayer coatings, very thick deposits and freestanding structures.

VACUUM EVAPORATION

Vacuum evaporation is a PVD process in which material from a thermal vaporization source reaches the substrate without collision in the gas phase (1). This means that there is no scattering during transport and the trajectory of the vaporized material is "line-of-sight". The vacuum environment also provides the ability to reduce gaseous contamination in the system to a very low level. Typically vacuum evaporation takes place in the pressure range of 10^{-5} Torr ** to 10^{-9} Torr depending on the level of gaseous contamination that can be tolerated. Figure 1a depicts a simple vacuum evaporation arrangement.

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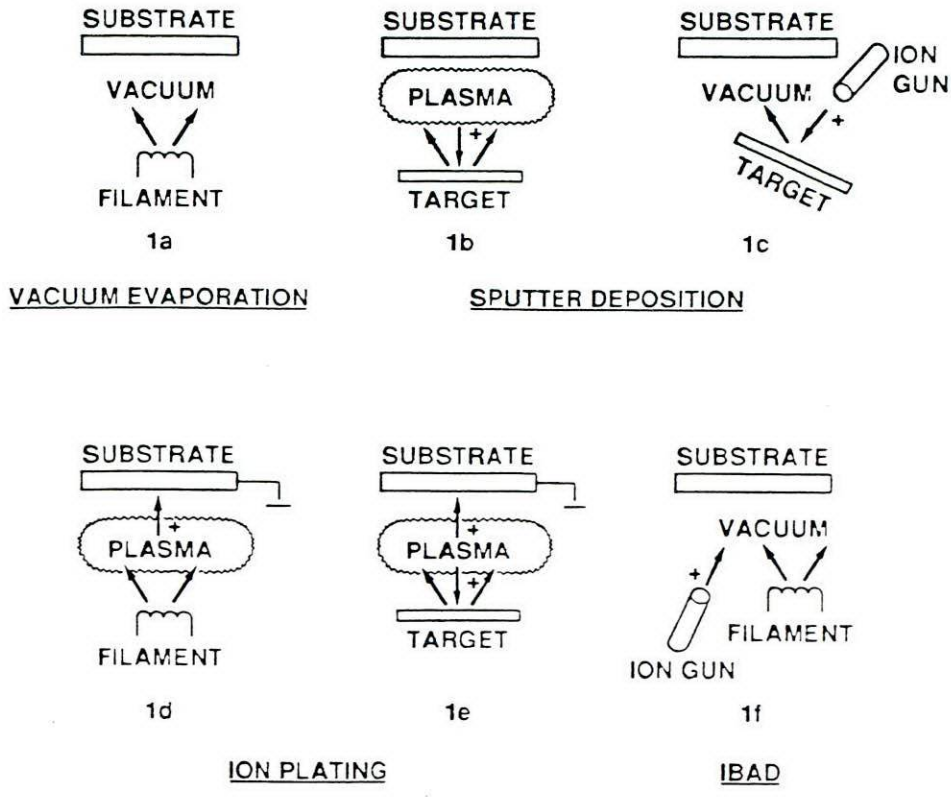

Figure 1: PVD processing techniques: 1a) vacuum evaporation, 1b) sputter deposition in a plasma environment, 1c) sputter deposition in a vacuum, 1d) ion plating in a plasma environment with a thermal evaporation source, 1e) ion plating in a plasma environment with a sputtering source and 1f) Ion Beam Assisted Deposition (IBAD) in a vacuum environment with a thermal evaporation source and ion bombardment from an ion gun.

Evaporation and sublimation

The vapor pressure of materials is very dependent on the temperature. Materials that have a high vapor pressure over the solid, such as chromium, sublime. If the material must be molten before the vapor pressure is substantial the material evaporates. Materials that have a high vapor pressure at a relatively low temperature may be vaporized from a resistively heated source such as a filament or boat. For more refractory materials, the material is vaporized using a focused electron beam source. In either case the area of vaporization is rather small resembling approximating a "point source". When vaporizing large amounts of material the source may be replenished using wire or pellet feeds to keep the level of the evaporant constant.

In most cases evaporation of alloys of materials results in a change in composition since the alloying materials usually have differing vapor pressures and thus evaporate at differing rates. In some cases the alloy composition can be retained using "flash evaporation" techniques where small amounts of material are completely evaporated. In the case of evaporation of compounds the composition of the deposited material often differs from that of the starting material because of decomposition and loss of a portion of the more gaseous material i.e. oxygen from an oxide. Thus substoichiometric oxides are normally deposited by vacuum evaporation.

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Other vaporization sources
In addition to evaporation and sublimation other specialized vaporization techniques may be used in a vacuum. Arc vaporization is used to vaporize electrically conductive materials in a high-current low-voltage electric arc. This technique produces high vaporization rates with a high percentage of the atomic vapor being ionized. These ions are accelerated away from the arc and achieve a kinetic energy much higher than thermal energy. In the arc vaporization process molten globules are formed which deposit along with the atomic species. These globules are often detrimental to the properties of the deposit and various techniques are used to try to eliminate them. Laser vaporization (laser ablation) is used to vaporize compound materials and has found particular application in the deposition of high quality high transition temperature (high T_c) superconductor oxides.

Thickness and surface coverage
Since the thermal evaporation is from a point source and the flux has a cosine distribution around the normal to the surface the distribution of the deposited material is determined by

the source-substrate distance, the angle of the substrate-source trajectory with the surface normal, and the angle of the substrate normal with the depositing flux. In order to increase the deposition uniformity the substrate is generally held in a moving fixture that randomizes the position and orientation of the substrate relative to the source during deposition. Another approach is to use multiple sources to produce an apparent large area evaporation source, although this approach makes thickness uniformity control more difficult.

The ability of vacuum evaporation to cover a surface depends on the surface topography. If the surface is smooth surface coverage will be good. However if the surface is not smooth, geometrical shadowing will prevent good surface coverage. Surface coverage can be improved by randomizing the deposition direction using fixturing that is moveable.

Advantages and disadvantages of vacuum evaporation
Some advantages of vacuum evaporation are:

- high purity materials can be deposited from high purity source material
- source of material to be deposited may be a solid in any form and purity
- line-of-sight trajectories and "point sources" allow the use of masks to define areas of deposition
- deposition monitoring and control are relatively easy

Some disadvantages of vacuum evaporation are:

- many alloy compositions and compounds can only be deposited with difficulty
- line-of-sight and point sources result in poor surface coverage on complex surfaces and in poor film thickness uniformity over large areas
- film properties depend on the "angle-of-incidence" of the depositing material
- fixturing with movement capability is necessary to improve surface coverage and thickness uniformity
- few processing variables are available for film property control
- substrate preparation is important to resulting film properties
- source-material utilization may be poor
- high radiant heat loads may exist in the system
- the liquid source material may move thus changing the source configuration

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Some applications of vacuum evaporation
Vacuum evaporation is widely used to form optical interference coatings, mirror coatings, decorative coatings, permeation barrier films on flexible packaging materials, electrically conducting films, and corrosion protective coatings.

SPUTTER DEPOSITION

Sputter deposition is the deposition of particles vaporized from a surface by the physical sputtering process (2). This PVD process is sometimes called just sputtering i.e. "sputtered films of --". Figure 1b and 1c show sputter deposition configurations.

Physical sputtering
Physical sputtering is a non-thermal vaporization process where surface atoms of a solid sputtering "target" are physically ejected by momentum transfer from an massive energetic bombarding particle. Usually the energetic particle is an ion accelerated from a gaseous plasma. Electrically conducting materials may be sputtered in a direct current (DC) diode plasma configuration. Dielectric materials must be sputtered using a radio frequency (rf) sustained plasma. In the magnetron sputtering configuration a magnetic field is utilized to contain the plasma-generating electrons and produce a high plasma density near the target surface thereby increasing the sputtering rate. There are many sputtering configurations and often the sputter erosion pattern from the target is non-uniform requiring movable fixturing to obtain a uniform deposition over a substrate surface.

Sputter deposition may be performed in a vacuum using an ion gun or in a low pressure (<5 mTorr) plasma where the sputtered particles and reflected high energy neutral particles do not suffer gas phase collisions between the target and the substrate. Sputtering may also be performed in a higher pressure (5-30 mTorr) where energetic particles from the sputtering target are thermalized by gas phase collisions before they reach the substrate surface. The properties of the sputter deposited films depend strongly on the sputtering conditions.

Sputtering targets
The sputtering target is a solid surface and sputtering can be attained over a large area of a surface. Solid targets provide a long-lived vaporization source with rather constant and reproducible vaporization rates. Fabrication of large-area sputtering targets is often costly and often the material utilization of the target is poor.

Reactive sputter deposition
By using a reactive gas in the plasma the deposited material may be made to react to form a compound material. The reaction is promoted by "plasma activation" of the reactive species.

Advantages and disadvantages of sputter deposition
Some advantages of sputter deposition are:

- elements, alloys and compounds may be sputtered and deposited
- the sputtering target provides a stable, long-lived vaporization source
- the solid sputtering target may be mounted in any orientation
- in some configurations the sputtering target provides a large-area vaporization source that can be of any shape

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- in some configurations the sputtering source may be a defined shape such as a line or a rod
- in some configurations reactive deposition may be easily accomplished because the reactive species are "activated" in a plasma (i.e. "reactive sputter deposition")

Some disadvantages of sputter deposition are:

- sputtering rates are low compared to those that can be attained in thermal evaporation
- in many configurations the deposition flux distribution is non-uniform requiring fixturing to randomize the position of the substrates in order to obtain films of uniform thickness
- film properties depend on the "angle-of-incidence" of the flux of depositing material
- sputtering targets are often expensive and material utilization may be poor
- most of the energy incident on the sputtering target turns into heat which must be removed
- in some configurations gaseous contamination is not easily removed from the system and gaseous contaminants are "activated" in the plasma thus making film contamination more of a problem than in vacuum evaporation
- in some configurations radiation and energetic particle bombardment from the plasma or sputtering target may change the film properties in an uncontrolled manner

Some applications of sputter deposition

Sputter deposition is widely used to deposit thin film metallization on semiconductor material, coatings on architectural glass, reflective coatings on compact discs, magnetic films, dry film lubricants and decorative coatings.

ION PLATING

Ion plating utilizes concurrent or periodic energetic particle bombardment of the depositing film to modify and control the composition and properties of the depositing film (3). Ion plating may be done in a plasma environment where ions for bombardment are extracted from the plasma or it may be done in a vacuum environment where ions for bombardment are formed in a separate "ion gun". The latter ion plating configuration is often called Ion Beam Assisted Deposition (IBAD) (4). Figure 1d and 1e show ion plating in a plasma environment. Figure 1f shows ion plating in a vacuum environment or IBAD.

Source of depositing species

The depositing material may be created either by evaporation, sputtering, or arc vaporization. The energetic particles used for bombardment are usually ions of inert or reactive gas, ions of the depositing material ("film ions") or ions of the reacting gaseous materials (e.g. oxygen or nitrogen).

Source of bias potential

Generally positive ions are accelerated to the depositing material due to a negative potential on the surface. This potential may be applied from an external source or be due to a "self-bias" on the surface. For electrical conductors such as metals, TiN, etc the applied potential may be DC. However if the film material is an insulator the applied potential must be rf in order to prevent a surface charge buildup which will cause the bombardment to cease. A self-bias can be caused

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to appear on the surface of a dielectric or electrically floating conductive surface by continuously bombarding the surface by high energy electrons.

Reactive ion plating

By using a reactive gas in the plasma the deposited material may be made to react to form a compound material. The reaction is promoted by "plasma activation" of the reactive species and the concurrent bombardment of the depositing material i.e. "bombardment enhanced chemical reaction". Materials such as TiN, ZrN and SiO_2 are routinely deposited by reactive ion plating.

Film properties

The concurrent bombardment can be used to modify and control the properties of the depositing material. The most common film properties that are modified include: adhesion, residual film stress, density of the deposited material and composition (stoichiometry) of deposited compound materials.

Surface coverage

Concurrent bombardment results in sputtering and redeposition of materials on surfaces that have a complex morphology. This effect, along with gas scattering at higher plasma pressures, can be used to give good surface coverage on complex surfaces such as ones having roughness, a complex geometry such as a doorknob or which have been patterned to form vias, metallization patterns, etc,

Other sources of concurrent bombardment

Concurrent bombardment of the depositing film can occur without a bias on the surface of the depositing material. For example, bombardment by the reflected high energy neutrals in low pressure sputter deposition and the ions accelerated away from the arc in vacuum arc evaporation can modify the film properties. Ion guns can be used to accelerate ions into a field-free deposition chamber.

Advantages and disadvantages of ion plating

Some advantages of ion plating are:

- in situ sputter cleaning of substrate surface
- surface coverage may be improved over vacuum evaporation and sputter deposition due to gas scattering and "sputtering/redeposition" effects
- bombardment may be used to modify film properties such as adhesion, density, residual film stress, optical properties, etc.
- film properties are less dependent on the "angle-of-incidence" of the flux of depositing material than with sputter deposition and vacuum evaporation due to gas scattering and "sputtering/redeposition" effects
- bombardment may be used to improve the chemical composition of the film material by "bombardment enhanced chemical reactions" and sputtering of un-reacted species from the growing film
- in some configurations the plasma may be used to activate reactive species, and create new chemical species that are more readily adsorbed and to aid in the reactive deposition process ("reactive ion plating")

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Some disadvantages of ion plating are:

- there are many processing variables to control
- it is often difficult to obtain uniform ion bombardment over the substrate surface leading to film property variation over the surface
- substrate heating can be excessive
- under some conditions the bombarding gas may be incorporated into the growing film
- under some conditions excessive residual compressive film stress may be generated

Some applications of ion plating

Ion plating is used to deposit hard coatings on surfaces, adherent coatings on surfaces, optical coatings with high densities, and conformal coatings on complex surfaces.

SUMMARY

There are a variety of PVD techniques, each with many variations. Each of these deposition options has advantages and disadvantages. The choice of technique to be used to accomplish a specific coating task depends on a number of factors that must be evaluated for each situation.

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DEPOSITION OF TiN AND OTHER PVD HARD COATINGS FOR NON-CUTTING TOOL APPLICATIONS

by

Michael E. Graham
BIRL, Northwestern University

INTRODUCTION

PVD hard coatings have been very successful in the cutting tool industry over the past 20 years. Titanium Nitride (TiN) has gained universal recognition and several other coatings have found a place in the manufacturers cutting tool arsenal. As it was discovered that TiN did not provide equal benefits for all applications, other materials have been developed, such as TiCN, ZrN, TiAlN , and more recently, CrN.

As the variety of coatings available for cutting tools has expanded, so has the interest in applying hard coatings to metallic and ceramic substrates for non-cutting tool applications. Materials such as TiN, while possessing excellent wear resistance in many instances, also are resistant to corrosion in most aqueous environments. In addition, the gold color of the transition-metal nitrides lends itself to decorative applications, and commercial applications have been developed for use on personal items such as writing instruments, watches, and rings. In the medical field, there is also interest in the use of TiN coatings on surgical instruments and other invasive instruments, since the TiN is not toxic to the human system and its presence as a thin coating can enhance the performance of substrate materials such as stainless steel.

Generally, the nitrides of Ti, Zr, and Hf (and alloy nitrides) are used to make a range of gold-yellow colors, while nitrides of metals such as Cr and Mo make silvery "metallic" surfaces. The carbides of these metal can be used to make dark-grey to black metallic coatings, and oxides can be used for a range of interference colors in very thin coatings to clear for thicker coatings. When using the PVD technology the oxides are often deposited with an amorphous structure, whereas, the nitrides and carbides are crystalline.

Table 1, while not an exhaustive list of the work done in this area, cites some representative work over the past several years, where the hard coatings have been evaluated for decorative applications. Included in the table are materials, colors, hardness, and references. Not every process is included in this list since there are a large number of variations on PVD deposition processes. A good review of the effect of process on microstructure is given by Håkansson, et.al.**[1]**.

The substrates used have been mostly very hard materials such as tungsten carbide and hardened tool steel. The newer applications involve softer metals, including steels, aluminum and copper alloys, and even

TABLE 1.
COATING MATERIALS AND PROPERTIES FOR DECORATIVE APPLICATIONS

Coating Materials	Color	Process	Hardness Vickers- (VHN)	Ref's
CrN_x, W-C:H	grey-metallic	Magnetron Sputtering (MS), Plasma Assisted CVD (PACVD)		2
Zr-B, Zr-B-N	grey-black	MS	2300	3
TiN, (Ti-Al)N	gold bronze, blue, black	MS	2200 2400	4
TiN, CrN_x	gold metallic	Activated Ion Plating (AIP)	2200 1740	5
SiO_2, Ta_2O_5, SiAl- Oxide TiN ZrN TiCN TiAlN TiNbN CrN	Interference colors gold brass lilac, bronze black pale gold metal	Unbalanced Magnetron Sputtering (UBM)	700 to 1200 2300-2600 2600-2800 2500-2800 2100-2400 2600-2900 2000-2200	6
TiN ZrN HfN TiC_xN_{1-x} ZrC_xN_{1-x} $Ti_xAl_{1-x}N$ $Ti_xZr_{1-x}N$	Golden Yellow Golden Green Yellow-Green Red gold-brn Golden Golden, brn-blk Golden	Cathodic Arc or MS	2400 3200 2750 2450-2900 3250-3450 2400-2900 2400-3250	7
$(Ti,Cr)N_x$	silv.to yel-brn	PVD	1400-2400	8

polymers. These softer materials present significant challenges in terms of meeting expectations of increased performance with hard coatings. The full potential of the hard films cannot be realized in mechanical wear applications when the coatings are not adequately supported, and where properties such as thermal expansion and elastic modulus are very different from the substrate. Nevertheless, the use of PVD hard coatings is being evaluated for such applications as erosion resistance in aircraft turbine blades, rolling contact fatigue resistance in bearings, and improved scratch resistance for simulated brass and gold in plumbing fixtures and door hardware **[9]**.

An example of the successful demonstration of an application for hard coatings was RCF test samples for NASA. Sproul et. al.**[10]**, showed that the nitrides of about eight different metals and alloys could all improve

the RCF performance of hardened steel (52100) by significant amounts. In some cases, the improvements in lifetime were more than an order of magnitude. In all cases, the best results were obtained with film thicknesses of less than one micron, eg., 0.5-0.75 μm. The coatings were applied by high rate reactive magnetron sputtering.

In another study **[11]**, the nitrides and carbides of Ti, Zr, and Hf were evaluated for their wear resistance. These materials were all deposited on M2 steel for general characterization and on 52100 steel for wear tests. All the coatings were able to provide significant improvements in wear resistance when applied as 1-2μm thick films. Under optimized conditions the hardnesses ranged from 2000 VHN for TiN to 3000 VHN for HfN, and the adhesion was excellent. The coatings were able to benefit the steels in part, because the steel was generally quite hard (Rc55-60), and the sputtering process was able to work at temperatures below 250°C so the steels would not soften.

We did learn something about the application of hard coatings in this study when some softer steels (Rc45) were coated with TiN and tested against the uncoated steel. It was evident that the best coating conditions for this steel produced a "softer" microstructure than was used on the harder steels. The ultimate wear resistance of these softer-coated steels was less than that of the harder coatings/substrates, but still much better than that of the uncoated steels. Hard coatings on the softer steel performed worse than uncoated steel.

CHROME NITRIDE RESULTS

The issue of coating softer materials is a recurring one, and one that requires a different approach to applying hard coatings. Intuitively, one might think that layered coatings, or graded coatings may offer solutions to this problem, and this is certainly an approach that is used. A coating material that lends itself naturally to this approach is CrN_x.

The use of sputtered CrN_x for protecting metals that are not as hard as fully hardened tool steel is attractive for a couple of reasons. First, there are many applications where it will be a logical replacement for electroplated hard chrome because of its corrosion resistance, scratch resistance, and appearance. Second, CrN_x can be sputtered in a range of compositions including solid solution Cr-N, the beta Cr_2N, and the cubic CrN phases. The advantages of the different phases ranges from greater ductility in the solid solution to increased oxidation resistance **[12]** and wear resistance with the higher nitrogen CrN phase. Even the low nitrogen phase is fairly hard compared to most metals, at about 1000 to 1400 VHN. The CrN phase has a hardness that ranges from 1300 to 2600 VHN depending on the deposition conditions. In a study to optimize adhesion on polished M2 samples, the associated hardnesses and thicknesses were determined and are shown in Table 2.

Further work was done in order to find the best conditions for depositing CrN on softer steels such as a tempered 440C (Rc38). A statistically designed experiment was utilized to vary the thickness, power and total

TABLE 2. OPTIMIZED ADHESION FOR CRN_x ON M2 STEEL (Rc60)

Optimized Parameter	Cr-N Phase	Cr_2N Phase	CrN Phase
Hardness (VHN)	1100-1300	1300-1400	1300-1500
Adhesion, Lc (kgf)	6.0-4.5	6.0-7.0	6.5
Thickness (μm)	0.5-1.0	1.0	5.0

pressure as the variable deposition parameters. Substrate bias and partial pressure of nitrogen were held constant at -125 V and 2 mTorr, respectively. The thickness was varied between 1 and 9 microns, the power between 2 and 8 kW, and the pressure between 4 and 12 mTorr. The partial pressure of nitrogen was controlled during deposition rather than nitrogen flow, although this is less critical with CrN_x than it is for TiN_x films.

Figure 1 summarizes the results by comparing the surface response plots for the data on both M2 and 440C. The plots show the adhesion critical load as a function of thickness and power. The total pressure was 10 mTorr for these plots. The results follow anticipated trends, since they show that thicker coatings are required for the best results on the softer substrate. It is also observed that the absolute value of the best adhesion load is lower for the 440C (3.25 kgf) than for the M2 (6.5 kgf), as expected.

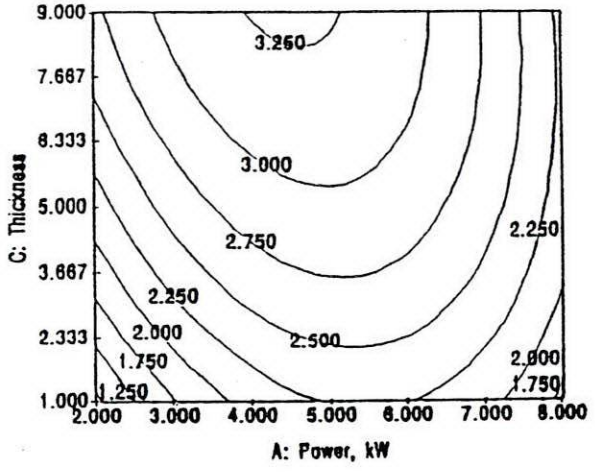

Fig. 1a. Adhesion Critical Load Response Surface for CrN on 400C Steel (Rc38)

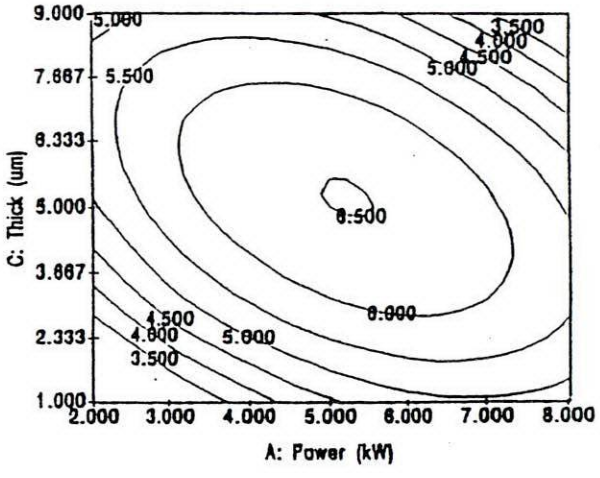

Fig. 1b. Adhesion Critical Load Response Surface for CrN on M2 Steel (Rc60)

The experiments were continued in a different sputtering system (dual cathode unbalanced magnetron), where the samples were coated in rotation. The conditions for deposition had to be modified to account for the different geometry and the more intense plasma to obtain the best results, but the guideline for 9-10 micron thick coatings was maintained for the 440C (Rc38) samples. The enhanced ion bombardment of this system (compared with the single target, balanced magnetron system) produced harder coatings, and, for the conditions tried, much better adhesion. Coatings with 9 microns of Cr-N exhibited adhesion critical loads of 7.5 - 8.0 kgf and a hardness of 1100 VHN. It was also found that 9-micron coatings with similar Lc's could be made as dual layers. For instance, 6 μm of coating Cr-N, topped with 3 μm of CrN (2000 VHN), also had an adhesion of Lc = 7.5 kgf. Single layer 9-μm films of CrN on the 440C attained critical adhesion loads of only 3.5 kgf. This result demonstrates that hard coatings can be successfully applied to softer substrates if the graded-coating approach is used.

CONCLUSIONS

A variety of hard coatings are now available by PVD techniques, and they offer the possibility for much enhanced wear and corrosion resistance if the proper match can be achieved between coating and substrate material for the application. Typical colors include silver/grey, yellow/golds and dark grey/blacks. Hardnesses can range from 1000 to 3000 VHN for the nitrides. The carbides tend to be at the higher end of this range of hardness. Some success has been demonstrated for deposition on steels with a base hardness of Rockwell-C 38 as compared to the normal cutting-tool applications on the harder (Rc55-60) steels. This was accomplished using the CrN_x system for coating, which can be deposited in three different phases that exhibit a range of hardnesses (1100-2300 VHN) and ductilities. Of course, the possiblity exists for other hard materials and even softer substrates to be used together in a similar way. Commercial success may depend on the nature of the application and the economic viablity of thick, graded coatings.

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Paper Not Available In Time For Publication

Replacements for Hard Chrome Electroplating

Keith Legg, BIRL, Northwestern University, Evanston, IL

Regulation of the solid and liquid waste streams and air emissions associated with hard chrome electroplating is becoming increasingly stringent. Various clean, dry-processing alternatives are available. This paper will present alternatives, their applications, and the critical issues involved in introducing them to the production environment.

For copies of this paper please contact:

Keith Legg
BIRL Northwestern University
1801 Maple Ave.
Evanston, IL 60201
708/467-1572
FAX: 708/467-1022

Optical Coatings - From Complex to Simple

By G. Caskey, Lakeshore Physics & Analytics
114 E 31st ST, Holland MI 49423

Abstract

Optical coatings span the range of surface finishes from simple metal films, to complex multilayer dielectric coatings, to optically active film stacks. Understanding optical interference empowers you to predict, based on individual film properties (which can be tailored), overall coating properties like transmitted or reflected color and intensity. Moreover, good measurement permits tailoring films to meet design needs, or to understand sources of failure when they occur.

Introduction

Thin film optical coatings deposited by various PVD processes are used for making a range of products. Principal characteristics desired by these coatings include specific mechanical properties, reflectances or transmittances, and/ or a specific color and appearance, and even electrical conductivity. If you understand more complex thin film stacks, then the issues related to simpler stacks are understood. That knowledge is a powerful tool in designing, developing and troubleshooting the processes used.

Complex thin film stacks include such commercially available devices as colored sunglass lenses, all-solid-state electrochromic mirrors, and even solar control coatings (low-e coatings). Other uses include photovoltaic, AMLCD (active matrix liquid crystal display) and electroluminescent display panels. These stacks may be pure dielectrics, or combinations of dielectrics and metals and even semiconductors, depending on the particular stack. Each process is selected for the materials to be used, the volume of product to be produced, the desired properties of the final product and the size of the coated parts. Brief descriptions of these coatings can provide insight into the simpler coatings discussed later.

Examples of PVD Coatings

Passive PVD Coatings

Colored sunglasses can be made by alternating layers of high and low refractive index dielectric materials.[1] Except for high energy-density applications, like laser filters, film absorption is low enough to be ignored. Each layer used is relatively clear but optical interference effects are used to produce a desired reflected color. If that color is nearly monochromatic, then the rest of the light transmits through the coatings, either leaving the transmitted light virtually undisturbed or to be spectrally-selectively absorbed by the substrate (lens). Figure 1 illustrates the spectral reflectance of such a coating. Note that the reflected light is nearly all blue and deep red (even into the infrared). The rest of the light is transmitted with little spectral selectivity, so the film stack acts much like a neutral density filter.

Sunglass coatings are perhaps 20 to 30 layers thick or more. It is only with a large number of layers that you can achieve the conspiring of interference effects to transmit all but a very restricted range of wavelengths using typical materials like silica and titania. The number, refractive indices and thicknesses of the layers determines completely the reflected color and

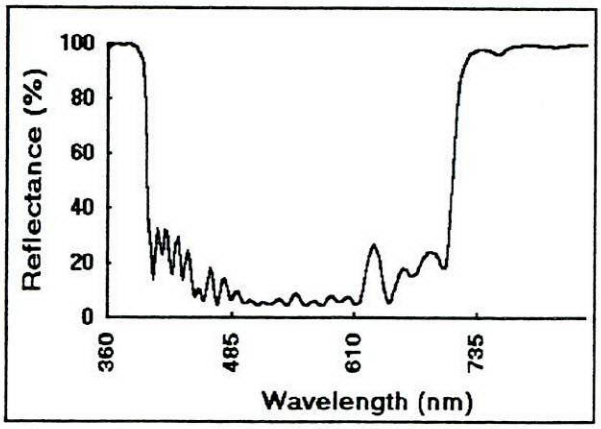

Figure 1 Spectral Reflectance of sunglasses coating computed similarly to reference 1, but with no absorption.

intensity. All three parameters (number of layers, thickness and refractive index) are selected by the design engineer. Of course, the substrate material you use may be different, and that needs to be added to the modeling done before coating to ensure you get what you want.

Active PVD Coatings

A more complex coating is a combination of semiconductor, dielectric, active, and metal films found in the all-solid-state electrochromic mirror.[2-5] Several companies have produced such devices, but only one is commercially available in any quantity. This attests to the problems that one can encounter in such dramatic combinations of effects needed to make this thin film device.

Figure 2 shows one form of film stack for electrochromic mirrors. The layers start with glass (basically silicon-dioxide), followed by a transparent conductor, then an anodic electrochromic layer, an electrically insulating layer that conducts ions, a cathodic electrochromic layer, and a metal reflective layer. The terms anodic and cathodic refer to whether the layers go from clear to highly absorbing during an oxidation or a reduction reaction, respectively.

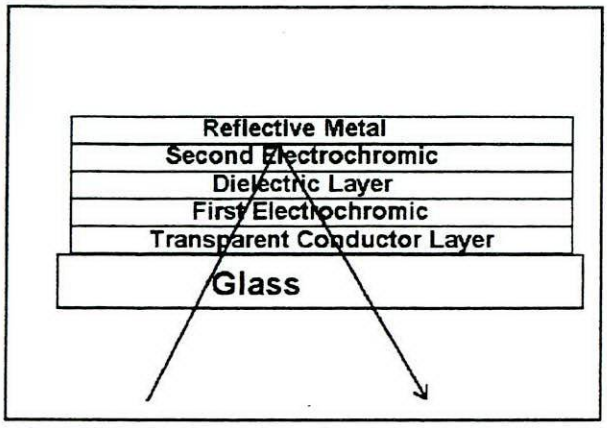

Figure 2 Schematic of a typical electrochromic mirror device showing the various layers involved. Light travels through all layers and reflects off the backmost metal layer (see refs. 2-5).

Clearly, obtaining all these properties in one device requires some sophistication in the processes themselves, as well as finding materials that color and un-color by the appropriate application of a few volts of potential difference across the stack. Nevertheless, such devices are available commercially and are the beginning of new markets for electro-active films for products. Aside from glare protection, applications of electrochromic technology include energy efficient smart- windows and privacy panels.

Solar Control Passive Coatings

The sunglass coating is an example of a passive film stack because the films themselves don't change, whereas the electro chromic mirror is an active film stack. Another passive film stack is that of a semiconducting layer, like tin-oxide or indium-tin-oxide (ITO). The former is used for electrostatic drains, window defoggers for ship windows or refrigerator cases. The

latter is commonly found in liquid crystal displays, after patterning to form the segments of the numerical or various shapes that will appear in the device. Other uses abound. But this layer can be used with or replaced by other material layers that all have characteristics that lead to energy efficient properties.

Energy efficient windows require that visible light be transmitted, but that infrared light be reflected. In the winter, when the sun is low, visible light enters the window. Once inside the room, the light is partly converted to heat. Heat, at temperatures that you and I like to be at, is radiated at wavelengths near 10μm, and is reflected back into the room by the window coating.

The term low-e comes from the low "emissivity" of the coating, which is a measure of the degree to which the coating acts like a perfect absorber, or black body.[6] If the emissivity is 1, the film would be acting like a perfect absorber. With emissivities significantly less than 1, like 0.1, about 90% of the heat is reflected back from the coating. In the simplest of terms, the emissivity is equal to 1-R, R being the reflectance (here in the infrared) ranging from 0 to 1.

Semiconductors, like tin oxide or ITO, have the nice property of reflecting IR light and largely transmitting visible light. This arises simply from the fact that they have free electron carriers but a large band gap. Some semiconductors are better than others for this purpose.

Angle of View Effects

In all these cases, the angle of viewing affects the perceived color of the film stack. This arises because as you look away from normal incidence, there is less difference in phase between light reflecting from upper and lower layers.[7] The resulting spectral reflectance is similar to that of normal incidence but for thinner films. That is, the spectral pattern shifts to shorter wavelengths (toward the blue end of the spectrum). Figure 3 illustrates schematically what a spectral reflectance curve might look like for both the normal and tilted coating. The more layers you have and the higher the refractive index, the more dramatic the effect can be.

The spectral characteristics of reflected or transmitted light will be, then, dependent on several factors like stack design or the angle of view. These factors are the same with simpler coatings, but the effects may not be so dramatic since the interference patterns are smoother and shallower for simpler film stacks. Yet even minor shifts in spectral response can be important.

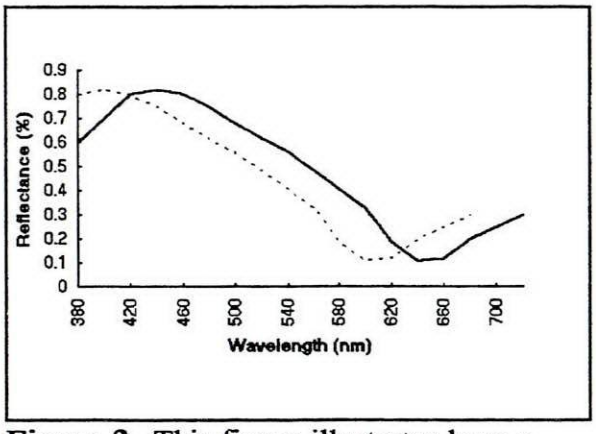

Figure 3 This figure illustrates how a spectral reflectance pattern (solid curve) might shift with a tilting of the coating away from the normal (broken curve).

Color is a complex property that arises from the combination of the illumina-

tion source, the spectral properties of the optical coating that is reflecting or transmitting light, and the spectral sensitivity of the person viewing the object. All three factors must be appropriately accounted for to know the apparent color. Our goal here is to combine some of the PVD coating properties with color theory to understand what happens as you change light sources or the coatings. But first, let's go back to the electrochromic mirror because it illustrates how careful attention to the optical design can reduce production costs.

Human vision is more sensitive in the green regions of the visible spectrum than to either the red or blue.[5] The peak sensitivity is at about 555nm and falls off on either side. Consumers like the color blue better than other colors, and passive blue mirrors are already accepted. Returning to the electrochromic mirror example, if you concentrate the interference effects to produce a reflectance minimum near a wavelength of 550 nm (in the colored state) then you don't need as much light absorbing power in the electrochromically active (i.e. anodic and cathodic) layers. Put simply, you can exploit optical interference to develop a PVD coating process that needs less coating to get the desired lower reflectance.[3] All this is done while maintaining a desirable blue color in the colored state and a silver color in the highly reflective or uncolored state.

Emphasis on optical design can give lower material needs and may mean less time in the high-capital-cost coater. Moreover, you also benefit from less problem with film stresses that accumulate with thickness.[8] This is one example of using the power of optical modelling for reducing costs and improving performance in PVD coatings.

If we can model these films adequately, then we can also predict the range of colors expected from a production process. That is, if the coating engineer can determine the range of actual thicknesses and refractive indices produced by a production process for each layer, then the resulting distribution of colors can be predicted by simple modelling. Software packages that model thin film stacks now usually include such "tolerancing" capability. If you then predict the range of color coordinates, and have a color specification from customers, you can predict a theoretical maximum yield. Then you can adjust your process to improve this yield.

Simple Coatings

So how about simple coatings. The automotive blue mirror is an example of a very simple coating. Take a substrate, coat an optically thick layer of metal with mid-range reflectance, like titanium or chromium or some other metal of like reflectance, and overcoat it with some thickness of a dielectric. The dielectric material might be silica, titania, or another oxide like chromium oxide. If the correct thickness of oxide is coated, the reflected color seen when looking at some object in the mirror will be blue if there is blue light in the source of illumination. A monochromatic or near monochromatic light source, like the sodium vapor lamps commonly used for plant floor illumination, won't have enough contrast between the blue light available and the yellow sodium-line light to provide the appearance of blue. But a tungsten or fluorescent light will give a blue appearance.

In the even simpler case of a metal coating, the color can be indicative of process problems. For example, if the color of a metal coating is not near that expected, the

coater may have a leak or the coating material may be contaminated. Starting materials for PVD coatings, such as evaporation charges or sputtering targets, may also show color or appearance shifts that indicate contamination of the source material.

Color and Appearance

Textured Surfaces

Color and appearance of coated or uncoated components or systems are attributes that combine several factors. These include the illumination source, the spectral reflectance characteristics of the parts, the surface texture, or other scattering features that affect gloss or haze, and other features such as the observer. For example, surface texture tends to shift color toward the color of the light source. So matching colors between materials of differing surface texture will require measuring this effect.

Measuring the effect on color from textured surfaces usually requires excluding the specular component. Colorimeters do this by design. However, if the specular component of reflected light contains the color of interest, such as is the case with many PVD coatings, then one must include the specular component. in fact, you might be interested in the specular component alone. There are even more complicated methods like goniospectrophotometry that require equally complicated instruments and methods[9] for pearlescent or metallic paint surface finishes where the specular component plays a significant role in the variation of color or appearance with angle.

Instrumentation

Color measuring instrumentation comes in a variety of forms. The basic instruments are the colorimeter and the spectrophotometer.

Colorimeters are designed to measure only diffuse reflectance for a single illuminant (standard light source), and a single geometry (e.g. diffuse light incident at 45 degrees from the normal and detected at 0 degrees). They work by filtering detected light with thee special filters designed to match the tristimulus or color matching functions. The sample is illuminated with a specific standard source. As such, specular, or mirror-like, reflectance is expressly excluded by the 0/45 geometry, and other illuminants are generally excluded by the filtering and light source available.

Spectrophotometers come in several varieties. All share the characteristic of measuring the reflectance or transmittance as a function of wavelength of light. Their varieties arise from differing geometries and illumination conditions. Here, the geometry of the device is important since the illuminant(s) is(are) simulated mathematically.

Mirror or other coatings I've used as examples above have little diffuse reflectance if made well. In fact, the diffuse reflectance they have is undesirable haze, which can also be measured. These coatings should be measured with a spectrophotometer using the specular component. When the coating is on a textured surface, the overall color can then be measured using only the diffuse component, or more complicated methods.

Quantifying color itself is relatively simple. It is a matter of determining the tristimulus values X, Y and Z, and then computing desired color coordinates (L*a*b*; x,y,Y; x',y',Y; L,u,v; L,u',v'; etc...) for a

given illuminant (e.g., A, D_{65}, F1, etc...). However, this can be done meaningfully only when you decide what you want to measure. Care in interpreting the results of color measuring instruments is imperative for those who want to make good use of the data. This is because quantifying color with just three parameters (tristimulus method) involves reducing an entire spectral response curve to just three numbers. While there are psychophysical bases for such methods, not all phenomena are characterized in any triad of numbers.

Most instruments today are excellent devices, but there remains much confusion about when to use the different devices and how to use their features to control quality. Colorimeters are used only when you want to know the effect of color with one light source. Metamerism, or the changing of color match between two or more samples that occurs with a change in light source, is excluded from detection using colorimeters. So is mirror-like, or specular, reflection. And no spectral (i.e. transmittance or reflectance vs wavelength) information is gained. However, colorimeters are less expensive than spectrophotometers. This makes them useful for quality control applications.

Generally, spectrophotometers are needed for good color measurement. Spectrophotometers measure the spectral response without regard to light source. Then a computational technique is used to generate color coordinates by simulating the light source mathematically. This is the most complete way to quantify color and appearance, but still there are considerations requiring attention.

Quantifying color and making use of the information provided is often fraught with misunderstandings that lead to concern over whether instruments are working correctly, whether one color coordinate system is better than another, or if color can be measured at all. The technical task is to develop clear understandings of color and appearance upon which meaningful control standards and procedures can be based.

Tailoring the Coating

The process you select for PVD coatings, both in terms of basic methods and the specific ways you use the equipment, will impact the coatings. For example, evaporated titanium dioxide may have a refractive index of about 2.2 in the middle of the visible spectrum, say green light (550 nm) while sputtering may give an index of as much as 2.5.[10-11] This largely arises from the more energetic nature of sputtering compared with evaporation. Also, the way you deposit the films in either evaporation or sputtering will result in variations in index. For example, heating the substrate prior and during evaporation can increase the refractive index of some materials. While these may seem troublesome facts, they are also opportunities to define and control your process better.

Selecting the process to obtain specific refractive indices is important for a variety of reasons. First, the number of layers, N, needed to produce a particular maximum reflectance or R in an alternating layer stack (like the sunglass coating) follows the approximate rule:

$$R \propto 1-\xi(n_L/n_H)^N \qquad \text{eq. 1}$$

where n_H is the refractive index of the high index material (e.g., titania) and n_L that of the low index material (e.g., silica), and ξ

is a factor that depends on n_H and the substrate index.[7] The larger the index difference, the fewer layers are required. Of course, the manufacturing cost is equally important and may involve more than just the number and type of layers.

Second, the materials used may or may not stand up to environmental exposures. Providing a good outermost protective layer may be important for a good product. Adjusting coating pressures and stack configuration can minimize residual stresses that tend to result in coating failure on exposure to the atmosphere. Even adjusting the substrate temperature affects the environmental resilience of PVD coatings. While these can seem menacing, they can be exploited by the coating engineer to provide exceptional product performance.

Tailoring the process to produce specific film properties permits obtaining optical properties that are, perhaps, not available in bulk materials. Even highly absorbing films are visually transparent if made thin enough. This alone gives many materials to the PVD designer that are not readily available to other processes.

One important capability is to be able to measure, at least approximately, the refractive index dispersion curves for the materials you use. This can be done by fitting transmittance and reflectance data where the indices are allowed to vary during the fit. Spectroscopic ellipsometry is another method. All methods have their strengths and weaknesses, but all are better than relying only on numbers out of a table. Tabulated numbers from books or papers are beneficial for initial designs, but care in use of these numbers can give you better understanding and control of your processes. In some cases, as in the electrochromic mirror, the indices are not available and must be determined from measurements on the coatings themselves.

Once you have the capability of determining the optical constants of your films, then you are set for even greater design capability. For example, you may want to mix materials to achieve some mix of optical properties. Such mixing can be modelled, at least approximately, by an effective medium approximation.[12]

Mixing of materials can be done by co-evaporation or co-sputtering, or in some cases by mixing the materials directly. Co-evaporation or co-sputtering involve using two independently controlled evaporation sources or sputter cathodes, respectively.[13] Material ratios are fixed by the power applied to each source. Care must be taken to ensure that the resultant films are of homogeneous composition. These methods permit formation of unique alloys or mixtures that can tailor the coatings to the needs of the manufacturer, albeit at added complexity to the process.

Summary

Complex films require understanding the detail of optical interference. This knowledge permits appreciating simples coatings and the requirements placed on their manufacture. New developments in optically active films make such understandings imperative, since optical properties may not even be knows for the materials involved. The tools developed for complex coatings can serve simple coatings well.

Other factors of importance are the commercially appreciable aspects of color and appearance, or specific optical response

from a coating. The area of color and appearance remains one in need of attention in order to provide specifications of value to the manufacturing community. Once needs for overall optical performance are determined, then the manufacturer of PVD coatings can begin to tailor the material composition, process and coating stack design to get the desired optical performance.

Knowledge gained by understanding the various effects that equipment and process have on the final product allows varied and new applications. Challenges still exist in the areas of coating process design, and of final product color and appearance. The latter is mostly a challenge in better understanding of color. Care in understanding color and appearance and the instruments used to measure these can resolve many of the problems that exist in matching components.

Finally, PVD processes themselves have many variables that can be exploited to produce specific film properties.

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Paper Not Available In Time For Publication

Diamond-like Carbon & Sapphire Coatings

Bruce Banks, NASA Lewis Research Center, Cleveland, OH

Diamond-like carbon and sapphire-like aluminum-oxide coatings can offer excellent abrasion and chemical barrier properties when applied to appropriate substrates. Amorphous diamond-like carbon is electrically insulating, moderately transparent, chemically inert and possesses a low coefficient of friction. Sapphire-like coatings afford excellent abrasion protection for polymers, while maintaining high optical transparency.

For copies of this paper please contact:

Bruce Banks
NASA Lewis Research Center
21000 Brookpark Road
Cleveland, OH 44135
216/433-2308
FAX: 216/433-6106

Wear Resistant Decorative Coatings

on Writing Instruments

SUR/FIN® 1994

June 23, 1994

Steven B. Tinkler - PVD Project Engineer
John H. Jacks - Engineering Manager
P.O. Box 5100, 1400 N. Parker Drive
Janesville, WI 53547- 5100

WEAR RESISTANT DECORATIVE COATINGS
SUR/FIN® 1994

Abstract:

Parker Pen USA, Limited of Janesville, Wisconsin, has been sputter-ion-plated writing instrument components for the past ten (10) years. The benefits of these PVD decorative coatings include superior wear resistance, brilliant colors, lowered manufacturing costs, and all environmentally friendly. This report discusses the equipment and some of the processes employed by Parker Pen to manufacture writing instruments. A number of process considerations are presented for those in the industry who may be investigating Sputter PVD technology. Authors: Steven Tinkler, ME, SVC and John Jacks, Eng. Mgr., Parker Pen USA, Limited.

Overview:

Parker Pen USA, Limited has been located in Janesville, Wisconsin for over 100 years. In the late 1970's the price of Gold increased to over $700 per ounce. At that time Parker was heavily into electroplating with both Silver and Gold for the coating of writing instruments. Parker R & D personnel researched the market for alternative coating possibilities and chose Sputter Ion Plating equipment and processes from Leybold AG, Germany. They are represented in the USA by Leybold Technologies, Inc., Enfield, CT. Parker Pen engineers worked with Leybold AG for three (3) years to develop their first "carousel" sputtering plant with four (4) target sources.

In early 1985 Parker Pen began using the Leybold Z700 sputtering plant to produce production pen parts. Then in 1992 Parker launched a new writing instrument model named The Insignia. It was to feature Sputter PVD coatings on seven (7) of the ten (10) product finishes. Additional capacity was planned and a larger Leybold Z1100 sputtering plant was sourced and placed into production. All of the part holding tooling was designed in-house and sourced from US machine shops.

Samples:

Samples of Sputter PVD finished pen components will be shown when this paper is presented. Color panel samples of Parker's production finishes will also be shown.

Benefits of PVD Decorative Coatings:

Basic PVD decorative coatings are metal Nitrides and/or Carbides of Titanium, Zirconium, Chromium, Aluminum, and alloys of these elements. Each metal and each reactive gas combination yields different coating characteristics. Titanium and Zirconium Nitrides are extremely hard. Aluminum Nitrides are rather corrosion resistant. Chromium and Aluminum Carbides produce different shades of grey, depending on how much Carbon is incorporated in the coatings.

Steven Tinkler, Ion Plate Project Engineer
John Jacks, PVD Factory Manager

Furthermore, Titanium and Zirconium Nitrides exhibit colors closely matching the Swiss Gold color standards of 2N and 3N. Several Leybold technical papers have been published covering PVD color variations available with their standard target materials. More exotic reactive gases can be used to produce a range of brown, lavender, and black colors. Gold target alloys can incorporate different elements to give many more hues of gold. Among these are Nickel, Vanadium, Ruthenium, and Indium.

Sputter PVD processes do not use any hazardous materials. Instead they transfer target materials in the form of a metallic gas by way of an Argon plasma. The typical reactive gases are Nitrogen and Acetylene (Carbon) which do not produce any hazardous wastes. Thus there are no restrictive EPA discharge regulations to be concerned with. These reactive gases are admitted into the processing chamber in a carefully controlled manner. A sophisticated closed loop feedback control system is necessary to control the flow of these gases into the chamber. Nitrogen is the most sensitive reactive gas. It reacts with both the substrates and with the sputtering targets. Leybold makes its own partial pressure gas control system to control N2. Argon, Acetylene, and Carbon dioxide gases can be controlled by simple mass flow controllers as available from MKS Instruments.

Coating hardness and Wear are important quality features of sputter PVD coatings. Parker Pen USA has developed and patented a PVD coating which is a micro-laminate of metal Nitrides and Gold alloy. Parker's marketing trade name for this coating is Dimonite-G®. It is a 14+ Karat gold, but is only 30 millionths of an inch thick! This wears as well as Gold electroplate that is five (5) times thicker, or 150 millionths of an inch. In our own wear tests, gold electroplated surfaces become rough as a corn cob, while Dimonite-G® coatings appear even more polished and brilliant than before. This thin-film coating is applied directly onto polished stainless steel substrates, and on bright Nickel electroplated brass parts.

Sputter PVD coatings are quite cost effective. Parker pen studies have shown that they can be about half the cost of standard gold electroplating. One typical Parker part costs $0.34 to Gold electroplate but only $0.15 to sputter coat with a Dimonite-G® finish. Actual cost advantages depend on how efficiently the sputtering tooling and equipment are utilized. The more parts that can be loaded into one sputtering run, the greater the efficiency. The thickness of PVD films is not as directly proportional to the deposition time and power levels as with electroplating. Sputtered materials do not build up on the holding racks as quickly on PVD tooling as it does on conventional electroplating racks. Sputter coatings are inherently low temperature, compared to some other PVD coating methods. Substrates, such as Zinc, which cannot tolerate temperatures above 200°C may be sputter PVD coated. The intensity of

the Plasma inside the chamber determines how hot the surface temperatures become. Lower power levels can be used for temperature sensitive substrates. However, a relatively high deposition rate produces a more dense thin-film. An increase in density produces a harder finish with less tendency to finger-print or corrode. Sputter PVD coatings can also be applied to non-conductive substrates, like plastic automobile headlight reflectors, and potato chip bags. The silver metallic finish on common snack food bags is put on there by sputter coating. Web-coating sputtering equipment is used to apply some of these films. The newest commodity to use sputter coatings is the CD, or compact disk for music and computer program storage.

Equipment:

Parker Pen has two (2) sputter coating plants. Both are made by Leybold AG. The Z700 plant was our first unit. Then a Z1100 plant was purchased in 1992 to satisfy the increase in product demand at Parker. The Z700 chamber size is nominally 700 mm tall and 700mm in diameter. The Z1100 chamber is 1100mm tall and 1100 mm in diameter. The comparative load sizes in the Z1100 is 2.5 times that of the Z700. Both pieces of equipment have a central carousel, and four (4) magnetron mounted targets in two directly opposing pairs. *(See Figure 1 attached.)*

A dedicated Cleaning system is needed to clean the components prior to PVD sputter coating them. The degree of component part cleanliness is an important factor in successful sputter finishing. Parker's experience has shown that this is best achieved with multiple de-ionized water rinse stages and both hot-air and vacuum drying. A five (5) stage system is recommended which has a sequence of Wash, Rinse, Wash, Rinse, Dry. Work with a reputable cleaning system manufacturer who has experience with PVD coating requirements and ask for references. A careful selection of pre-PVD cleaning chemistry is a critical requirement. Parker Pen has cleaning agents supplied by the Macdermid Company. The equipment builder and your chemical supplier must work together so that the cleaning chemistry that is chosen is totally compatible with the cleaning system tanks, plumbing, valves, gauges, pumps, etc. Together they must demonstrate that the cleaning chemistry is effective when used in the physical system as it was designed and fabricated.

Process Considerations:

Sputtered PVD films require a corrosion resistant substrate on which to be deposited. For Brass and other Copper based substrates a bright Nickel or Palladium electropled corrosion barrier must be applied before PVD films can be successfully deposited. This is because PVD films are all slightly porus and subject to chemical attack. PVD films grow as tiny needle-like columns. SEM pictures depict this film growth. *(See attachment #2)*. The corosion barrier must be thick enough to level the brass surface grain and also bright enough

to meet the end customer's visual standards.

Stainless steels (type 300 series) do not normally require a separate corrosion barrier. When properly cleaned and passivated this material resists corrosion in most user environments. The processing trick is to get a very high polish on the stainless steel surfaces to be PVD coated. Parker had to develop their own in-house polishing process. It features both plastic media "wet-cut-down" tubbing, and barrel tumbling in a proprietary organic media. The polishing leaves a film residue which is completely removed by the cleaning system chemistry.

Parker Pen Janesville, WI has a sister company in France who recently installed a Leybold Sputter PVD coating system. They chose to install a modular enclosure around their PVD plant and work area. Their Z1100 coating plant is installed through a wall of that enclosure. Air conditioning, heating, and make-up air filtration systems keep this processing environment at a 3,000 grade clean room status. Water vapor is a major factor in successful PVD coating processes. Vacuum pumping systems have a hard time pumping out water vapor. The best way to minimize water vapor in any vacuum processing chamber is to control the humidity and temperature in the zone where the chamber door is opened. A satisfactory relative humidity value is between 30 and 50.

A good technical and maintenance support staff is essential. Members of this team schedule production, manage materials, and direct manufacturing efforts. They also keep an inventory of spare parts on hand and perform a number of preventive maintenance tasks. Examples of these are:

Changing Shields that cover chamber walls.
Change & clean coated carousel tooling.
Replace O-ring seals that age and leak.
Clean & replace process control sensors.
Change oil & filters in vacuum pumps.
Service carousel feed through hub.
Troubleshoot coating performance problems.
Repair electrical & mechanical defects.

Conclusions:

Sputter PVD Coatings are becoming much more plentiful in the consumer marketplace. Decorative coatings are now being applied to such diverse products as Door and Window hardware, Writing instruments, Watches and Bands, and Eyeglass frames. Technical or functional sputter PVD coatings are being used on automotive pistons, Japanese structual stainless steels, architectural glass, and metal cutting tools. The third class of sputter PVD coatings go onto digital recording media, like computer disks and Compact disks (CD's).

The four (4) essential elements of Sputter PVD coatings are:

- Vacuum chamber and pump systems.
- Target materials and reactive gases.
- Substrate choice and preparation.
- Accurate Control systems.

WEAR RESISTANT DECORATIVE COATINGS
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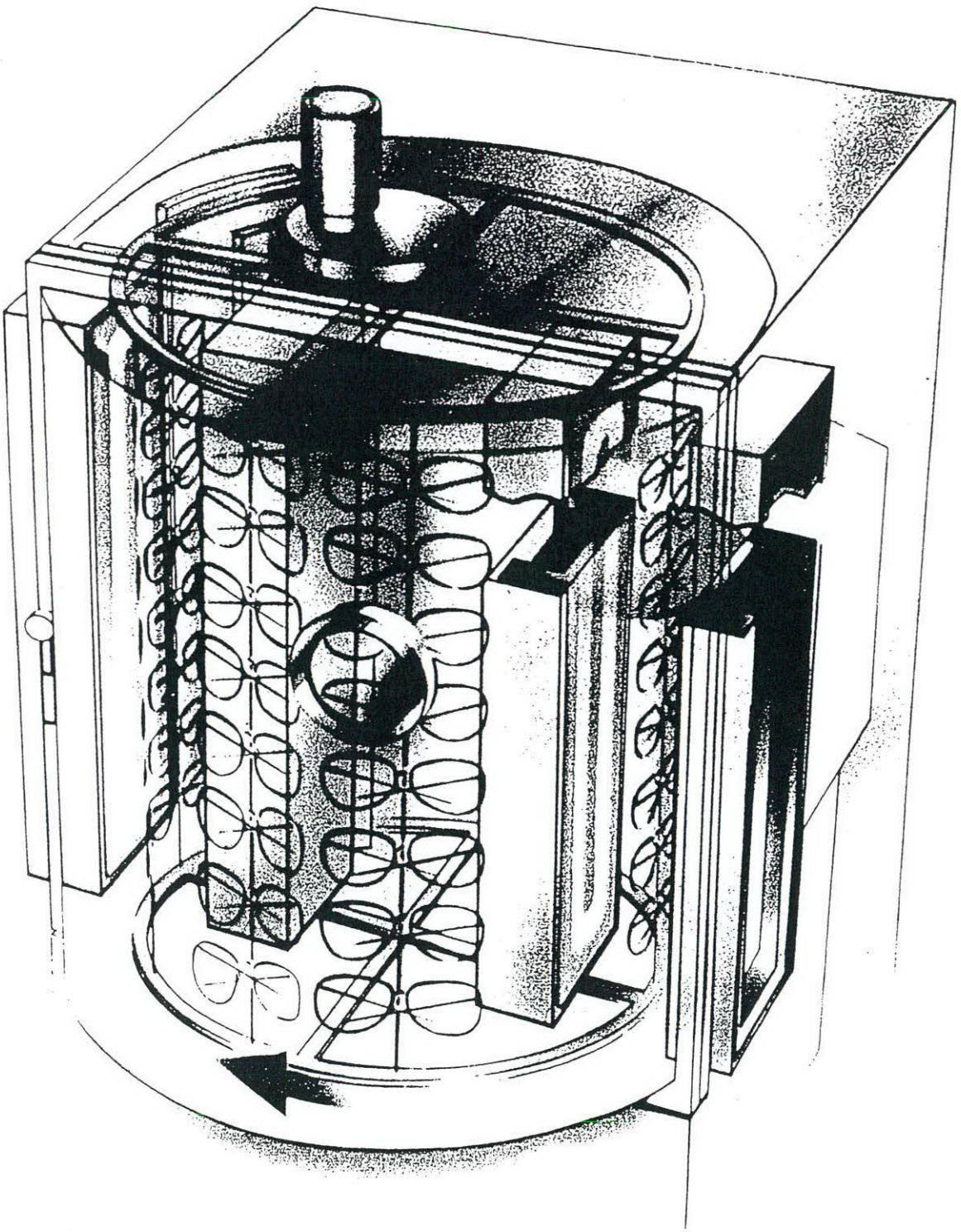
Benefits of Sputter PVD decorative coatings include:

- Excellent Wear resistance.
- Environmentally friendly.
- Cost effective
- Can be applied in many colors.
- Rack tooling has a long service life.
- Low temperature processing

Schematic of Deco Systems



JS
Sample "D"
LEYBOLD