84

SUR/FIN

American Electroplaters' Society
SUR/FIN '84

71st Annual Technical Conference



July 16-19, 1984
New York Hilton
New York, NY

Session C - General Interest

AMERICAN ELECTROPLATERS' SOCIETY, INC.

71ST ANNUAL TECHNICAL CONFERENCE - NEW YORK CITY

GENERAL INTEREST

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General Interest
Session C

Surface Integrity and Surface Finishing

Dr. Aviezer Israeli
Tel Aviv, Israel

SURFACE INTEGRITY AND SURFACE FINISHING

Dr. Aviezer Israeli
Tel Aviv, Israel

The effects of some mechanical, physical and chemical finishes of the surface integrity of various substrates will be discussed. Technology used to analyze and measure surface integrity will be presented. These techniques should result in a better understanding of the correlation of finishing processes, operating parameters, surface properties and product performance.

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C-2

General Interest Session C

Rotating Electrodes: A Universal Tool for the Control and the Optimization of Plating Baths

Dr. J. Vanhumbeeck
Siemens N.V., Oostkamp, Belgium

ROTATING ELECTRODES : A UNIVERSAL TOOL FOR THE CONTROL AND THE OPTIMIZATION OF PLATING BATHS

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Introduction

The deposition of metals from high speed plating electrolytes as used in reel to reel machines for the selective plating of contact surfaces is mainly based on heavy electrolyte movement.
Due to these special process conditions a control of the bath performance with common instruments such as the Hull cell is not any more possible. Especially the strong electrolyte movement cannot be simulated accurately in these devices.
Rotating electrodes which are already used since a long time for electroanalytical purposes offer the possibility to simulate, to control and to reproduce accurately electrolyte movement. These electrodes are therefore a helpful tool for the control and for the optimization of high speed electrolytes.

Type of rotating electrodes

Rotating disc electrodes (RDE)

The rotating disc electrode is the most used and best known electrode in electrochemical studies. The electrode consists of a metallic disc embodied at the top of a cylindrical shaft made of isolating and chemical resistant material e.g. PTFE (fig. 1). The disc is contacted through a brush contact and an internal connection in the shaft. Typical diameter of the disc is 2-5 mm. The choice of the disc material depends on the application. Most used is platinum. The tip of the electrode including the disc can be removed for evaluation of the deposit. The shaft is driven by an electrical motor with adjustable rotation speed mostly in the range 0-5000 RPM sometimes even up to 10.000 RPM.
The rotation of the electrode causes a pumping action of the electrolyte to the disc resulting in a laminar flow at the disc surface in a relative broad range of rotation speeds.
An advantage is the relative constant diffusion layer thickness over the disc surface and consequently a stationary concentration distribution.
A turbulent flow happens only at very high rotation speeds.
This electrode system is especially suited for electroanalytical purposes but also for the control of electrode mechanisms where the stability of the laminar flow is extremely valuable.

Rotating cylinder electrode (RCE)

The rotating cylinder electrode has a similar construction as the RDE. The active electrode is a cylindrical ring at the outside of the electrode shaft (fig. 1). This type of electrode is less well known than the RDE. Mass transport can also be controlled and the concentration fluctuations at the electrode surface can be calculated. The electrolyte movement is mostly turbulent even at low rotation speeds. The RCE is very well suited for the simulation of industrial process which are naturally turbulent as is the case e.g. with high speed jet applications.

Other types of electrodes

For the study of the kinetics and the mechanism of electrochemical reactions other types of electrodes are used such as : ring disc electrodes, multiple ring-disc electrodes, splitted ring disc electrodes. For the control of the performance of plating baths these systems are actually not used but their tremendous potentialities suggest an increased significance as analytical tool.

Simulation of the electrolyte movement

For the control of the bath performance with rotating electrodes it is important to simulate as close as possible the process conditions. With the rotating electrodes a rotation speed must be chosen which produces at the electrode surface the same electrolyte movement as in the process.
A simple method is to adjust the rotation speed for a given current density to the point at which a critical layer property such as brillance, appearance changes. The current density to be used is the one which causes under the process conditions the same change in deposit property.
A more accurate measurement is principally possible through the registration of current potential curves and the determination of the limiting current.
A reliable registration of these curves in the plating cell is however most of the time difficult due to the turbulency of the electrolyte and the resulting instability of the measured current or due to the difficulty to arrange measuring electrodes in the plating cell.

Applications

Influence of current density and electrolyte movement on deposit properties.

A very simple experimental set-up can be used here (fig. 2). At a fixed rotation speed deposits can be made at different current densities. The influence of current density on typical properties of the deposits such as appearance or brillance can be evaluated.
The current density working range for the electrolyte can thus be defined very accurately. This experiment simulates the Hull cell test in a more accurate way.

As the tip of the rotating electrode can be removed other layer properties as hardness, morphology or wear and contact resistance can also be controlled as a function of current density.
This experiment can be repeated for different rotation speeds adding a third dimension to the test. In this way for a given electrolyte an operation window considering current density and electrolyte movement can be defined.
In practice when the rotation speed of the RDE which simulates the same electrolyte movement as in the plating cell is known then the value of the used current density versus the limits of the operating window can be evaluated. When this window moves or narrows due to aging of the bath or due to contammination the current density or eventually the electrolyte movement can be adapted in order to remain in the save region of the working window. This method is already used to control the bath performance of high speed palladium electrolytes in reel to reel machines (fig. 3).
The RDE has become therefore a classical tool in our production control laboratories.

Optimization of the bath and process conditions

With the same experimental set up of fig. 2 the influence of the process conditions as e.g. temperature, anode-kathode dimensions on the deposit properties can be controlled and optimized. Also the effect of the bath composition as e.g. brightner concentration on the bath performance and the influence on the working window can easily be checked. This technique is particularly interesting for noble metal plating baths because only small bath volumes are necessary to run the test.
In the case of gold electrolytes it was e.g. possible to define an optimal bath composition and an optimal electrolyte movement and current density range to achieve a desired deposition rate and keep certain deposit properties constant.

Other applications

Rotating electrodes can also be used as working electrode i.e. cathode in other electrochemical measurement techniques which give valuable information on the plating bath condition. A long known measurement technique but unfortunately not used in a wide extend is the registrations of current-potential curves. The measurement requires a more elaborated experimental set-up (fig. 4) with an additional reference electrode to define the potential of the working electrode.
P. Kohl (1) has shown that in solder baths the slope of the S-shaped curves gives an indication on the additive concentration in the bath. In the case of high speed gold plating baths we observed that lead contaminations under 1 ppm resulted in supplementary peaks and could thus be detected before the layer properties were affected (fig. 5). The same experimental set-up can also be used to measure the current efficiency of plating baths.
This method was already described earlier (2).

Conclusion

The rotating electrode is a powerfull tool for the control of the performance but also for the optimization of plating baths and especially high speed electrolytes. Under these process conditions classical instruments such as the Hull cell cannot be used due to restrictions in the electrolyte movement.
In a relatively simple experimental set-up the influence of electrolyte movement, current density, bath composition and process conditions can be controlled.
The instrumentation is not expensive and easy to run. The RDE is already used for the process control of high speed gold and palladium electrolytes in our production control laboratories.

References

(1) P. Kohl, J. Barnes, R. Collins, R. Buckley
Proc. AES 69th Annual Conf. S1 (1982)

(2) J. Vanhumbeeck, F. Vangaever
Proc. AES 69th Annual Conf. B4 (1982)

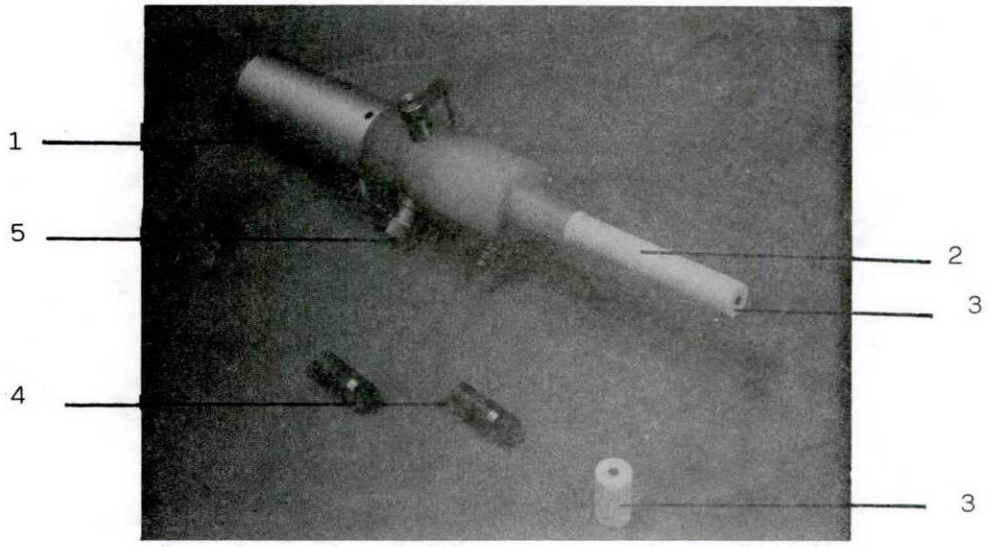


Figure 1 : Rotating electrode with mounted disc electrode tip.
Not shown is the electronic speed regulation box.
1. Motor housing
2. Rotating electrode shaft
3. Disc electrode tip
4. Cylinder electrode tip
5. Electrode contact

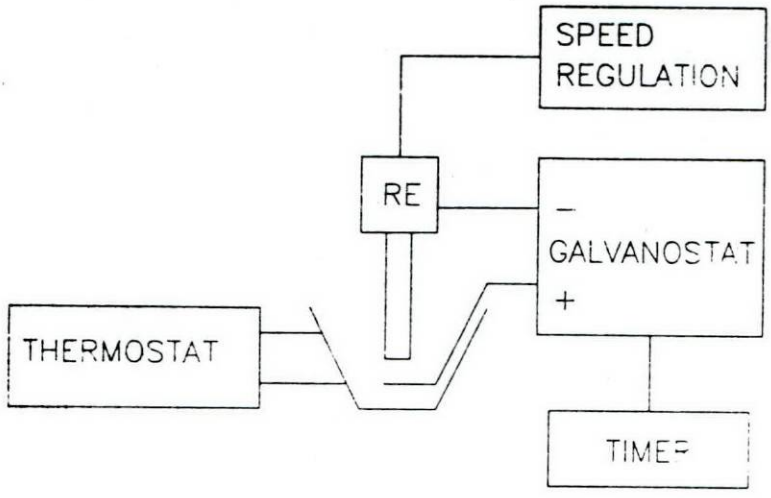


Figure 2 : Schematic experimental set up for testing plating bath performance with a rotating electrode.
RE : Rotating Electrode

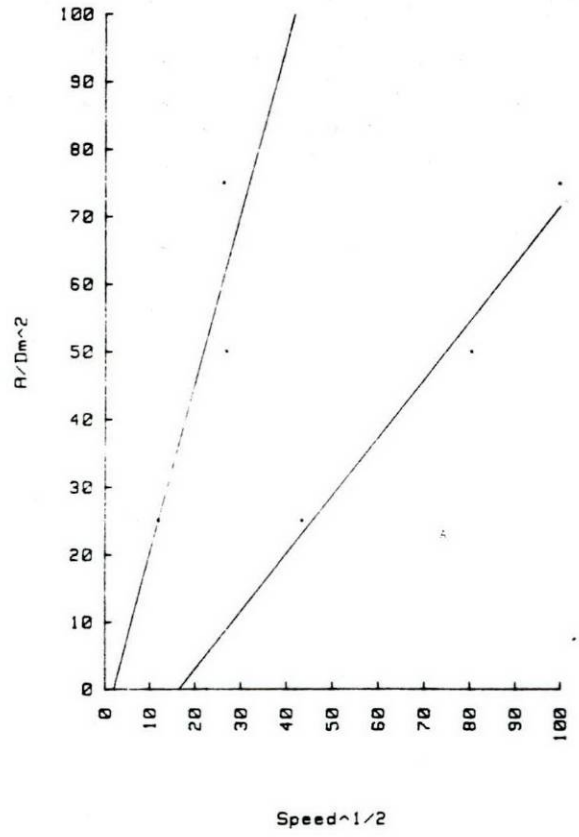


Figure 3 : Operation window of a high speed palladium bath with 30 g/l palladium at pH 7,3 and 60°C.
The influence of the electrolyte movement i.e. rotation speed of a rotating disc electrode (diameter tip : 10 mm; diameter electrode : 4 mm) and current density on the layer appearance is indicated.
Region A : semi bright smooth deposit
Region B : dark grey burnt deposit
Region C : white grey dull deposit

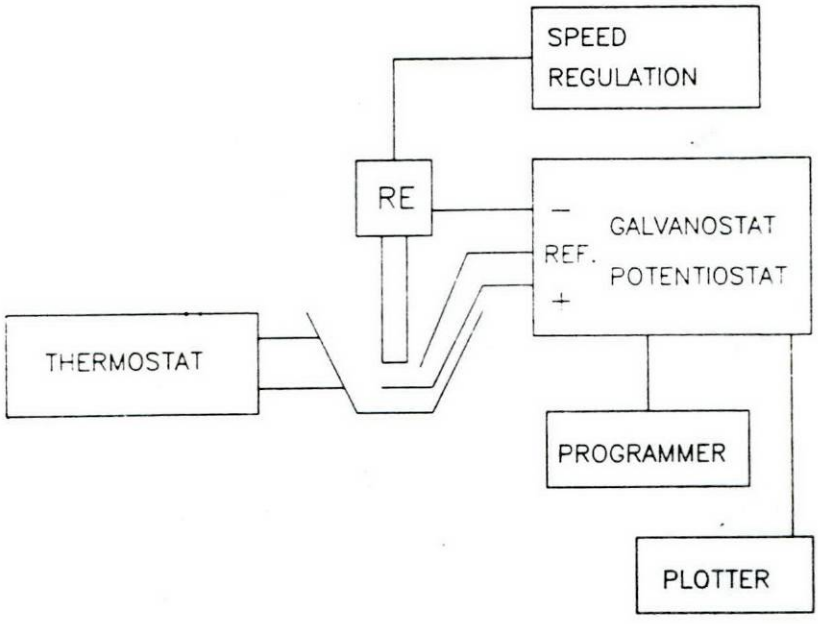


Figure 4 : Schematic experimental set-up for the registration of current-potential curves and the measurement of current efficiency (2)
RE : Rotating Electrode
Ref : Reference Electrode

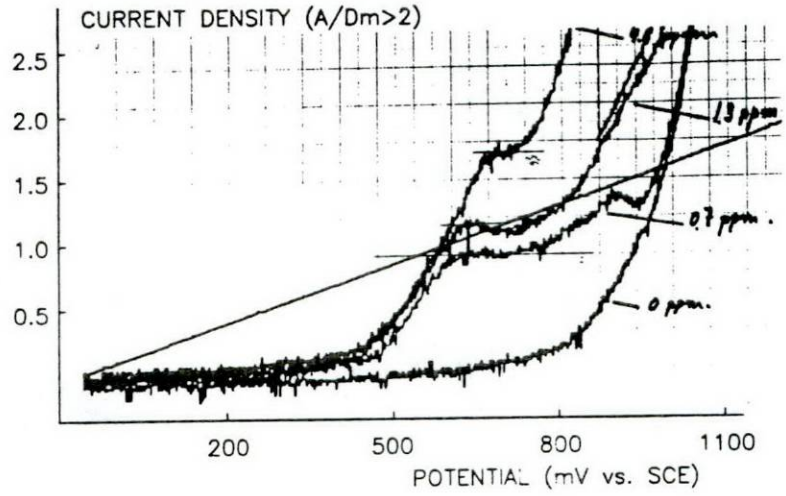


Figure 5 : Current-potential curves of a proprietory high speed gold bath (gold 15 g/l pH 4,5 55°C; Kobalt 500 mg/l). The rotating electrode was a platinum disc with diameter 3 mm. Measurement was done at 5000 RPM.
The influence of increasing amounts of lead contammination in the bath 0,7-1,3 and 4,6 mg/liter is shown.

C-3

General Interest Session C

Automatic Plating Equipment Justification/ Selection

J. Roger DeBusk
Genicom Corp.
Waynesboro, VA

AUTOMATIC PLATING EQUIPMENT JUSTIFICATION/SELECTION

J. Roger DeBusk
Genicom Corporation
Waynesboro, Virginia

In 1975, the Waynesboro General Electric Plant had a major decision to make concerning its plating facility. The plating facility was over twenty years old, most of the equipment, which was original equipment, was worn out. The processes reminded one of a hop-scotch game as operators dashed from tanks to buckets and lines to lines trying to process parts. One rinse tank had rags stuffed in holes which permitted water to flow in faster than it flowed out. The twenty-year old dryer allowed so much steam to escape that it became an art of drying parts with live steam. Safety hazards were too numerous to mention and Cost Accounting was unhappy with plating cost which was obviously labor intensive. Chemical and metal usage, especially gold, was extremely high. Along with all these problems, the drains below the floor were in bad shape and would have to be repaired. Many alternatives were reviewed with only three given serious consideration. A fourth alternative was decided for us.

The alternatives were as follows:

I. Do nothing.

   Exit plating in three years.

II. Maintain status guo.

   - Keep productivity at present level.
   - Requires expenditure of $300K over next two years.
   - Increase buy content.

III. Renovate plating room.

   - Improve efficiency, productivity, effectiveness.
   - Require expenditure of $735K over next two years.
   - Provide capacity through 1980.

IV. New plating facility.

   - Moratorium on space.

Reviewing the cost of operations for providing plating to meet production requirements, it was determined that alternative I for doing nothing, was cost prohibitive, while the one for remaining status guo would result in a negative cash flow of 1.5 million dollars. It was quite obvious from a cost standpoint that alternative III of modernizing the plating facilities was the most acceptable since any new facilities had been ruled out by a moratorium on space. (Fig. 1)

Now that we had determined that modernization of the existing facilities was the most viable alternative, a project was established which would enable us to carry out this assignment.

Project: Modernization of existing plating facilities.

Objective: Finish parts in-house to meet 1980 production requirements at minimum cost.

Goals:

- o Improve material flow
  - Each line a complete process
  - Increased efficiency
  - Faster inventory turnover
- o Expand capacity
  - Deburr
  - Barrel Line
  - Zinz
  - Electroless Nickel
  - Copper/Nickel
  - Deionized Water
- o Automate zinc line
- o Eliminate farm out

Strategy:

- o Develop process flow
- o Determine required capacity
- o Establish layout
- o Determine cost impact of project
- o Provide equipment and processes

Program:

- Schedule all projects to make changes with minimum interruption to production
- Review new technologies to improve existing processes
- Update processes

Source Review:

- Five-year forecast (Advanced Manufacturing Engineering)

Assumptions:

- Existing header line (relays) will meet five-year forecast requirements
- No major new processes will be introduced or required
- Cadmium would be replaced by zinc

Projects:

- Make plating room layout using straight line approach
- Develop product schedule
- Repair drains
- Provide safer, more functional wall grating
- Install new exhaust plenums to improve ventilation
- Install new tanks and related equipment
- Initiate bulk storage of hydrogen and chemicals
- Provide new office space for foreman, quality, and laboratory
- Provide additional space for rack storage and repair
- Install automatic zinc plater
- Improve safety
- Motivate personnel by making area more attractive and conducive to good work habits
- Reduce water consumption and waste treatment load

Projects:
(continued)

- Provide quality water for solution make-up and replinishment
- Provide clean environment for gold plating
- Improve environment for QC equipment
- Expand storage for racks, barrels, work in process
- Improve water conservation with dragout sprays and conductivity controls on rinse tanks
- Paint work area and equipment
- Relocate utilities to accommodate new layout
- Provide improved and enlarged racks
- Improve drying facilities
- Install new gold plating equipment
- Replace deionizer
- Redesign rack and unrack stations
- Install suspended ceiling
- Initiate preventive maintenance program
- Remove degreaser
- Restrict traffic flow in the plating room
- Place eye wash stations and safety showers in strategic locations

Recommendations:

- Proceed with outlined projects
- Schedule projects to cause least interruption of production
- Begin immediate study of new facilities which will be required beyond 1980
- Provide Manufacturing Engineer - Metal Parts with Chemical technician
  - Assist in expediting program
  - Review new technologies

Recommendations:
(continued)

-Update processes

- Train and provide technical assistance for plating room personnel

Conclusion:

o Modernization project will provide capacity to meet 1980 requirements for:

Barrel Line	Zinc
Black Oxide	Electroless Nickel
Alodine	

Action Plan for Automatic Plating System:

	Time Schedule
Notice of Intent submitted	12/03/76
Appropriation submitted	1/31/77
Installation Complete	12/31/77

The first phase of the plating was completed in 1976. Much of the worn-out equipment was upgraded and replaced as a result of the three major accomplishments being achieved. The first was the development of a solder plate barrel plating process which replaced tin plating that required labor intensive racking. Not only did we save $300K per year, but it enabled us to procure orders which required solder plate only and to eliminate a very dangerous hot fat flow operation. The second was a $250K savings which resulted in being able to control gold thickness requirements between .000030" - .000060". This was accomplished by the installation of new gold jet plates with their automatic timer and current density controls. The third major savings was in materials for our electroless nickel plating process. By using the straight line approach for processing, our supplier was able to formulate and provide us with less expensive plating chemicals, which still continues to do an excellent job.

Final Equipment Phase - Automatic Plating Equipment

With the completion of the first phase of the plating room modernization a second decision had to be made. Should we automate not only the zine but also the copper-nickel line or replace the existing hand lines with modern equipment using larger racks, overhead hoist and the straight line approach.

The Advantages of Automatic Platers are:

- o Increased capacity
- o Reduced labor

The Advantages of Automatic Platers are: (continued)

- o Reduce material cost
- o Improved quality
- o Reduced waste treatment
- o Consistency

Capacity - Zinc

An in-depth study of parts requirements showed that we did not have capacity in 1976 to meet production requirements, resulting in an increasing farm-out program which was very costly and hard to administer. The new modern manual zinc line would only meet our production requirements through 1980 and then we would be forced into another farm-out program. A zinc automatic would provide the capacity required through 1980 and unlimited capacity through 1985 based on a 15% - 20% growth each year. So the decision was made to automate. (Fig. 2)

Benefits of a Zinc Automatic Plater

- o First year savings of $259K with an initial investment of approximately $198K
- o Discounted rate of return is 94%
- o Break-even point is approximately one year
- o Meets production requirements through 1980 -- one shift
- o Meets production requirements through 1985 -- two shifts

Copper-Nickel Capacity

The capacity requirements were even more dramatic. One shift would not have met our 1977 production requirements and two shifts would have met them through 1981. By 1985 we would have reached our total capacity and have been required to look for methods to meet our production requirements. (Fig. 3)

Advantages of a Copper-Nickel Automatic Plater

- o First year savings of $216.8K with an initial investment of $220K
- o Discounted rate of return is 91%
- o Break-even point is approximately one year

Advantages of a Copper-Nickel Automatic Plater (continued):

- o Meets production requirements through 1981 -- two shifts
- o Meets production requirements through 1985 -- three shifts

Now that the decision had been made to automate, one must understand what makes up an automated plating system before they can specify and select the equipment.

To properly present this program, I must ask a few basic questions. The answers will explain an automatic plating system. The questions are:

1. What is an automatic plating system?
2. What does an automatic system consist of?
3. What features should be considered when you decide to buy a system?

1. What is an automatic plating system?

An automatic plating system is a device designed to mechanically move a work piece through a series of production operations. This device does not require coffee breaks, lunch, or dinner breaks, or a good night's sleep. It will continue to repeat it's predetermined operations with a minimum of preventive maintenance for as long as the predetermined process is valid. However, it is an extremely hungry device and to be properly used, a continuous flow of fresh material must be avaialble for processing.

2. What does an automatic plating system consist of?

An automated plating system consists of the following items:

A. Control center - nerve center

B. Lift transport assembly

C. Process tanks

A. Control Center:

The control center system is provided as the basic logic control unit. The basic logic of the system is the program which determines when an operation is to be performed, whether or not a particular machine command is correct and safe to be performed during that step in the automated process sequence and then command the lift/transport assembly to perform the operation. The solid-state control-

A. Control Center (continued):

ler system is capable of performing the same functions as relays, static controls or card logic control systems.

B. Lift Transport Assembly:

The lift transport assembly, which may be mechanical or hydraulic, is complete with lifting and traversing drives to transport the work through the designed plating cycle. After transfer the lifting mechanism lowers the work into a predetermined station where the rack engages saddles located in the process plant.

C. Process Tanks:

The process tanks, for the most part, are the items that are taken for granted. As everyone knows a tank-is-a-tank and there is never any problems with the tanks. I would like to take some time to review some of the basic considerations taken in tank selection and fabrication. Some of these are:

- o Construction material
- o Lining
- o Size
- o Corrosion protection on the outside of the tank
- o Color code
- o Placement of utilities and accessories (heater, filters)
- o Plumbing - valves
- o Overflow
- o Flat bottom
- o Drain placement
- o Dye checked for leaks
- o Rack size
- o Rack weight
- o Anode centers

C. Process Tanks (continued):

- o Steam pressure
- o Water temperature
- o Electrical service
- o Auxiliary heaters
- o Exhaust

3. What features should be considered when you decide to buy?

A. Interface and Control:

The manufacturer has a staff that can work with your Engineering and Process personnel to optimize the final process you have selected.

B. Service Personnel:

A staff of service personnel to support the installation and start-up plus supply adequate training of your "in-house" personnel on all phases of mechanical, electrical, and programming of the system. This determines when the warranty should start.

C. Simplicity of Design:

Specify the use of "off-the-shelf" type components and that the manufactures supply you with a set of drawings to be used in ordering any spares so that all standard parts would be noted to allow you to go directly to the OEM for standard parts.

D. Expandable System:

Plan into the original system the capability of expanding for future needs.

E. Complete System:

Assure yourself that what you think you have purchased is what you received. Make sure all quotes are complete and do not leave out items such as: exhaust system, scurbbers, motor control centers, and duct wiring.

F. Select a Complete Manufacturer:

Make sure the supplier selected has compared "in-house" manufacturing capability. This will assure you of a

F. Select a Complete Manufacturer (continued):

high quality product. A manufacturer that is only an assembly house must rely on the quality he purchases and does not have the capabilities to back up all parts of the product he is supplying. He can only pass on any warranties provided by his supplier.

G. Manufacturing Procedures:

Review the perspective supplier's manufacturing and quality procedures to assure yourself that they are using state of the art.

H. Efficiency:

Plan on only a 75%-90% utilization factor. This will allow for proper maintenance and down time.

I. Specifications:

Complete review of your present process is essential. You must be able to actually define requirements. Consider your power requirements. Make sure that you and your supplier understand your needs.

Rectifiers - ripple

Filters

Flow rates

Operating temperature

Total cycle

J. Engineering:

Determine that your supplier has a complete Engineering Staff:

Mechanical

Electrical

Chemical (waste treatment)

Architectural

K. Process Control:

Develop your "in-house" process control capability and

K. Process Control (continued):

completely define your process before looking into automatic equipment.

Vendor Selection:

Once the decision had been made to automate the zinc and the copper-nickel lines the following procedure was used to select the vendor.

- o Major vendor's contacted
- o G.E. requirements reviewed with above vendors
- o G.E. requested Dunn & Bradstreet on all vendors. All were satisfactory
- o G.E. personnel visited locations, both inside and outside the company, to observe equipment from various vendors in operation and to obtain inputs from these users
- o Vendors visited Waynesboro and presented their design proposal. Various concepts and alternatives were discussed
- o Vendors visited Waynesboro and presented revised design proposal
- o G.E. prepared detailed technical specification which would be included in their request for quotations
- o Quotations submitted by all five potential vendors were reviewed and comparatively analyzed
  - Three were too high, cost wise and included major deviations which did not offer any significant technical advantages
- o Three candidates were eliminated and the other two invited to Waynesboro to review their quotations. Both vendors were requested to submit revised quotations
- o Quotations were received from both vendors and reviewed
- o Equipment proposed by both vendors were quality equipment and would meet the requirements of the General Electric Company
  - One vendor was several thousand dollars lower than the other with technical equivalent equipment

Vendor Selection (continued):

- o G. E. personnel visited the low bidder to inspect their manufacturing facilities to assure they were capable of fulfilling contractural requirements
- o Request for material was issued
- o Equipment was installed

Results:

Total Program

Total cost of modernization program $1,042K

Cost reductions $1,783K

Each dollar spent generated $1.55 in cost reductions.

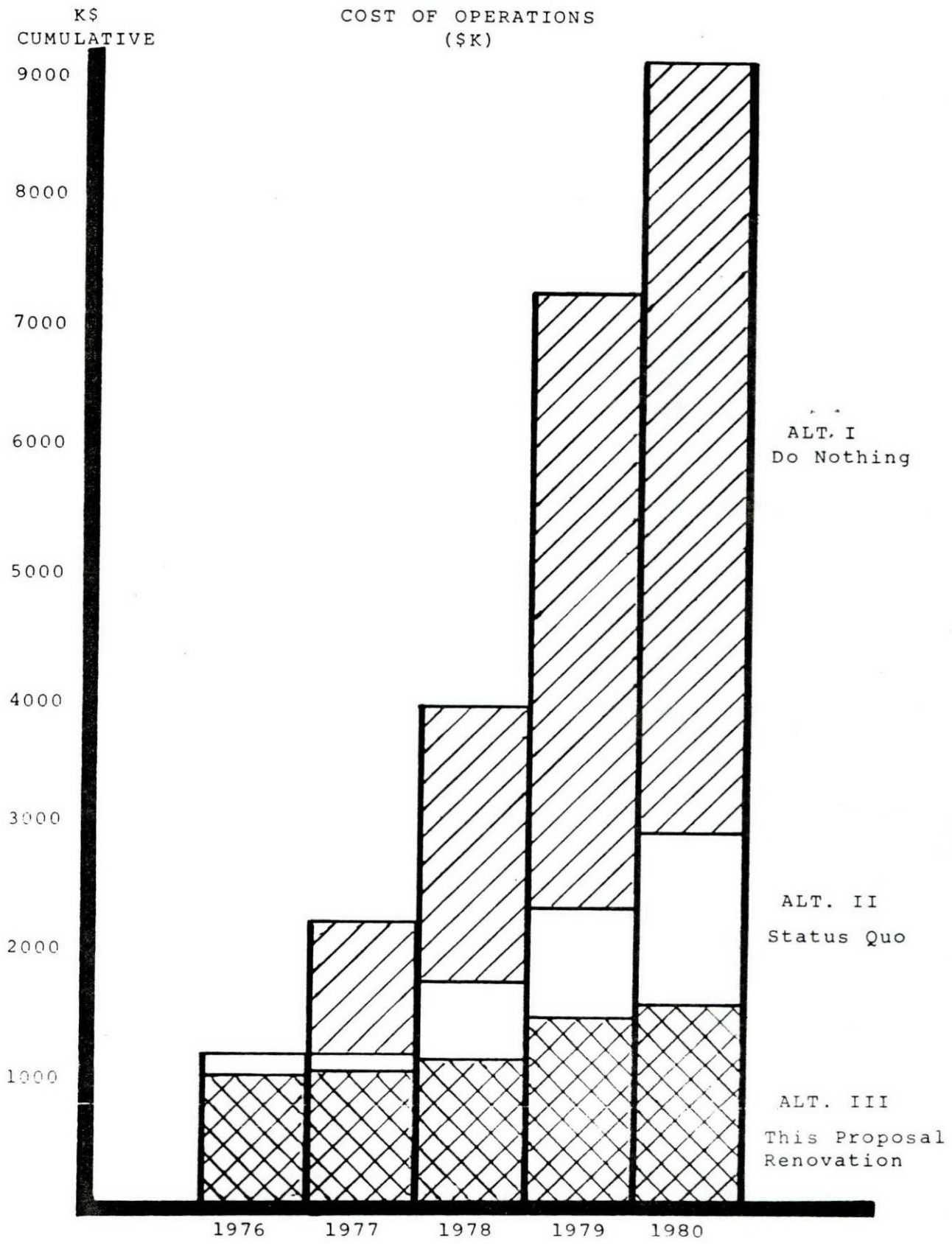
Augomated System:

Total cost of the automation system $496.9K

Cost reductions $473.00

Each dollar spent generated $0.96 in cost reductions

FIGURE 1


K$
CUMULATIVE
COST OF OPERATIONS
($K)
9000
8000
7000
6000
5000
4000
3000
2000
1000
ALT. I
Do Nothing
ALT. II
Status Quo
ALT. III
This Proposal
Renovation
1976
1977
1978
1979
1980

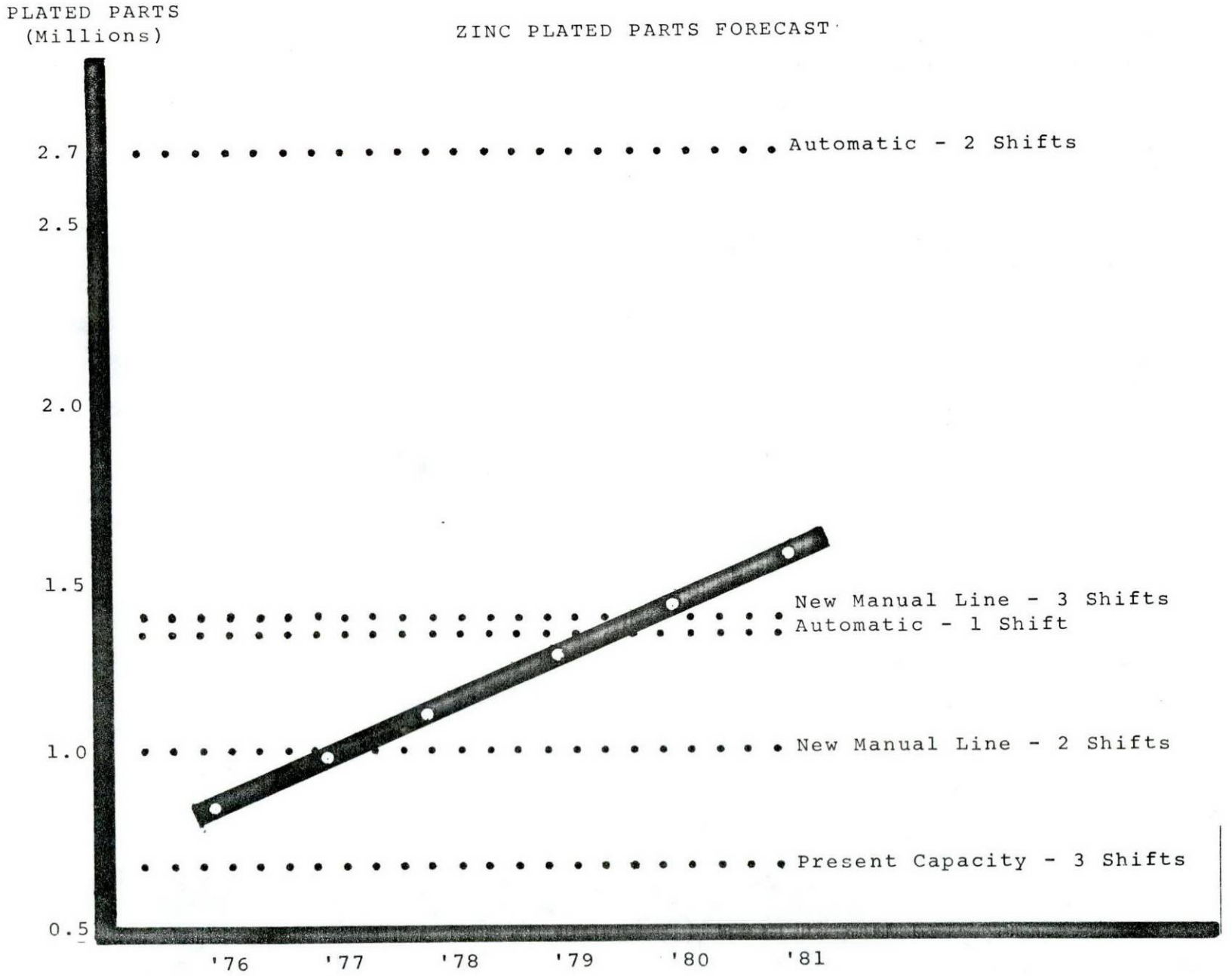

PLATED PARTS
(Millions)
ZINC PLATED PARTS FORECAST
2.7
2.5
2.0
1.5
1.0
0.5
Automatic - 2 Shifts
New Manual Line - 3 Shifts
Automatic - 1 Shift
New Manual Line - 2 Shifts
Present Capacity - 3 Shifts
'76
'77
'78
'79
'80
'81

FIGURE 2

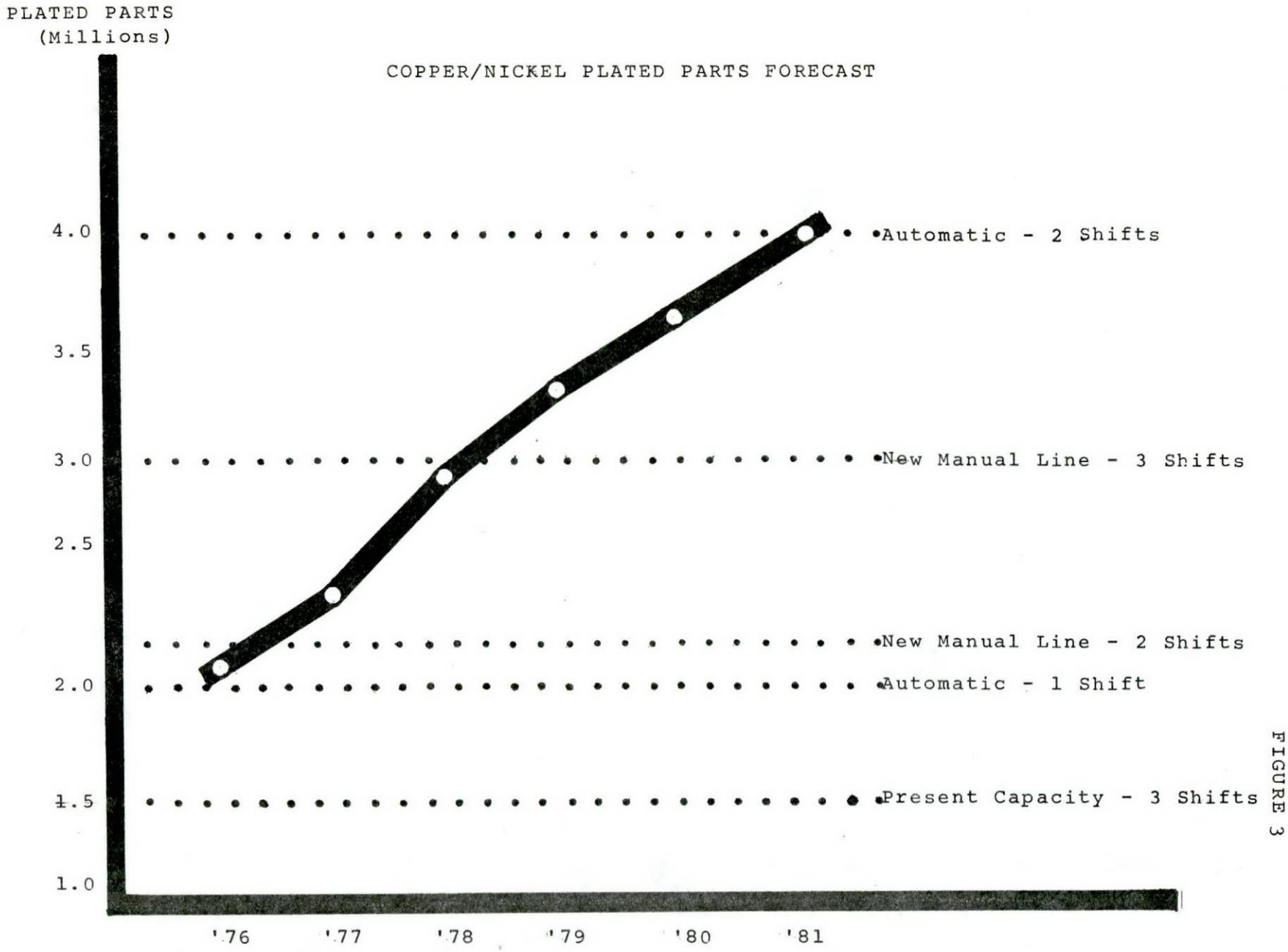

PLATED PARTS
(Millions)
COPPER/NICKEL PLATED PARTS FORECAST
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Automatic - 2 Shifts
New Manual Line - 3 Shifts
New Manual Line - 2 Shifts
Automatic - 1 Shift
Present Capacity - 3 Shifts
'76
'77
'78
'79
'80
'81

FIGURE 3

C-4

General Interest Session C

Control of Production Copper Electroplating Baths Using Cyclic Voltammetric Stripping Analysis

Rita Gluzman
UPA Technology
Syosset, NY

CONTROL OF PRODUCTION COPPER ELECTROPLATING BATHS USING CYCLIC VOLTAMMETRIC STRIPPING ANALYSIS.

by: Rita Gluzman, CVS Technical Specialist
UPA TECHNOLOGY, INC.

The current technological progress and sophistication of manufacturing techniques in the printed circuit board industry has produced an increased demand for a better comprehension and control of the copper plating baths.

Cyclic Voltammetric Stripping (CVS) analysis can be used as an AIDE and a MULTI-PURPOSE TOOL to the operator of acid copper baths. It functions to:

ROUTINELY MONITOR THE WORKING ACID COPPER BATH.

1. Confirm proper bath performance by determining the concentration of the additive components (suppressors and anti-suppressors) in:
   A. Freshly prepared or noncontaminated production baths.
   B. Used or contaminated production baths.
2. Monitor contaminants.
3. Establish an acceptable chloride concentration range.

EVALUATE ADDITIVES DURING INCOMING INSPECTION TO ENSURE CONSISTENT ADDITIVE STRENGTH.

INDICATE THE NECESSITY FOR CARBON TREATMENT AND EVALUATE ITS EFFECTIVENESS.

TROUBLESHOOT PROBLEM BATHS BY:

A. Performing diagnostic tests.

PERFORM RESEARCH WORK BY:

A. Evaluating new additive systems.
B. Evaluating performance of different types of baths/ additives.

THEORY OF OPERATION

Voltammetry is an electrochemical technique in which an applied potential is used to cause the oxidation or reduction of a substance at the electrode surface in an electrolyte solution.

In Cyclic Voltammetric Stripping (CVS) method the potential of an inert rotating electrode immersed in a sample of the bath is cycled at a constant rate so that a small amount of copper is alternately deposited on the electrode and stripped off by anodic dissolution. The charge required to strip the copper is related to the deposition rate and, therefore, to the additive concentration in the plating bath. (1)

Experimental Details

All data was taken on acid copper baths containing 75 gr/l of $CuSO_4 \cdot 5H_2O$; 10% b/v H_2SO_4; 75 ppm of Cl^- with various components of Copper Gleam PCM additive from LeaRonal.

CVS parameters were obtained by using QUALIDERM -1000 system which contained the following electrodes:

Working - platinum electrode mounted in the rotating disc configuration.

Auxiliary - copper rod.

Reference - saturated calomel electrode (SCE) immersed in a salt bridge filled with 10% sulfuric acid.

The rotating working electrode was cycled at 100 mV/sec. between -0.20V and 1.60V vs. double-junctioned SCE.

I. DETERMINATION OF ADDITIVE COMPONENTS IN ACID COPPER BATHS.

Most of the additives have four major components: brightener, carrier, wetter, and leveler. Each component can be a single compound or a mixture of several compounds. In some cases the same compound can perform several functions (For example: the same compound can be a leveler and a carrier).

Terminology note: Additive refers to the mixture of the components; Brightener refers only to the brightener component.

The above-mentioned four components can be divided into two major groups: suppressors and antisuppressors. The brightener component is usually the antisuppressor, while the other three are suppressors.

Explanation of the suppressing effect: The suppressor components have the effect of decreasing the rate of copper deposition.

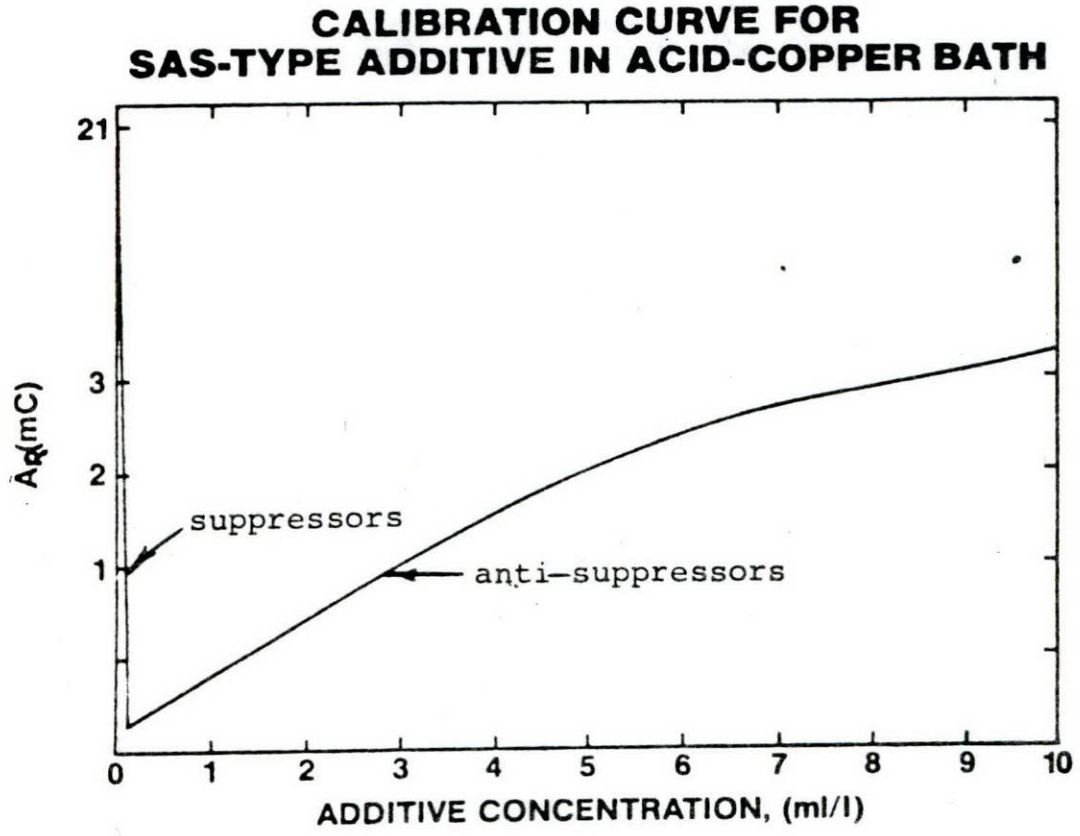
For proper bath operation, both suppressors and antisuppressors should be controlled and maintained in a balanced combination.

Based on additive nature, most of the acid copper baths can be divided into two major groups:

1. Sulfoniumalkanesulfonate-based (SAS)
2. Polyether-sulfide-based (PES)

A plot of CVS parameter (A_R) versus concentration of additive shows the sensitivity of the method to the concentration of proprietary additive, as can be seen from Figure 1.

Figure 1



During extensive research work on SAS-type additives, it was determined that the steeply descending portion of the calibration curve for SAS-type additives is caused only by the suppressing components (wetters and carriers) of the additive system (see Figure 1).

On the other hand, the rising portion of the calibration curve is sensitive only to the anti-suppressor (brightener) component of the additive system. This phenomenon may be used to independently determine the additive components in SAS-type acid copper baths.

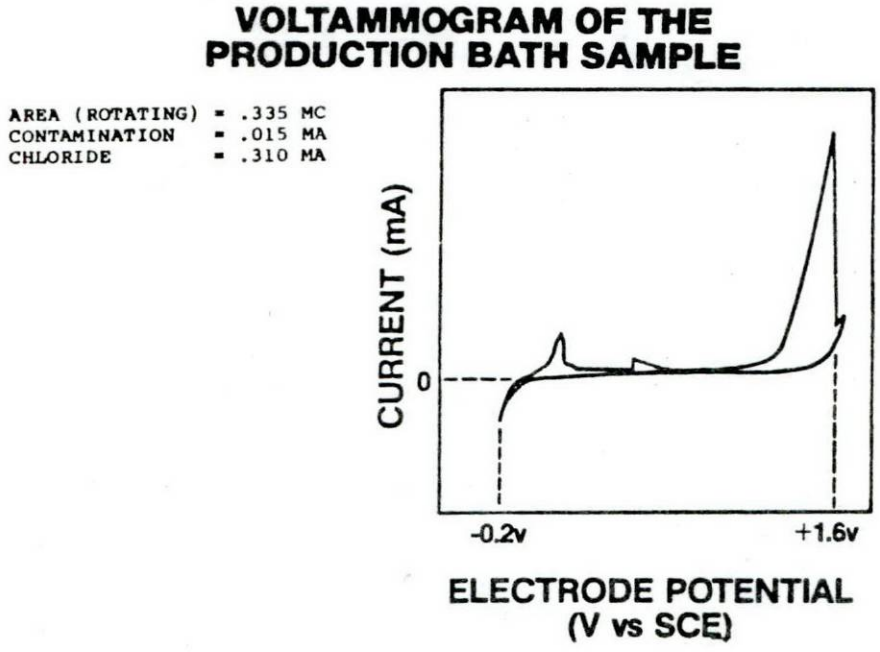
The concentration of the brightener component can be accurately determined by one of two methods.

A. For freshly prepared or non-contaminated bath samples, the standard addition calibration curve should be utilized.

EXAMPLE # 1

CVS ANALYSIS OF THE PRODUCTION ACID COPPER BATH SAMPLE WITH PCM ADDITIVE

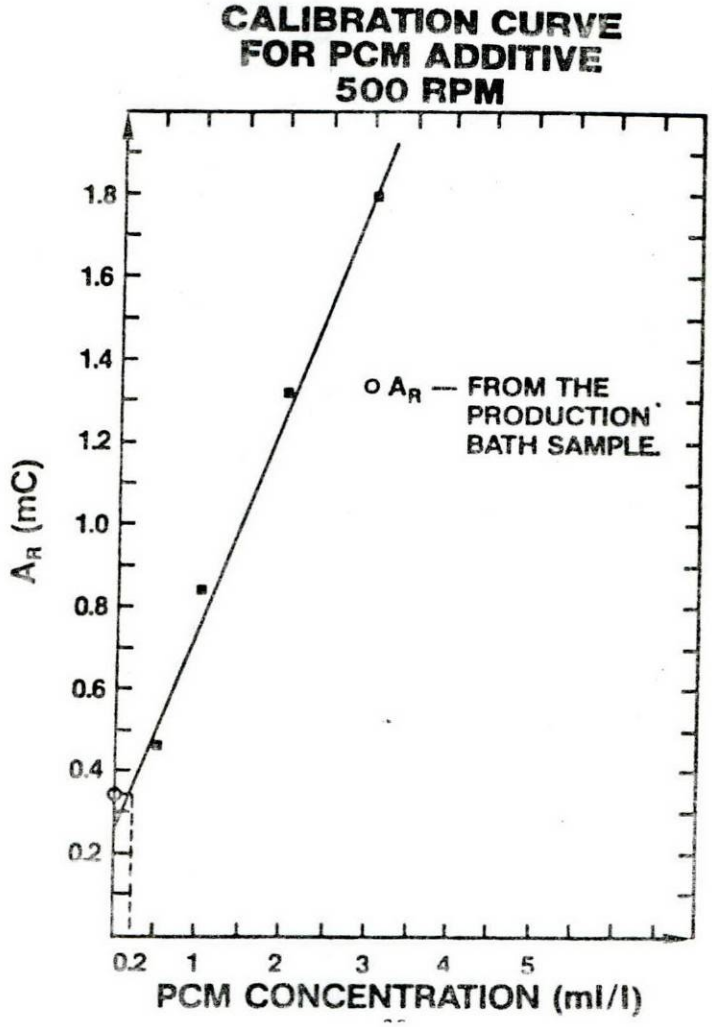
Figure 2



Explanation: From the calibration curve (Fig. 3) the brightener concentration in this production bath is 0.2 ml/l.

The contamination current is very low; the bath practically does not have any oxidizable organic contaminants.

Figure 3



B. For used or contaminated production baths the Linear Approximation Technique (LAT) should be followed.

When the contamination current is greater than 0.050 mA (empirically-chosen value) the acquired bath impurities, additive breakdowns and other contaminants have a great effect on the rate of copper deposition, thereby interfering with CVS analysis and changing the calibration curves.

The "standard additions" techique, described earlier can no longer be used for brightener determination in these production baths.

The Linear Approximation Technique (LAT) assumes that at low brightener concentrations (<5ml/l), the relationship between the CVS rate parameter A_R and the brightener concentration is linear and can be described by an equation of a type:

$$y = a + bx$$

where b (the slope) can be easily determined when 1 ml/l of the additive is added to the sample of production bath. Then:

$$y = a + \frac{y_{(x+1)} - y_{(x)}}{(x+1) - x} \cdot x$$

or

$$y = a + [y_{(x+1)} - y_{(x)}] \cdot x$$

or

$$x = \frac{y - a}{y_{(x+1)} - y_{(x)}} \quad \text{and if } y_{(x+1)} = y',$$

or

$$x = \frac{y - a}{y' - y}$$

where: y = A_R of production bath sample

y' = A_R of production bath samples after 1 ml/l of brightener addition

The intercept a (A_R at zero brightener concentration) has to be experimentally determined for every specific production bath sample.

Note: As calculated, x will have "ml/l" units.

The formula is: $x = \frac{y - a}{y' - y} \cdot 1 \text{ (ml/l)}$

For simplicity, the coefficient "1" is omitted.

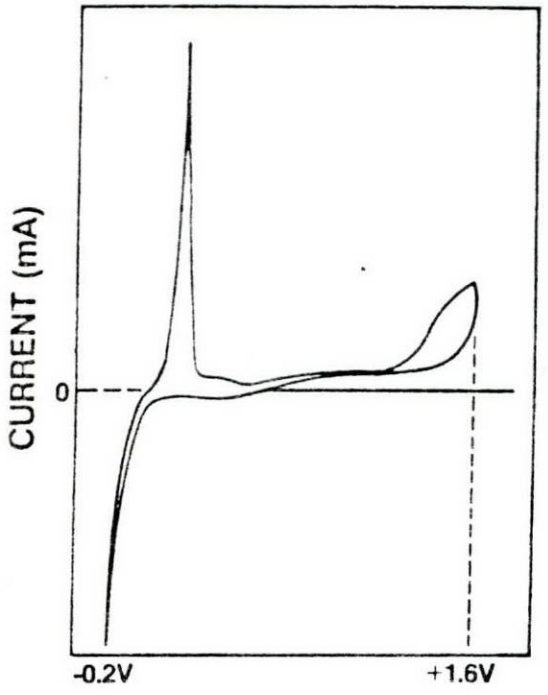
EXAMPLE # 2

CVS ANALYSIS OF THE PRODUCTION ACID COPPER BATH SAMPLE WITH PCM ADDITIVE AND ORGANIC CONTAMINATION ABOVE 0.050 mA.

AREA (ROTATING) = 1.134 MC or: y = 1.134 mC
CONTAMINATION = .101 MA
CHLORIDE = .449 MA

Figure 4

TYPICAL VOLTAMMOGRAM OF A SAS-TYPE PRODUCTION BATH SAMPLE WITH HIGH ORGANIC CONTAMINATION



After substituting the corresponding values in the formula for brightener determination:

$$x = \frac{y - a}{y' - y}$$

or

$$x = \frac{1.134 - 0.460}{1.645 - 1.134}$$

$$= 1.32 \text{ ml/l}$$

The concentration of the suppressors (wetters and carriers) can be determined by using the dilution titration technique. (3)

It has been established experimentally that during normal copper plating, the suppressor components of the additive are consumed at lower rates than the anti-suppressor components. As a result, the concentration of the suppressor components tends to increase with time. It is normally found that acid copper plating baths are operating at suppressor concentrations much higher than optimal levels. The bath/additive manufacturers and suppliers should assume the responsibility to establish upper limits for the concentration of these components in a production plating tank.

EVALUATION OF THE ADDITIVE ACTIVITY

Keeping additives in a proper range of concentration in an acid copper plating bath is mandatory for obtaining high quality copper deposits. The major difficulty stems from the fact that such systems consist of mixtures of proprietary components that in most cases are not pure compounds. As side products of major organic synthesis, these components may differ in strength and activity from batch to batch. It has also been observed that individual batches change with time. Therefore, variations in effective activity may be attributed to the additive aging after manufacture. All of this obviously introduces serious process control problems.

Cyclic Voltammetric Stripping analysis can provide PC board manufacturers with valuable information concerning the activity and stability of their additive systems. By using CVS analysis to inspect and calibrate incoming batches and by continuous control of plating baths and additive stocks, problems related to stability and differences between batches can be minimized.

CVS ANALYSIS AS A POWERFUL TOOL IN REGULATING CARBON TREATMENT PROCEDURE.

Over a period of time, a normal production plating bath will accumulate organic contaminants that are introduced from rack coatings, photoresists, breakdowns of the additive components, and other drag-in chemicals. Usually these organic contaminants are removed from the bath during the carbon treatment procedure.

Currently the procedure is performed on the basis of a previously established schedule or when plating in the existing bath results in a poor deposit. When the latter occurs, it is already too late and too costly to perform the carbon treatment. The losses from the rejected product can be tremendous.

Therefore, there was an obvious need for a technique that would forecast the need for carbon treatment and afterward establish its effectiveness for every specific bath. CVS provides such a technique and will:

1. Reduce the cost of plating due to premature or unnecessary carbon treatment.
2. Reduce the rejects due to copper plating in highly contaminated or just "bad" plating baths.

The CVS method can successfully establish a carbon treatment schedule and evaluate the effectiveness of the carbon treatment procedure. Based on CVS feedback, carbon treatment schedules can be streamlined to efficiently maintain acceptable bath purity under normal conditions.

Figure 5 shows voltammograms from a fresh bath and a contaminated production bath, both containing the same concentration of the additive. For the fresh bath, only a single oxidation wave of chloride is evident beginning at 1.2 V vs SCE. However, in contaminated production baths, two waves are obtained; the chloride wave and a second broad wave beginning at 0.9 V, corresponding to the oxidation of bath contaminants.

In this case, the chloride wave is superimposed over the contaminant wave. The diffusion-limited current for the contaminant wave, measured at 1.1V is directly proportional to the concentration of the oxidizable organic contaminants present in the bath. Therefore, theCVS limiting current measurement provides an accurate, reliable means for monitoring and controlling the level of oxidizable organic contaminants in acid copper production baths. (2)

EXAMPLE # 3

This is the information given in a printout from a CVS analysis of a typical production bath.

RATIO (AR/AS)	=	1.859
AREA (ROTATING)	=	1.894 MC
AREA (STATIC)	=	.568 MC
CONTAMINATION	=	.124 MA
CHLORIDE	=	.337 MA

The current from oxidizable contaminants is 0.124 milliamps.

The CVS analysis of a virgin bath with the same copper and sulfuric acid composition produces a "contamination" current of 0.027 milliamps:

RATIO (AR/AS)	=	1.182
AREA (ROTATING)	=	31.45 MC
AREA (STATIC)	=	28.53 MC
CONTAMINATION	=	.027 MA
CHLORIDE	=	.178 MA

Based on extensive experimental data, it was established that when the current from oxidizable contaminants at 1.1V does not exceed 0.100 milliamps the bath is considered comparatively clean. When the current from oxidizable contaminants exceeds 0.100 milliamps, the bath starts to approach dangerous levels of organic contamination, and starting from that point, a carbon treatment should be considered.

It is the responsibility of the bath and additive manufacturers to establish acceptable upper limits of contamination and their values should be used in lieu of these values.

Figure 5

Effect of Organic Bath Contaminants on CVS Voltammograms

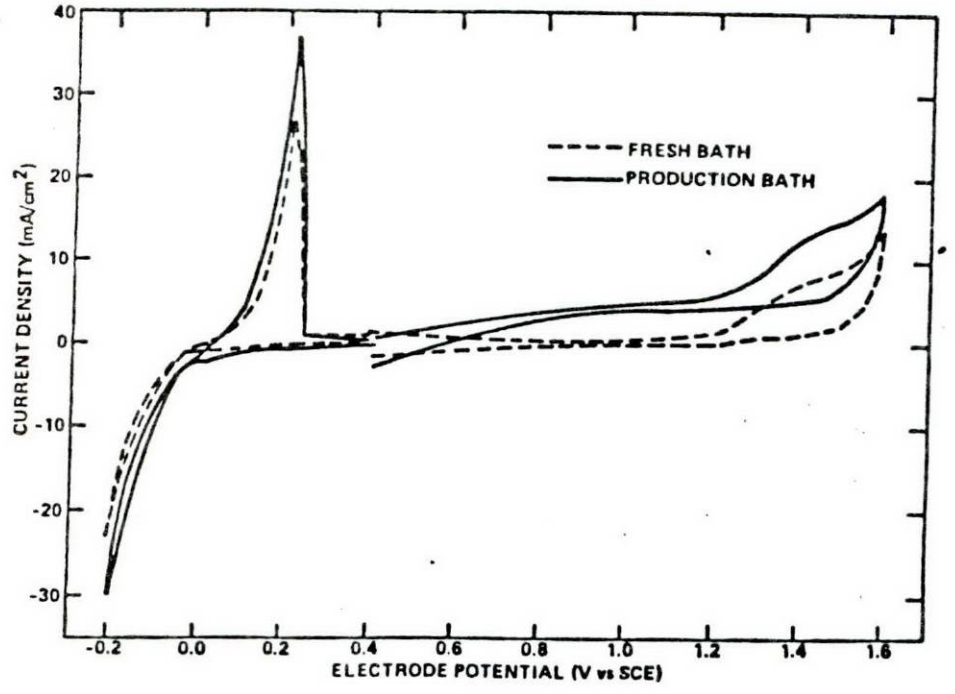
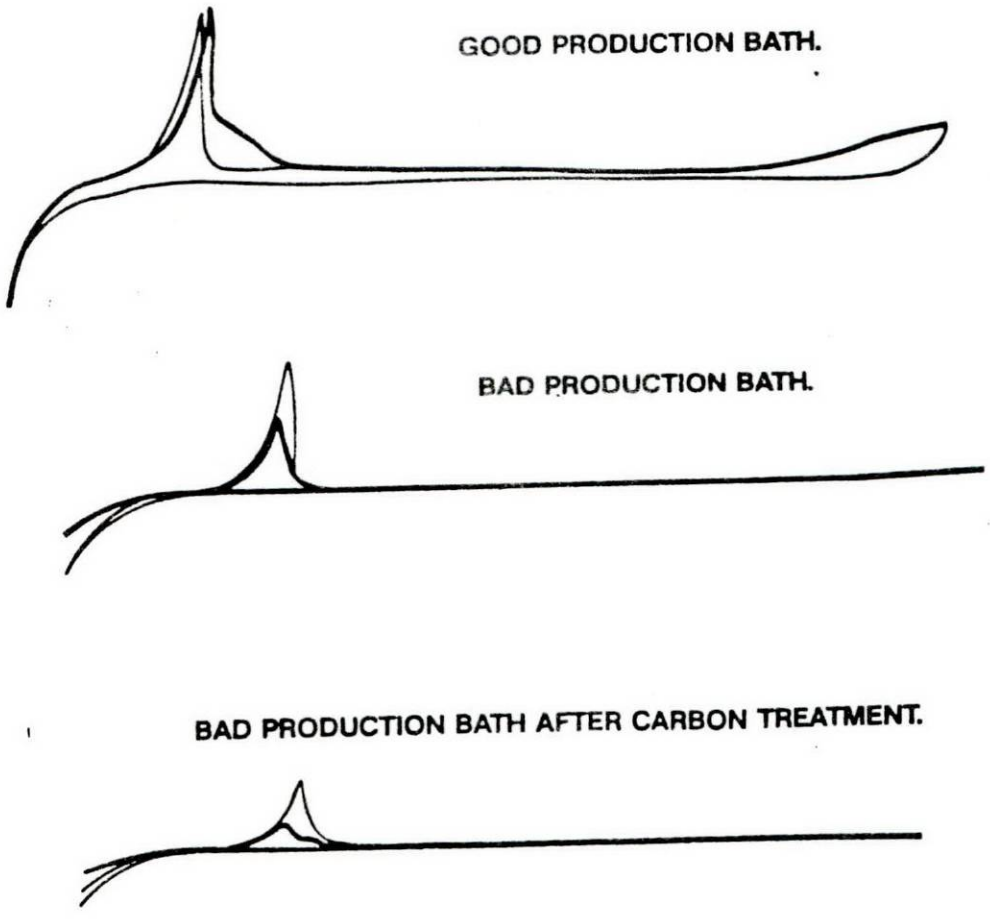


Figure 6 shows voltammograms of "good", "bad", and "bad after carbon treatment" copper plating baths with the PCM additive system. The typical double peaks for the PCM additive can be observed only on the voltammograms for the"good" and "after carbon treatment" baths. Such double peaks are missing on the voltammogram of the "bad" bath, suggesting an abnormal behavior.

Figure 6

TYPICAL VOLTAMMOGRAMS OF PRODUCTION SAS-TYPE BATHS



CONCLUSION

CVS analysis can be used as a useful tool to provide improved control of the acid copper plating process; specifically, control of additive components, evaluation of additive acitivity, indication of necessity for carbon treatment and evaluation of its effectiveness. Such analysis is required to obtain optimum results in reducing reject rates, additive waste and unnecessary carbon treatments.

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General Interest Session C

Quality Development for Minimum Total Cost

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Quality Development for Minimum Total Cost

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Abstract

Production processes, such as electroforming, produce variations in the parts. Variations represent loss of quality and financial loss. Dr. Taguchi's methods, widely used in Japan, evaluate quality loss, develop stable processes, and provide best quality control during production. Dr. Taguchi's methods lead to high quality and low manufacturing cost.

Introduction

Dr. G. Taguchi has developed comprehensive methods for the development of quality (1,2,3). Dr. Taguchi's methods are widely used in Japan, but they have only recently become known in the United States. This paper is a brief description of the application of Dr. Taguchi's methods to fabrication processes, such as electroplating and electroforming.

Figure 1 shows the relationships among the different activities that we will consider here. Our prime attention is focussed on the Fabrication Process. We wish the Fabrication Process to produce uniform parts economically. The parts can never be completely uniform because of three types of noises:

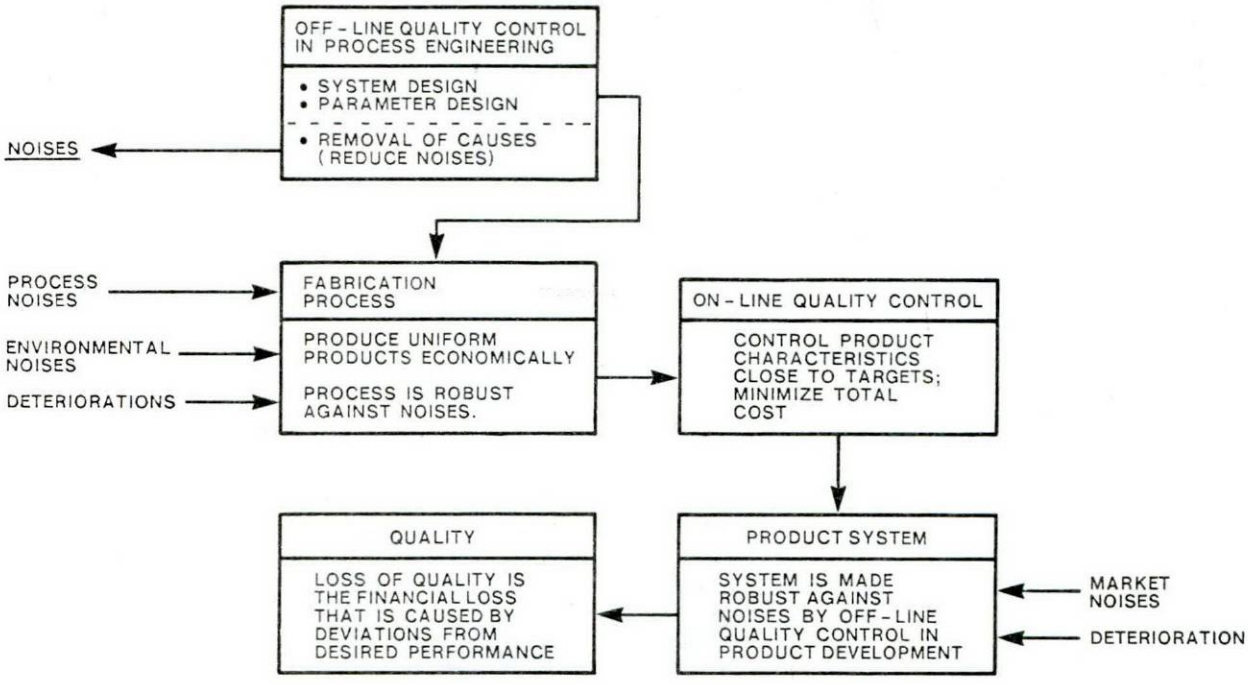


Figure 1

- **Process Noises**

  Variations in primary fabrication factors, for example, electrolyte concentration and pH.

- **Environmental Noises**

  Variations in other factors such as relative humidity and the concentration of trace elements.

- **Deteriorations**

  Degradation with time and use such as contamination of the plating bath.

Of course, the parts will vary unacceptably if the noises are excessive. We wish to develop the fabrication process to produce uniform parts in the presence of the relatively small noises that are typical of good industrial practice.

The Fabrication Process is developed by Off-Line Quality Control in Process Engineering which has three steps:

- **System Design**

  Selection or design of the fabrication equipment, materials, operations, and standard operating procedures.

- **Parameter Design**

  This is a critical step in Dr. Taguchi's method. The nominal values of the fabrication factors are optimized to make the Fabrication Process robust against noises. The variance of the parts is reduced even though the noises are typical of good industrial practice. Also, the production time can often be reduced.

- **Removal of Causes**

  For some critical tolerances, special action may be required to minimize some of the noises. However, this should be used only as a last resort because it will increase the manufacturing cost.

After the Fabrication Process is fully developed, it is put on line for commercial production. Deviations from target values can be reduced by On-Line Quality Control that checks the critical characteristic(s) at constant intervals, and adjusts the process if the adjustment limit is exceeded. Dr. Taguchi optimizes the checking interval and the adjustment limit to minimize the total cost - factory cost plus field cost.

The variance of a part becomes a noise within the Product System. A key feature of Dr. Taguchi's methods is the use of Off-Line Quality Control in Product Development to make the product system robust against noises. In this paper, this activity is not described; the concentration is on production.

Finally, the variance of a part decreases the quality of the product. This loss of quality is financial loss, such as service cost, because the customer is dissatisfied. Dr. Taguchi quantifies the quality loss to guide our development and production activities.

The remainder of this paper describes in more detail:

- Parameter Design in Off – Line Quality Control in Process Engineering.
- Quality
- On – Line Quality Control

Parameter Design

In Parameter Design, the nominal values of the fabrication factors are optimized to make the Fabrication Process robust against noises. The basic concept is to take advantage of nonlinearities in the process. The operating point is found where the critical characteristic(s) of the part has relatively little response to the noises. Then, all of the parts will be relatively uniform even though the process has the noises that are typical of good industrial practice.

We start on our journey to find the operating point that is most robust against noises. Consider an electroforming process that has 10 critical fabrication factors. From early works, we have a value for each factor. Now we seek a better value. We carefully select a larger value and a smaller value for each factor. Now we have three levels for each of the 10 factors. This gives a total of 3^{10} or 59,049 combinations.

We need an efficient development procedure to find the best of the 59,049 combinations. Dr. Taguchi uses orthogonal arrays to select a few combinations for evaluation. Here we use the L_{27} orthogonal array (See Table 1). In combination with the table of three alternative values for each of the 10 factors, the L_{27} orthogonal array defines 27 experiments or production trials.

The 10 fabrication factors are assigned to the first 10 columns of the L_{27} orthogonal array. Then each row of the L_{27} represents an experiment or production trial. For example, in Trial 1 (first row) all 10 factors have their Level 1 values. In Trial 2, the first four factors are at Level 1, and the last six factors are at Level 2. Thus, Tables 1 and 2 together define 27 production trials. Note that in the L_{27} orthogonal array, each level of every factor is present nine times. Also, for any two columns, i.e., any two factors, each combination, 1 – 1, 2 – 2, 3 – 3, 2 – 3, 3 – 1, 1 – 2, 3 – 2, 1 – 3, and 2 – 1, is present three times. Orthogonal arrays have been found to be very useful in development work.

For each of the 27 trials, a small number of parts are made. The critical dimension, or other characteristic, is measured. The mean value, m, and variance, σ^2, are calculated for each trial. The signal – noise ratio, SN, is calculated for each trial:

Table 1
L_{27}

	1	2	3	4	5	6	7	8	9	10	11	12	13
1	1	1	1	1	1	1	1	1	1	1	1	1	1
2	1	1	1	1	2	2	2	2	2	2	2	2	2
3	1	1	1	1	3	3	3	3	3	3	3	3	3
4	1	2	2	2	1	1	1	2	2	2	3	3	3
5	1	2	2	2	2	2	2	3	3	3	1	1	1
6	1	2	2	2	3	3	3	1	1	1	2	2	2
7	1	3	3	3	1	1	1	3	3	3	2	2	2
8	1	3	3	3	2	2	2	1	1	1	3	3	3
9	1	3	3	3	3	3	3	2	2	2	1	1	1
10	2	1	2	3	1	2	3	1	2	3	1	2	3
11	2	1	2	3	2	3	1	2	3	1	2	3	1
12	2	1	2	3	3	1	2	3	1	2	3	1	2
13	2	2	3	1	1	2	3	2	3	1	3	1	2
14	2	2	3	1	2	3	1	3	1	2	1	2	3
15	2	2	3	1	3	1	2	1	2	3	2	3	1
16	2	3	1	2	1	2	3	3	1	2	2	3	1
17	2	3	1	2	2	3	1	1	2	3	3	1	2
18	2	3	1	2	3	1	2	2	3	1	1	2	3
19	3	1	3	2	1	3	2	1	3	2	1	3	2
20	3	1	3	2	2	1	3	2	1	3	2	1	3
21	3	1	3	2	3	2	1	3	2	1	3	2	1
22	3	2	1	3	1	3	2	2	1	3	3	2	1
23	3	2	1	3	2	1	3	3	2	1	1	3	2
24	3	2	1	3	3	2	1	1	3	2	2	1	3
25	3	3	2	1	1	3	2	3	2	1	2	1	3
26	3	3	2	1	2	1	3	1	3	2	3	2	1
27	3	3	2	1	3	2	1	2	1	3	1	3	2

$$SN = 10\log_{10}\frac{m^2}{\sigma^2} = 20\log_{10}\frac{m}{\sigma} \quad . \qquad (1)$$

Larger values of SN are better. We wish to minimize the standard deviation, σ, relative to the mean value, m. Now we have 27 SN ratios, one for each trial. For each level of each factor, the average SN ratio is calculated. For example, for Factor 1, the average of the nine SN ratios for Trials 1 – 9 gives the average SN ratio for Level 1. The average SN ratio is similarly calculated for Levels 2 and 3. The level that gives the largest average SN ratio is the best level. Thus, if Level 3 of Factor 1 gives the highest value for the average SN ratio, then Level 3 is the best value for Factor 1. The same procedure is used to find the best level for all of the fabrication factors.

Table 2

Electroforming Nickel Belts Using a Nickel Sulfamate Electrolyte

Fabrication Factors	Levels 1	2	3
1 pH	3.5	3.9	4.3
2 Plating Temperature(°F)	130	140	150
3 Current Density	200	300	400
4 Agitation(rpm)	30	40	50
5 Nickel Concentration(oz/gal)	10	12	15
6 $NiCl_2$/Ni	0.08	0.1	0.12
7 Mandrel Material	Al	Cu	S.S.
8 Saccharin Concentration(ppm)	25	65	100
9 Temperature Differential(°F)	60	70	80
10 Anode Material	EDNi	SDNi	

The above procedure of Parameter Design gives the best combination of nominal values for the fabrication factors. The process has been made robust against noises. The inherent standard deviation of the product of the process has been minimized, even though the process variations (noises) that are typical of good industrial practice are present. The complete Parameter Design will usually include additional analyses of the data, and verification trials are used to verify that the operating point that has been selected does produce the expected uniform product. The complete process is described in more detail in Reference 1. The application of Parameter Design to integrated circuit fabrication is described in Reference 4.

Quality

Quality loss is the financial loss after the product is shipped. If a critical part dimension deviates too far from its target value, then the product performance will not conform to customer requirements. It is the job of Off – Line Quality Control in Product Development to develop the product so that Δ_C can be as large as possible. Now we assume that the Product Development has been done well, and Δ_C is the largest deviation that can be tolerated before customer dissatisfaction occurs. Figure 2 shows Δ_C as the customer tolerance.

When the customer is dissatisfied with the performance of the product, some action – such as service – will be required. The action costs money.

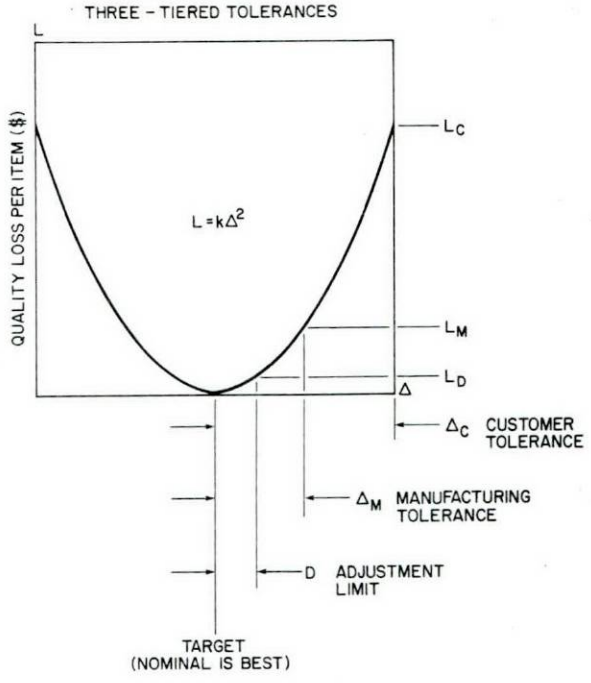


Figure 2

- Important Quality Fact No. 1:

  We must associate a financial loss, L_C, with the customer tolerance, Δ_C. Otherwise, we would be misleading ourselves with the foolish notion that lack of quality is free.

- Important Quality Fact No 2:

  Consider two units of production, one with Δ slightly larger than Δ_C and the other with Δ slightly smaller than Δ_C. Is there a significant difference between the two units? Of course not. Conclusion: Quality loss, L, is a smooth curve. It doesn't suddenly jump from $L = 0$ to $L = L_C$ when $\Delta = \Delta_C$. L increases smoothly from $L = 0$ when Δ is on target to $L = L_C$ when $\Delta = \Delta_C$.

- Important Quality Fact No. 3:

  The quality loss, L, is symmetrical. Negative deviation is just as bad as positive deviation. The quality loss, L, is zero when Δ is on target ($\Delta = 0$).

The simplest curve that satisfies all of the above requirements is

$$L = k\Delta^2 \quad . \tag{2}$$

Because $L = L_C$ when $\Delta = \Delta_C$, Equation 2 becomes

$$L = \frac{L_C}{\Delta_C^2} \Delta^2 \quad . \tag{3}$$

This simple equation is sufficient to guide us in making economical decisions about our manufacturing practices.

On-Line Quality Control

In production, if Δ deviates too far from target, we can take action in the factory, scrap or rework, to avoid quality loss after the product is shipped. The cost of this action, L_M, is usually much smaller than the quality loss at the customer's site, L_C. Action in the factory is cheaper than action at the customer's site. The manufacturing tolerance, Δ_M, is from Equation 2:

$$\Delta_M = \left(\frac{L_M}{L_C}\right)^{1/2} \Delta_C \quad . \tag{4}$$

The manufacturing tolerance, Δ_M, is considerably smaller than the customer's tolerance, Δ_C. If the deviation, Δ, is larger than Δ_M, then the quality loss in the field would be larger than L_M. The economical decision is to take action in the factory at a cost of only L_M. Of course, we actually wish to also avoid scrap or rework and its cost, L_M. The On-Line Quality Control to avoid scrap and rework and minimize total cost is described below.

If the deviation can be controlled to be less than D, then it is clear from Figure 2 that much quality loss will be avoided. However, the process control will cost something. We wish to minimize the total cost:

$$C_T = C_C + L \quad , \tag{5}$$

where: C_T = total cost of quality,

C_C = cost of control, and

L = quality loss.

$$C_T = C_C + \frac{L_C}{\Delta_C^2}\,\sigma_M^2 \quad . \tag{6}$$

In Equation 6, σ_M^2 is the variance, the average of Δ^2 averaged over all of the units that are produced. In Parameter Design, described above, the manufacturing process was optimized to reduce σ, the standard deviation, during relatively short production runs. If σ is very small compared to D, and very stable, additional action may not be necessary. If σ is very large, for example, approximately equal to Δ_M, then we probably should return to System Design and find a better process. Commonly, σ is smaller than D, but, over the full production run, the variance, σ_M^2, will become excessive unless control action is taken.

The process can be controlled by checking every n parts. If the check shows that Δ is less than the adjustment limit, D, then no action is taken. If Δ is larger than D, then the process is adjusted towards the target. With checking and adjustment, Equation 6 becomes

$$C_T = \frac{B}{n} + \frac{C}{\mu} + \frac{L_C}{\Delta_C^2}\,\sigma_M^2 \quad , \tag{7}$$

where: B = cost of checking,

C = cost of adjustment, and

μ = average adjustment interval.

Once the dependence of σ_M and μ on n and D are determined, then the values of n and D are optimized to minimize the total cost, C_T. One method of doing this is described in detail in Chapters 9 and 10 of Reference 2.

Summary

Dr Taguchi uses Parameter Design to make the process inherently consistent, defines the quality loss function to determine the value of quality, and uses On - Line Quality Control to minimize the total cost. Dr. Taguchi's methods provide a significant advantage in achieving high quality and low cost.

Acknowledgements

All credit belongs to Dr. Taguchi whose methods are briefly described here. The author values the discussions that he has had with Dr. Taguchi. However, Dr. Taguchi did not have an opportunity to review this paper before it was submitted, and all shortcomings are the responsibility of the author. The author also wishes to thank Mr. Ray Bailey for suggesting this paper and for his discussions of the electroforming example.

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General Interest Session C

Improved Corrosion Resistance by Water-Soluble Organic Polymers

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INTRODUCTION

Sacrificial zinc coatings are used throughout the world to protect steel from corrosion on both small and large discrete parts and on continuous lengths of wire, rod, conduit and strip. Most of the applications involving discrete parts further use a chromate conversion coating in order to retard the white corrosion products that form readily on the zinc surface. Many of the continuous processing applications, on the other hand, are finished with an organic topcoat to provide additional protection and the desired appearance. Development of organic topcoats on chromated zinc parts is a logical step toward the overall objective of improved quality.

The fact that chromated zinc coatings may not provide satisfactory corrosion protection was recognized by Schulz, et. al.[1] This conclusion pertains not only to the optimization of the inorganic chromate matrix and its adhesion, but also to the need for special inhibitors and pore-closing agents. A major area of concern is the automobile industry where increased performance is required for assembled parts, such as those found in the engine compartment. It has been determined that the parts in this environment, which are subjected to widely variable temperatures, plus moisture and salt, prematurely produce excessive corrosion of zinc, and even basis metal. It has also happened that in the case of shipment by sea, the chromated zinc coated parts often show white corrosion upon arrival at the dealer's showroom.

After several years of development work and detailed studies in Germany, a new family of resin based post-treatments has been introduced to provide enhanced corrosion protection of zinc coated steel. The purpose of this paper is to describe the technical features and benefits of these new coatings.

CHROMATE COATINGS

As noted above, chromate coatings are incapable of providing the full measure of corrosion protection required. These films are formed from hexavalent chromium as it oxidizes and dissolves the zinc layer, thereby raising the pH near the surface which produces insoluble trivalent chromium and precipitates as a gel[2]. Bishop[3] describes this gel as a film of polymeric hydrated chromium hydroxide.

Upon exposure to temperatures of 80°C or above, dehydration occurs causing shrinkage and other structural changes in the chromate gel. Thus, the effectiveness of chromate conversion coatings for corrosion protection is reduced at elevated temperature. Also, in the case of yellow chromates, the special corrosion inhibiting effect of soluble hexavalent chromium compounds is decreased by the formation of insoluble derivatives[4].

The effects of heat and salt spray on chromate conversion coatings are illustrated in the scanning electron micrographs shown in Figures 1 - 6. As illustrated in Figure 1, drying a yellow chromate coating at 80°C produces a fine network of microcracks. Subjecting a yellow chromate coating to a thermal stress of 120°C for 24 hours causes massive deterioration of the film, as revealed in Figure 2.

Similar phenomena are also observed with black chromate coatings. In Figure 3, the pronounced network of cracks formed by drying at 80°C is evident. An even more pronounced cracked network is formed after 24 hours at 120°C (Figure 4) which creates cracks approximately 1 um wide. Subsequent exposure of thermally treated black chromate coatings to a neutral salt spray for a short time leads to the formation of corrosion products in the cracks (Figure 5), as one would expect from previous work[5]. After 72 hours of salt spray exposure, a thermally stressed black chromate coating is completely covered with zinc corrosion products (Figure 6).

One conclusion that can be drawn from these studies is the need for a suitable post-treatment or topcoat to provide improved protection against the combined effects of temperature and salt spray.

POST-TREATMENT METHODS

Various water soluble resins have been evaluated in terms of their ability to prevent chromate film dehydration and deterioration in salt spray. In addition to establishing the performance of specific resin systems, it was found that combined systems which incorporate chromates and phosphates within the structure of the water soluble resin provide additional benefits (Figures 7 and 8).

The organic polymers studied were chosen from the following groups: acrylate, acrylate/styrene, and alkyd resin based molecules. The mode of cross-linking, i.e., curing, depends on the specific polymer structure; mainly, one is dealing with thermally induced poly-addition and poly-condensation. Thus, in the case of acrylic resin dispersions, the cross-linking reaction of the n-methylol group containing amides is substantially accelerated by increased temperature.

In general, only a specific resin system and curing condition will produce the desired results. Best results are obtained from treatment solutions with a solids content in the range from 5-15%. When working with parts on racks, it is advisable to maintain a solids content of less than 10%, while handling of small parts in barrels, baskets, or centrifuges normally

requires a solids content close to 15% in order to achieve the desired increase in corrosion protection.

As a result of this work, several resin systems have been introduced commercially. To avoid use of commercial names, the two most important systems* will be referred to as the simple organic resin system and the combined resin and inorganic system which includes hexavalent chromium and phosphate compounds.

PROCESS PARAMETERS

The process parameters of the simple resin system are as follows:

Solids Content	5-15%
pH	8.5-9.0
Temperature	20-40°C
Drain Time (after rinse)	30-60 seconds
Treatment** Time	10-60 seconds
Drain Time	1-2 minutes
Drying Temperature	60-120°C
Drying Time	5-15 minutes

To prevent solids separation, it has proved beneficial to maintain the pH level between 8.5 and 9.0. The pH value may be adjusted by use of an ammonia solution or by amines such as dimethylaminoethanol or triethylamine. When removing the part from solution, it should be allowed to drain well before drying in an oven or centrifuge. In a centrifuge, rotation speeds should be set typically at 40-70 rpm to reduce loss of the coating and consequent reduction in thickness. Solution concentration can be determined approximately from density measurements and exactly based on solids content. Consumption rates depend on the type of part, solution concentration, and specific method of application. Experience has shown that consumption rates will be in the range of 5-15 grams of concentrate per square meter.

The process parameters of the combined resin and inorganic system containing hexavalent chromium and phosphate compounds are as follows:

Solids Content	2-10%
pH	1-2
Temperature	15-25°C
Immersion Time	10-15 seconds
Drain Time	1-2 minutes
Drying Temperature	80-160°C
Drying Time	10-30 minutes

*AQUARES 3 and AQUARES 6B, trademarks of Blasberg Oberfläechentechnik, GmbH.

**Treatment can be immersion or spray.

A noteworthy feature of this system is the solution pH which should be maintained under 2.0 and adjusted with phosphoric acid. Drying temperature is important, as it affects corrosion resistance. Treated steel surfaces should be dried at 140-160°C while treated zinc surfaces should be dried below 140°C. Coatings from this system will hold lacquer and are excellent as adhesive and primer coatings for subsequent application of a decorative powder coating.

While the above treatment system is most often used on non-chromated surfaces, it also provides excellent corrosion protection on black chromate coatings. In such cases, the solids content should be about 4% and drying temperatures of 80-100°C should be used to avoid deterioration of the chromate layer.

The performance features of both resin systems are outlined in the following sections.

CORROSION RESULTS

This section deals first with post-treatment by the simple organic resin (Figures 9 - 13), followed by the results for the combined resin containing hexavalent chromium and phosphates (Figures 14 - 16).

In Table I, a simple post-treatment is seen to provide at least a factor of 2 improvement in salt spray tests with 15 µm thick zinc deposits for standard barrel and rack conditions.

TABLE I

Effect of Post-Treatment on Salt Spray* Performance

Process	Treatment	Zinc Corrosion	Basis Metal Corrosion
Barrel	Yellow Chromate	48 - 96 hours	N/A
Rack	Yellow Chromate	72 - 200 hours	190 - 440 hours
Barrel	Yellow Chromate plus Organic Resin	120 - 240 hours	N/A
Rack	Yellow Chromate plus Organic Resin	240 - 330 hours	600 - 1000 hours

*Per Test SS DIN 50 021 (Equivalent to ASTM B-117).

The simple post-treatment process has enabled several German automotive companies to make their specifications more stringent. The example shown in Table II illustrates the changes which have been implemented[6]. Coating classification is determined by the zinc deposit thickness. Categories 3

and 6 correspond to 8 and 15 um zinc thickness, respectively, followed by yellow chromate. The new specifications with and without post-treatment in terms of salt spray test requirements are as follows:

TABLE II

Salt Spray* Test Specifications[6]

Coating Classification	Process	Chromate Only	Post-Treatment	Criteria
3,6	Rack	72 hours	192 hours	No zinc corrosion.
3,6	Barrel	48 hours	192 hours	Maximum 5% zinc corrosion.
3	Rack/Barrel	144 hours	240 hours	No base metal corrosion.
6	Rack/Barrel	240 hours	360 hours	No base metal corrosion.

*Per SS DIN 50 021

Figure 9 shows two automobile lock parts after 120 hours of exposure to salt spray. Both parts were plated in cyanide zinc (10-12 um), followed by a blue-bright chromate. The part on the left with no post-treatment has failed, while the one on the right with a post-treatment in a solution containing > 2% solids is fully acceptable. Figure 10 shows similar results for yellow chromated parts after 500 hours of salt spray. In addition to the significant improvement in corrosion protection, it is also noteworthy that the yellow color is fully maintained on the post-treated part, indicating that the corrosion inhibiting chromium VI compounds are still intact. Figure 11 shows two production parts from Daimler-Benz, Sindelfingen where a 700 hour salt spray test was used. The left part with only yellow chromate shows both zinc corrosion and red rust on the total surface, whereas the sealed part shows only red rust at the top.

The results from the Kesternich industrial atmosphere test** also show remarkable improvement for post-treated parts. Figure 12 contains photographs of two springs which were also plated by Daimler-Benz with 6-10 um of zinc and yellow chromated. The part on the left shows red rust after only three cycles, while the sealed part on the right shows only zinc corrosion beginning after 12 cycles. Similar results are evident in Figure 13

**Per SWF 2.0 S DIN 50 018, which is equivalent to ISO 3231, is a humidity test with 2.0 liters sulfur dioxide.

where production cast iron parts with the finish of zinc plate (8-10 um) followed by blue chromate have been subjected to different post-treatments in four cycles from the industrial atmosphere test. The part at the upper left with no post-treatment shows significant red rust. A slight improvement is shown for the part at the upper right, which received a post-treatment in a solution producing a low solids content (less than 1%). However, the part shown at the bottom received a post-treatment in a solution containing 8% solids and is only beginning to develop zinc corrosion products.

Test results from an automobile company study of zinc plated and chromated parts subjected to washing cycles indicate a notable corrosion resistance improvement of the post-treatment process. The cycle used was cold water rinse followed by steam spray and standard salt spray. It was found that zinc corrosion was evident on the parts without sealing after only 48 hours, whereas sealed parts lasted 120 hours to the first sign of zinc corrosion.

Salt spray test results for unplated automobile lock parts without and with the combination post-treatment are shown in Figure 14 after a 24-hour exposure. For comparison, Figure 15 shows two zinc plated parts without chromate after a 400-hour salt spray test. In both cases, the part on the right was post-treated and is shown to be in excellent condition compared to the untreated control sample. Similar results are shown in Figure 16 for zinc plated parts with black chromate after 400 hours salt spray. It should be pointed out that the parts used to obtain these high performance results were prepared under optimum conditions. Production experience has shown that the corrosion resistance of both rack and barrel plated parts subjected to the combined post-treatment, as measured by salt spray, are as follows:

Finish	Time To Corrosion
Bare Steel	24-48 hrs to red rust
Plated Zinc	150-400 hrs to zinc corrosion
Black Chromated Zinc	100-200 hrs to zinc corrosion

OTHER APPLICATIONS

The resin post-treatments described above are also useful over other finishes such as zinc alloys. Recent work in the U.S., based on salt spray tests per ASTM BII7, has shown that barrel plated parts with 7.5 um thick zinc - 0.7% cobalt coatings, followed by a yellow chromate and simple post-treatment will last 350 hours to base metal corrosion. Similar parts with 15 um of zinc cobalt followed by the combination post treatment were able to withstand 550 hours salt spray exposure to base metal corrosion.

In the assembly of zinc plated fasteners, mechanical and physical damage to the chromate film can result in severe corrosion problems of the unit in service. Post-treatment with the new resin systems can prevent this

problem from occurring and also allow for improved mechanical assembly of the fasteners.

Still other applications for these resin systems are as a topcoating for phosphated or polished articles, especially for use where there are severe galvanic couples, such as between stainless steel and mild cold rolled steel joints. Another area of application is to make nickel and chrome plated parts, such as tools, less sensitive to deterioration of the finish from handling.

CONCLUSION

The present study demonstrates that the use of suitable resin post-treatments for chromated zinc can provide a significant improvement in corrosion protection. Production experience by such companies as Audi/VW, BMW, Daimler-Benz and Opel indicates that salt spray test specifications can be made more stringent by at least a factor of two with post-treatment. The impact of these developments on the quality of automotive parts more than justifies the modest increase in finishing costs. As the trend towards long warranty life of vehicles continues, additional improvements in the technology for organic and mixed post-treatments can be anticipated.

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Fig. 1 Scanning electron micrograph, yellow chromate coating dried at 80°C. Bar represents 10 μm on all SEM photos.
(1800 X magnification)

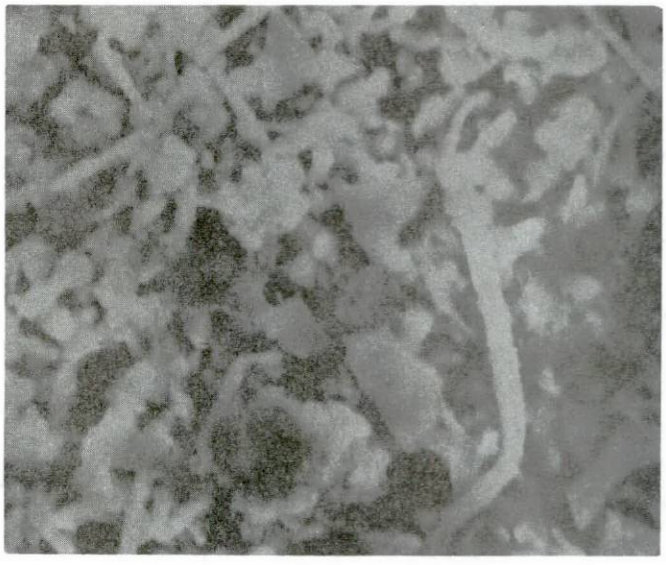


Fig. 2 Scanning electron micrograph, yellow chromate coating temperature treated at 120°C for 24 hours.
(1600 X magnification)

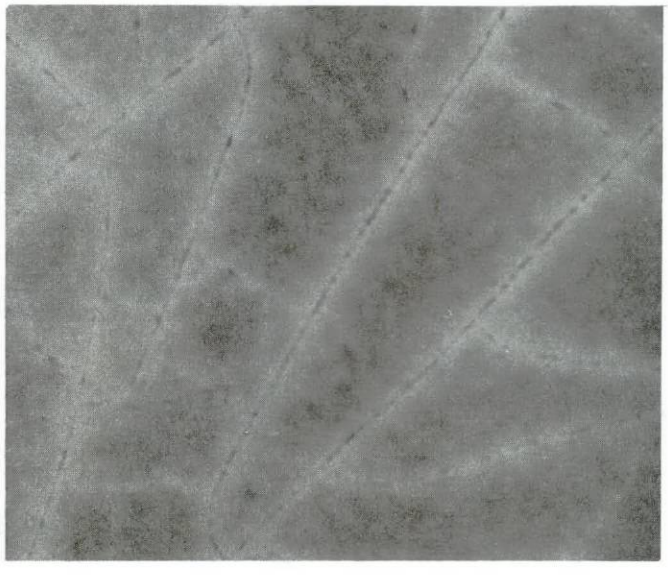


Fig. 3 Scanning electron micrograph black chromate coating dried at 80°C.
(2000 X magnification)

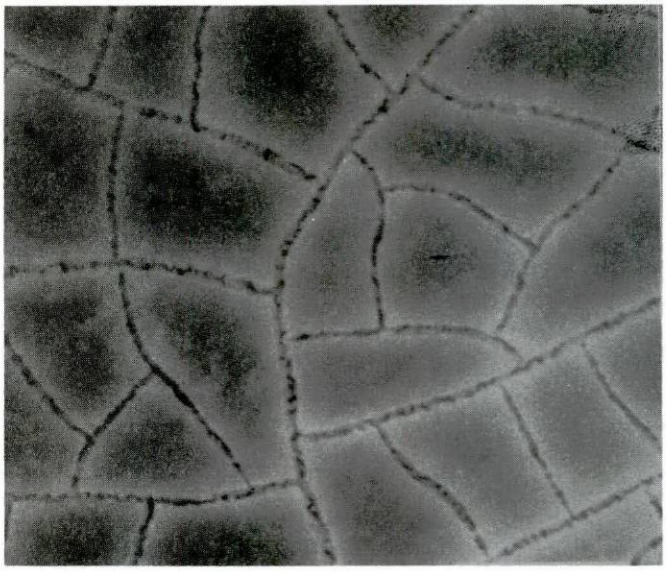


Fig. 4 Scanning electron micrograph, black chromate coating temperature treated at 120°C for 24 hours. (2000 X magnification)

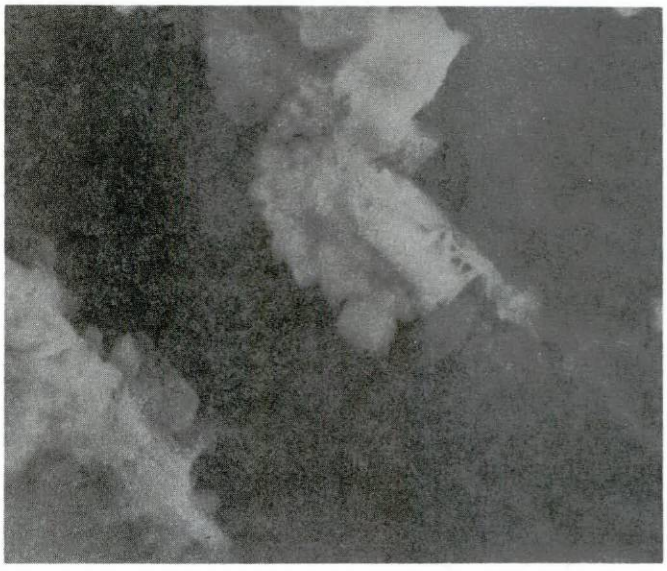


Fig. 5 Scanning electron micrograph, black chromate coating temperature treated at 120°C for 24 hours after a short salt spray test. (1600 X magnification)

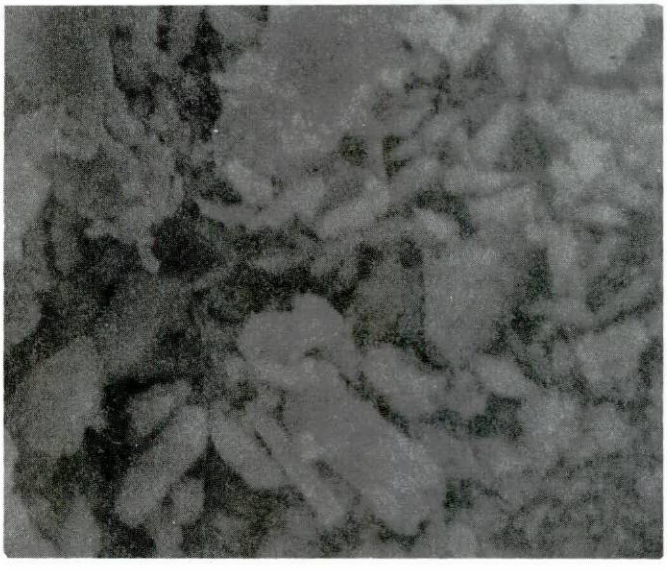


Fig. 6 Scanning electron micrograph, black chromate coating temperature treated at 120°C for 24 hours after 72 hours of SS DIN 50 021. (1600 X magnification)

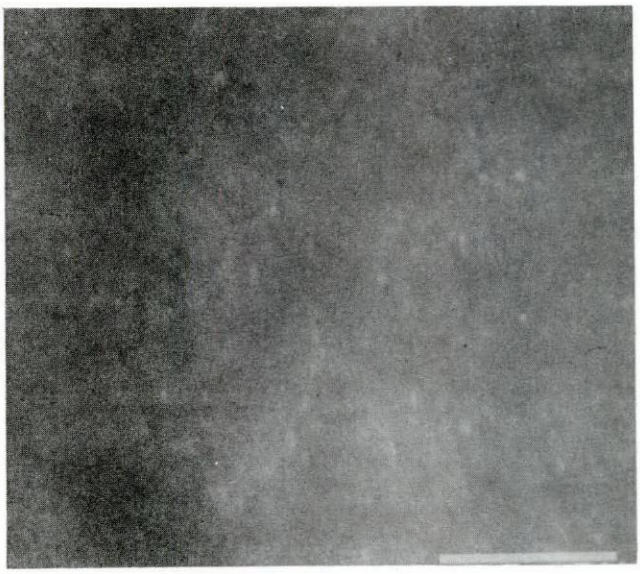


Fig. 7 Scanning electron micrograph, black chromate coating sealed and dried at 80°C.
(1800 X magnification)

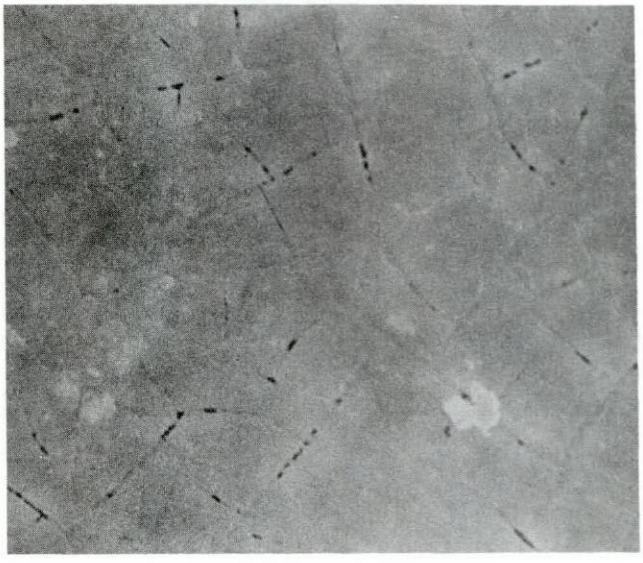


Fig. 8 Scanning electron micrograph, black chromate coating sealed and temperature treated at 120°C for 24 hours and subjected to 72 hours salt spray test.
(1600 X magnification)

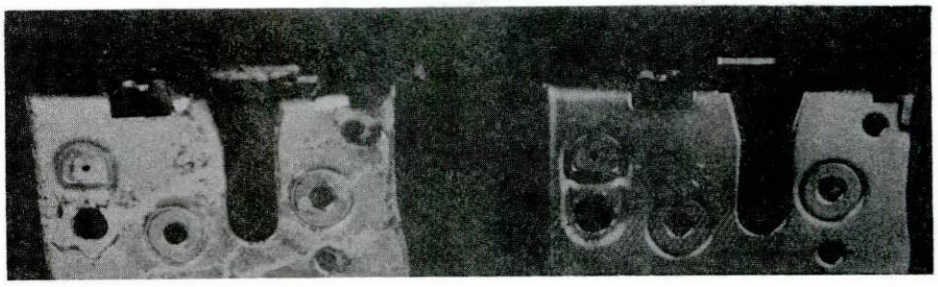


Fig. 9 Door lock plates with cyanide zinc (10-12 μm thick) and blue chromate after 120 hours of salt spray. Part on right has simple resin film.

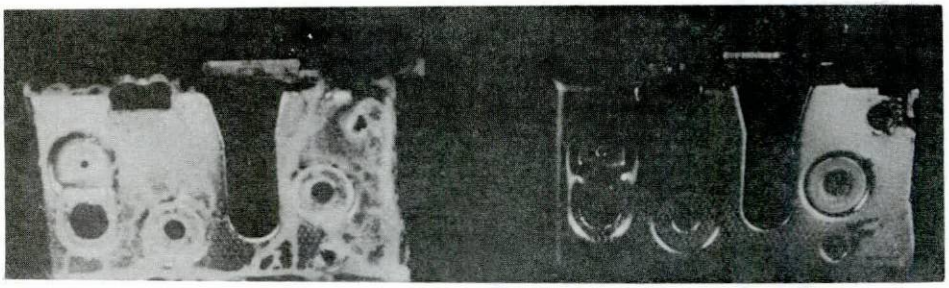


Fig. 10 Similar to Figure 9, yellow chromate, after 500 hours salt spray.

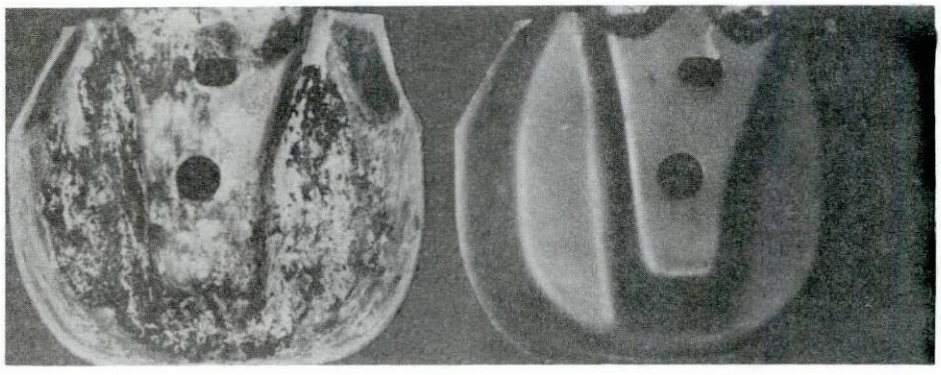


Fig. 11 Production parts without and with resin treatment after 700 hours salt spray.

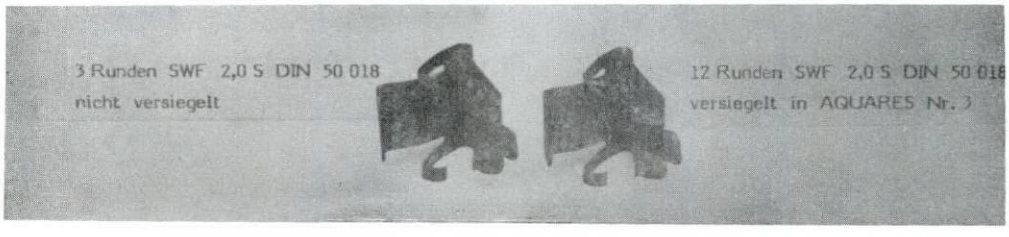


Fig. 12 Spring assemblies subjected to industrial atmosphere test SWF 2.0 DIN 50 018. Photograph on left indicates failure after 3 cycles for chromated zinc, whereas right photo shows effect of simple resin treatment after 12 cycles.

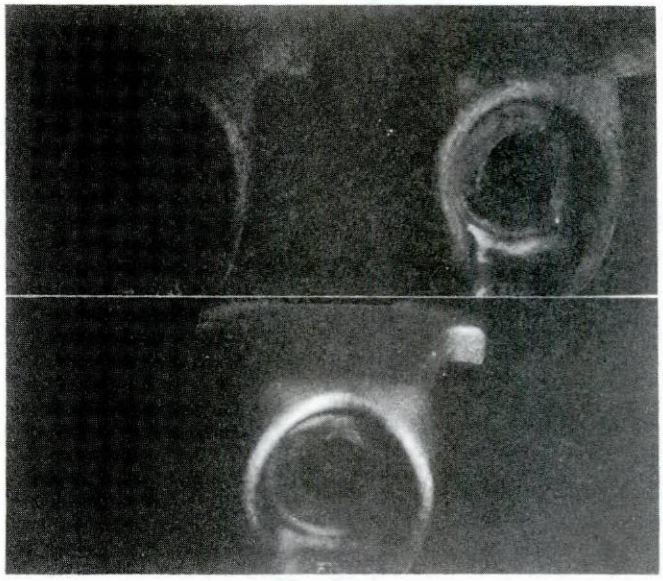


Fig. 13 Cast iron parts with blue chromate after 4 cycles of industrial atmosphere test. Top left shows severe failure without post treatment, top right shows improvement with low solids (< 1%) post-treatment and lower photo demonstrates benefit of treatment.

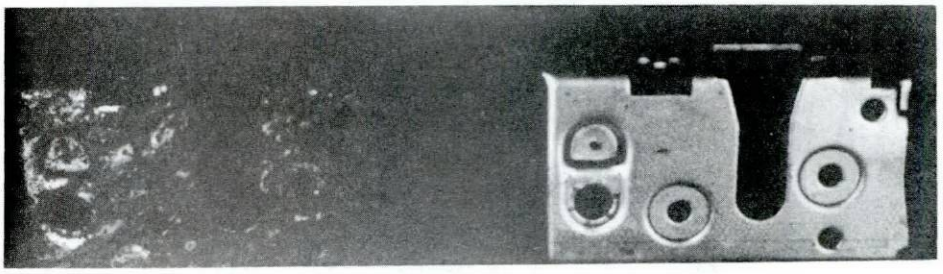


Fig. 14 Bare steel door lock plates without and with combined post-treatment after 24 hours salt spray.

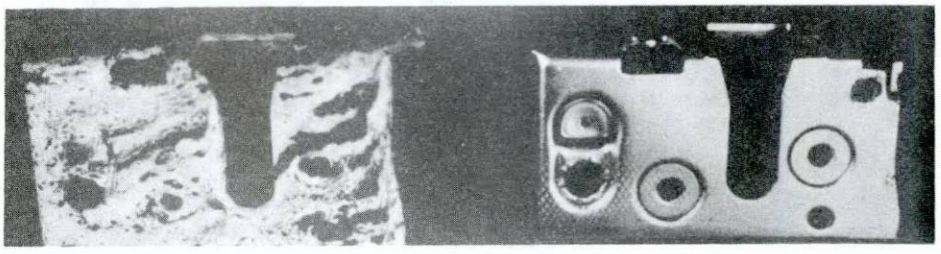


Fig. 15 As Fig. 14, cyanide zinc (10-12 µm thick) after 400 hours salt spray. Resin baked at 140°C.

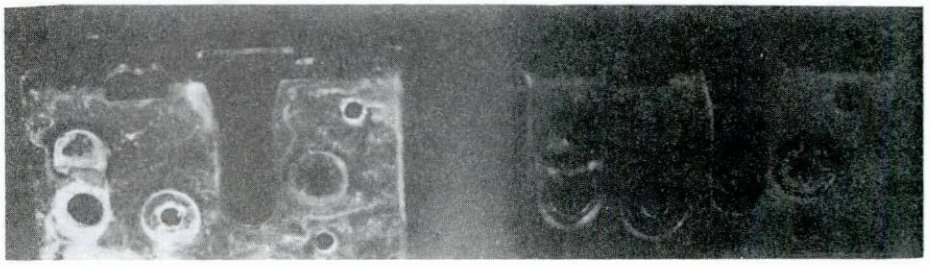


Fig. 16 As Fig. 15 with black chromate, baked at 100°C.

C-7

General Interest Session C

An Approach Based on Similiarity Rule to the Engineering Scale-up of A Continuous Electro-plating Line

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An Approach Based on Similarity Rule to the Engineering Scale-up of a Continuous Electroplating Line

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ABSTRACT

Flow control plays a decisive role in industrial electrolytic alloy-plating. Interest in developing an electrogalvanizing line, which assures uniform alloy-plating quality at high current density and high-speed operation, has stimulated this investigation. Experiments have been conducted utilizing a high-speed pilot-line and a hydrodynamic model with a moving endless strip. It is shown that alloy-plating behaviour at a continuous plating cell with fluid injection can be predicted quantitatively through the use of empirical correlations of dimensionless parameters.

1. INTRODUCTION

Electrolytic zinc-based alloy-plated steel sheets, such as Zn-Ni, Zn-Fe and so forth, have been recently developed and also supplied to the market for automobile body applications in Japan. Practical interest of this work lies in the development of a versatile and efficient electrogalvanizing line which can provide various alloy-plated products of the highest quality at high current density and high speed operations. Furthermore, it also presents features of fundamental scale-up technique for a continuous electroplating line.

Many experimental studies have been reported about the major influence of fluid flow on the electrodeposition of zinc-based alloy-plating, utilizing a flow-channel cell (Ref. 1, 2) or a rotating cylinder electrode system (Ref. 3). Much less is, however, known about the availability of process data obtained from beaker-scale laboratory experiments for scale-up and process design of commercial size electroplating line (Ref. 15). A scale-up technique based on similarity rule is advanced in the present investigation, in order to provide an approximation method capable of predicting alloy-plating behaviour in a continuous electrogalvanizing line.

2. EXPERIMENTAL

(1) Measurement of Fluid Velocity Field

All the measurements were made in a hydrodynamic model with a moving endless strip, which is installed in Hiroshima Technical Institute of Mitsubishi Heavy Industries, Ltd. Its geometric dimensions were identical to those of a

plating cell of the pilot-line for electrolytic alloy-plating.

First, macroscopic flow pattern in the model cell was investigated through the use of tufts method on a moving strip and in addition red dye injection method, in order to describe the flow field qualitatively.

Secondly, velocity profiles between a dummy anode-plate and a moving strip at various streamwise and spanwise stations were measured using pressure probes and also hot wire probes.

(2) Electrolysis Apparatus and Procedure

The experiments were performed galvanostatically in a flow system containing a rectangular flow channel cell, in which interchangeable electrolyte injection angles were employed. Alloy composition of deposits along the streamwise location of cathode was measured. Trace metal cations were added to the solution to examine the mass transfer rates varying with streamwise position of cathode steel sheet, along the line of Winand et al. (Ref. 4).

(3) Full-sized Pilot-Line Operations for Alloy-Plating

Electrodeposition of alloys were made in a continuous high-speed pilot-line varying line speed, fluid injection direction &/or velocity at various current densities, whose dimensions are comparable to those of a commercial size plant except for the strip width. It is located in Central Research Laboratories of Sumitomo Metal Industries, Ltd.

3. RESULTS and DISCUSSION

(1) Electrolysis in Flow-Channel Cells

The results of Zn-Ni electrodeposition in rectangular flow-channel cells varying electrode separation and solution flow rate clearly show that Ni content in deposits is a function of Reynolds number under given plating operation conditions, whose representative length is equal to the hydrodynamic equivalent diameter calculated from electrode separation gap, as is seen in Fig. 1 and Fig. 2.

It is known that the mass transfer entry length for a parallel plate electrochemical reactor in turbulent flow is considerably short (Ref. 5), even when flow separation exists at the sharp-edged inlet (Ref. 6). In case a jet of electrolyte issued from a nozzle incidents on a cathode at an inclined angle, it would be expected that mass transfer rate should depend on the distance from the stagnation point in contrast to the turbulent flow case in parallel plate reactors (Ref. 7, 8, 9). As shown in Fig. 3, results of Zn-Ni alloy-plating in a flow cell with variable injection angles are relevant to the explanation of the characteristics of wall-jet flow. It is suggested that a downstream transition of velocity profile from wall-jet flow to Poiseuille (pipe) flow occurs gradually.

Fig. 4 shows how the Ni content depended on overall rate constant $\bar{k}$ of the trace metal ion added, regardless of flow systems involved. It would imply that an empirical correlation for electrolytic alloy-plating may be obtained in terms of dimensionless parameters. Namely, any dimensionless quantity Q concerning alloy-plating, Ni content for instance, is given by the following dimensionless expressions.

$$Q = \Phi\ (Sh) \qquad [1]$$

Sherwood number is expressed by equation

$$Sh = \psi(Re,\ Sc) \qquad [2]$$

where local Reynolds number is

$$Re_{\tilde{u}} = \zeta(\tilde{u}(\xi),\ d_e) \qquad [3]$$

Here $\xi = x/d_e$ denotes dimensionless distance.

Simultaneous hydrogen evolution at the cathode exerts a great influence on electrolytic alloy-deposition by both rising the pH value in the vicinity of the cathode and promoting mass transfer in the concentration boundary layer. Several investigators have observed a marked enhancement of mass transfer at gas-evolving electrodes (Ref. 4, 10, 11, 12). Results obtained from codeposition of trace species with Fe-Zn alloy-plating varying solution flow rate is shown in Fig. 5. The overall heterogeneous rate constant $\bar{k}$ is given by,

$$\frac{1}{\bar{k}} = \frac{1}{k_R} + \frac{1}{k_{MT}} \qquad [4]$$

, where $\bar{k}$ is determined by measurements.

$$\bar{k} = \frac{N}{C_\infty} \qquad [5]$$

To account for the gas-bubble stirring effect, enhancement factor ε is introduced to the empirical dimensionless relationship (Ref. 13) for the parallel plate electrodes in turbulent flow. The mass transfer coefficient can be written as

$$k_{MT} = 0.023\ \varepsilon \left(\frac{D}{de}\right) Re^{0.8} Sc^{1/3} \qquad [6]$$

It was found that values 3.0×10^{-2} m/min. and 4.1 for reaction rate constant k_R and bubble enhancement factor ε respectively, give a good fit for the data shown in Fig. 5.

(2) Velocity Distributions in Electrode Separation

The variation of the velocity profiles between a dummy anode plate and a moving strip was measured over the length and width of the model. It is seen from Fig. 6 that the velocity profile resembles that of the modified Couette flow with the superposition of fluid injection corresponding to its direction and velocity of incidence.

In order to obtain dimensionless correlation in this system, its representative velocity should be defined properly. Since velocity distribution in the vicinity of a cathode strip intensively affects the electrodeposition phenomena, a relative velocity of solution in a coordinate system with the

moving strip is employed to characterize this complicated system as a first approximation. Neglecting the flow velocity component normal to the cathode, relative velocity can be calculated from the measured velocity profile according to the following equation, as indicated in Fig. 7.

$$U = \frac{2}{h}\{ \int_0^{y_{max}} U(y)dy + U_{max}\left(\frac{h}{2} - y_{max}\right)\} \qquad [7]$$

Local Reynolds numbers were obtained for a particular cell configuration and a specific flow injection mode, in this manner, which are tabulated in Table 1. For this example, distribution of local Reynolds number in the longitudinal direction along the moving strip was non-uniform. This case, which may be unfavourable to alloy-plating, is chosen to put emphasis on the importance of careful cell design for uniform mass transfer.

(3) Electrolytic Pilot-line Experiments

Extensive experiments have been performed using the pilot-line with a variety of operation conditions, such as line-speed, fluid injection mode (direction &/or velocity), type of nozzles, plating bath composition, pH and temperature, current density, cell type (i.e. vertical and horizontal cells), geometric configurations in the cell, and etc. One of the results of Zn-Ni alloy-deposition is depicted in Table 1. Fe-Zn alloy-plating was also carried out with the addition of trace indicator metal ion in order to examine the overall mass transfer characteristics of the cell. Fig. 8 illustrates the comparison of pilot-line data with pertinent calculated values.

Rigorously, similarity does not exist between the flow-channel cell in our laboratory room and the large-sized pilot-line. Thus, relaxation of model rules (Ref. 14) may well be introduced into the physical picture described in Fig. 9 through the geometric sectioning of a plating cell of the pilot-line into a series of small parallel plate reactors, assuming current density, electrolyte temperature, bath pH and composition are uniform. For each unit cell in Fig. 9, the Buckingham pi theorem can be written as

$$Q_x = \Phi(Sh_x) \qquad [8]$$

, and local Sherwood number is given by

$$Sh_x = \psi(Re_x, Sc) \qquad [9]$$

These functions Φ and ψ can be determined experimentally by use of flow-channel cells. So that, overall dimensionless quantity can be estimated by integration with respect to x.

$$\bar{Q} = \frac{1}{L}\int_0^L \Phi(Sh_x)dx \qquad [10]$$

by substitution from eqn. [9] into eqn. [10],

$$\bar{Q} = \frac{1}{L}\int_0^L \Phi[\psi(Re_x, Sc)]dx \qquad [11]$$

Moreover, average mass transfer coefficient is determined from

$$\bar{k}_{MT} = \frac{D}{d_e L} \int_0^L \psi(Re_x, Sc)dx \qquad [12]$$

The data of Table 1 are intended to show the comparison of observed Ni % in deposit with that calculated in view of the foregoing procedure. The results obtained from the pilot-line agreed approximately with those predicted.

Table 1 Comparison of experimental observation of the pilot-line with calculated values based on Eq. [8] - [12]

Line Speed	Re_x at measurement ports #1	#2	#3	#4	Ni % avg. calc.	Ni % obs.
50	2.5×10^4	2.0×10^4	4.4×10^4	6.9×10^4	—	—
m/min.	(27.5)	(31.5)	(14.0)	(11.5)	21.1	18.5
100	4.8×10^4	3.8×10^4	6.6×10^4	9.3×10^4	—	—
m/min.	(14.0)	(19.0)	(11.5)	(10.7)	13.8	14.8

Substituting value 2.1 for ε into Eqn. [6], the local k_{MT} can be calculated using local Reynolds numbers in Table 1. Taking the average of the local mass transfer coefficients and also by substitution of $k_R = 3.0 \times 10^{-2}$ m/min., calculated values for overall rate constant $\bar{k}$ are obtained, as shown in Fig. 8, and are in agreement with the observed results. Differences in gas-bubble enhancement factors between the flow-channel cell and the pilot-line may be attributed to the variation of convective flow induced by moving bubbles along the cathode (Ref. 12), yet the physical features of gas-bubble enhancement factor have to be clarified in future studies. It seems likely that the prevalence of the universal velocity distribution adjacent to the cathode at high Re and Sc numbers have furnished the basis of the foregoing scale-up procedure.

4. CONCLUSIONS

A generalized scale-up method of a continuous electroplating line with the help of empirical correlations of appropriate dimensionless numbers has been obtained. The characteristic quantities for this system are the so-called hydrodynamic equivalent diameter, d_e and in addition the mean relative flow velocity, $\tilde{U}$ in a coordinate system with the movement of a strip (i.e. Eqn. [7]).

Due consideration should be given first to a number of engineering design factors, such as anode length, separating gap, fluid injection and its control, number of anodes and solution injection ports per each cell, cell configuration, cell type (vertical v.s. horizontal), number of cells and etc., so as to facilitate both high and uniform mass transfer and current distribution in the cell, for attaining uniform alloy plating quality throughout the coil.

NOTATION

$\bar{k}$	overall heterogeneous rate constant
k_R	electrode surface reaction rate constant
k_{MT}	mass transfer coefficient
C_∞	bulk concentration
N	mass flux
x, y, z	distance
d_e	hydrodynamic equivalent diameter
D	diffusion coefficient
U(y)	relative velocity
$\tilde{U}$	mean relative velocity
$U_{max.}$	maximum relative velocity
$Y_{max.}$	value of y when $U = U_{max.}$
h	electrode separation gap
L	electrode length
Q_x	a pi number concerning electrodeposits
$\bar{Q}$	average of Q_x
Re_x, Re	local and average Reynolds number
Sh_x, Sh	local and average sherwood number
Sc	Schmidt number
ξ	x/de dimensionless distance
Φ, ψ, ζ	dimensionless correlation functions
ε	gas-bubble enhancement factor

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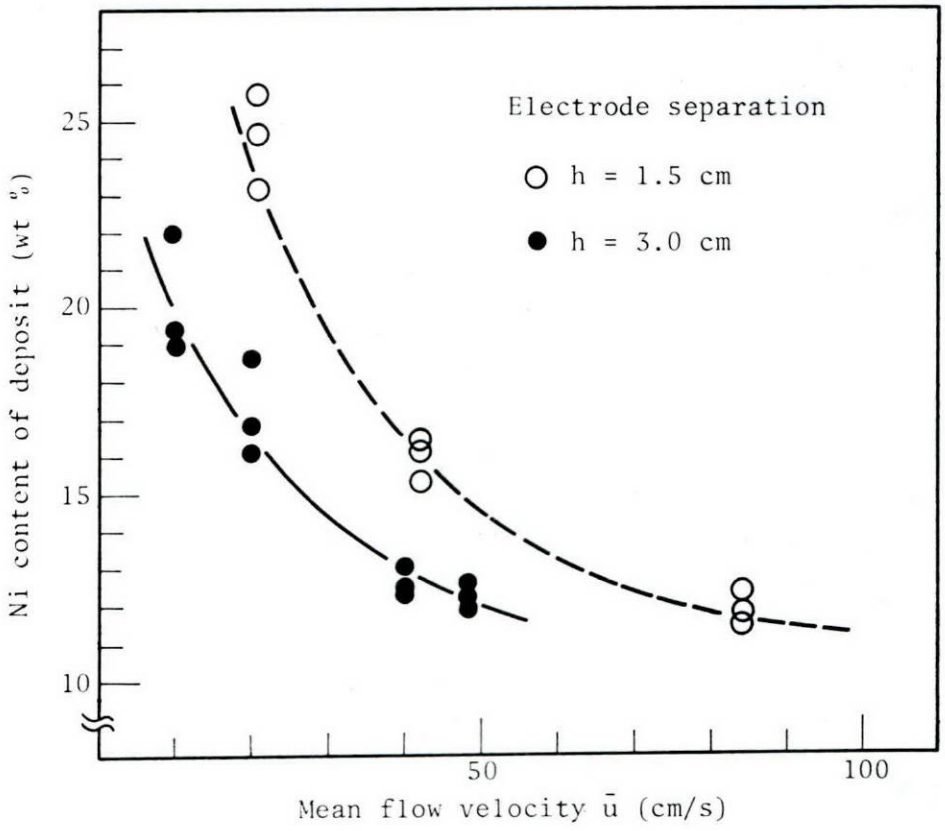


Fig. 1 Effect of electrode separation gap on Ni content in deposit.

Plating conditions:

$[Ni^{2+}]$ = 1 M, $[Ni^{2+}]/[Zn^{2-}] \simeq 2.7$

pH 1.9, Temp. 60°C

Current density 80 A/dm^2

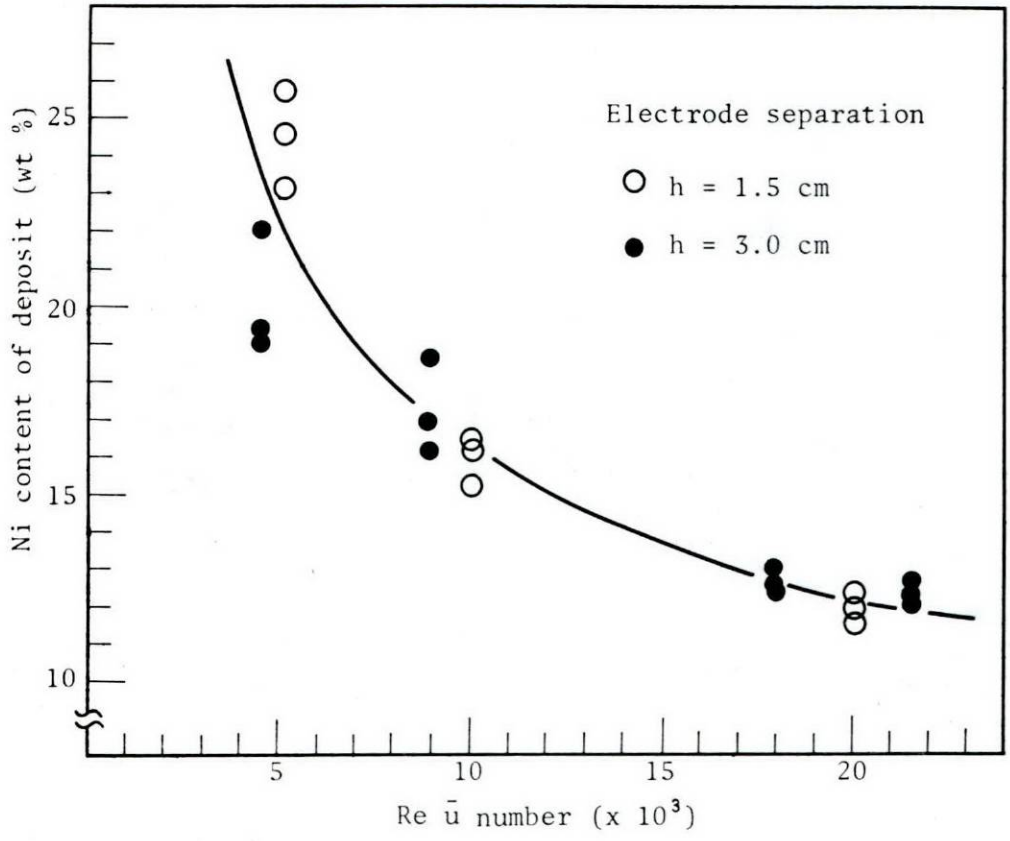


Fig. 2 Influence of Reynolds number on Ni content in deposit.

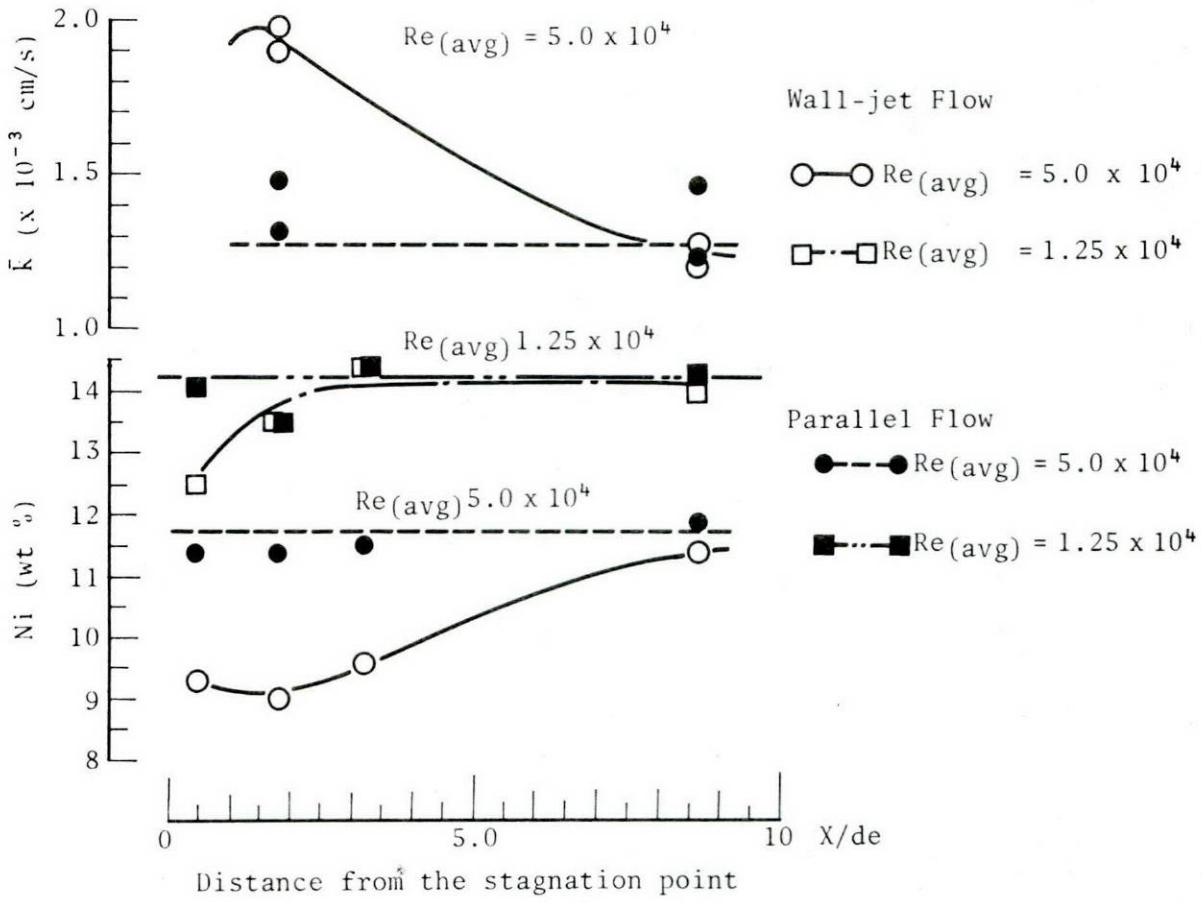


Fig. 3 Comparison of electrodeposition characteristics between wall-jet flow and parallel flow.

Plating conditions:

$[Ni^{2+}]$ = 1 M, $[Ni^{2+}]/[Zn^{2+}] \simeq 2.5$

pH 1.9, Temp. 60°C

Current density 80 A/dm^2

Incident angle 45°

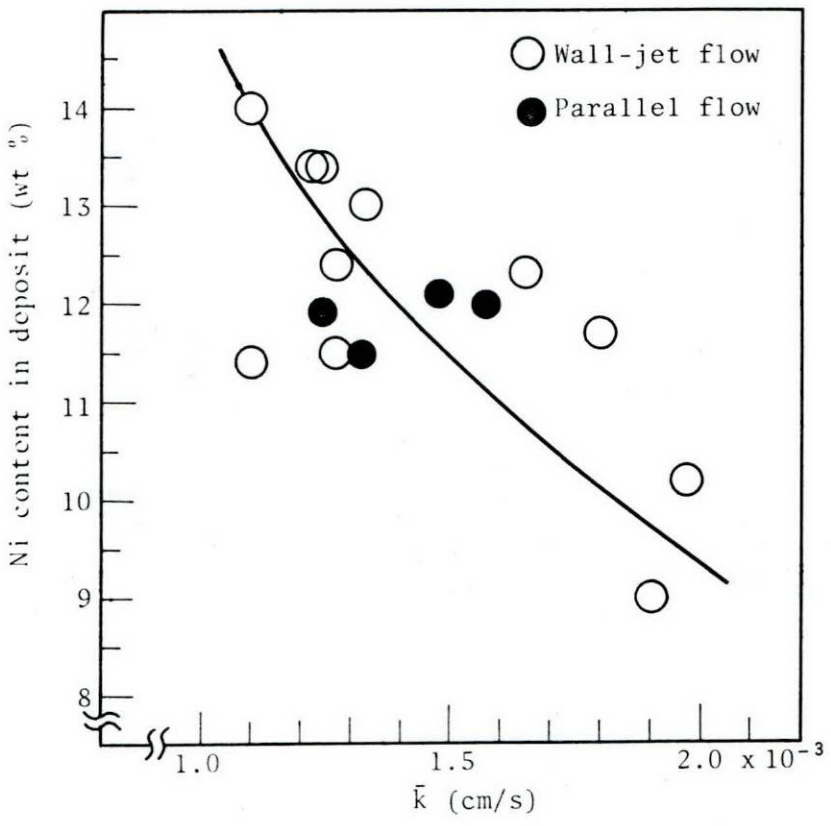


Fig. 4 Variation of Ni content in deposits with overall rate constant $\bar{k}$ of the trace indicator ion.

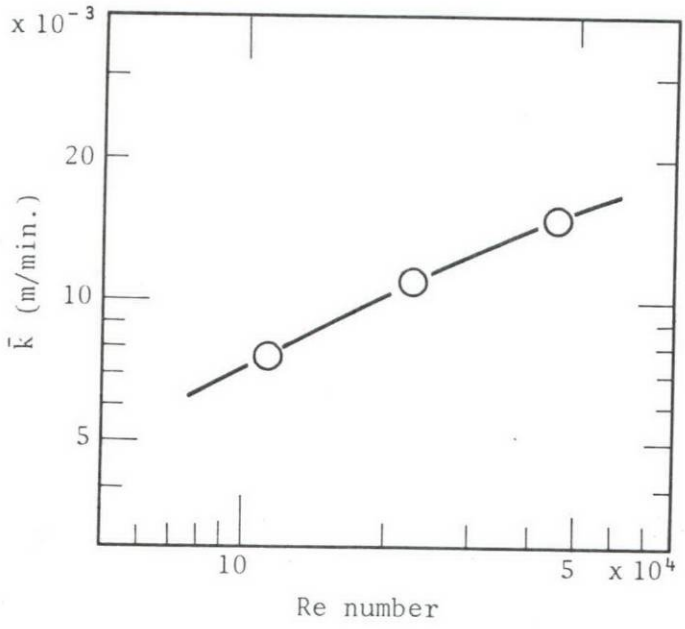


Fig. 5 Overall rate constant $\bar{k}$ of the minor indicator ion as a function of Reynolds number

Plating conditions:

$[Fe^{2+}]$ = 0.9 M with the addition of small quantity of $[Zn^{2+}]$

pH 1.8, Temp. 50°C

Current density 80 A/dm^2

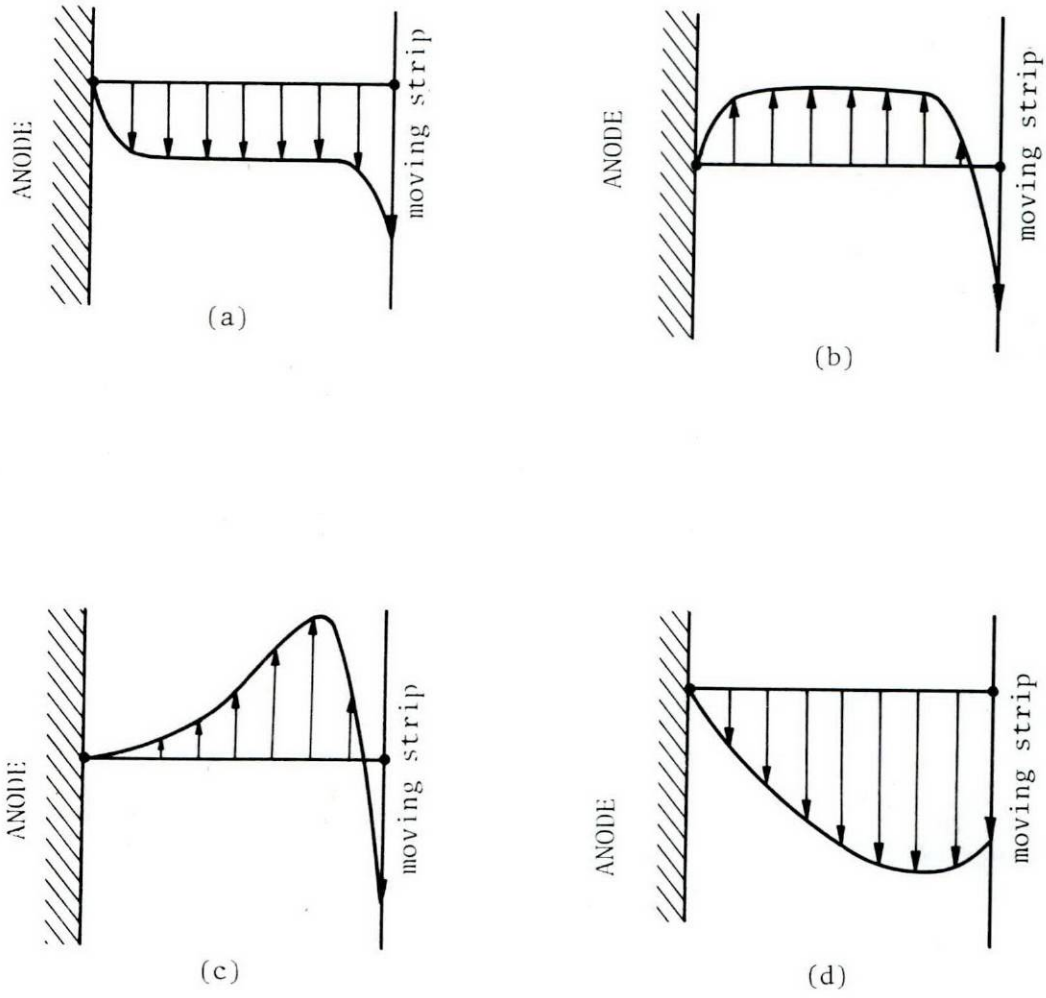


Fig. 6 Schematic representation of flow in the electrode separation of a continuous electroplating cell.

(a) without fluid injection.

(b) with counter-flow injection

(c) with wall jet flow injection

(d) with co-flow injection.

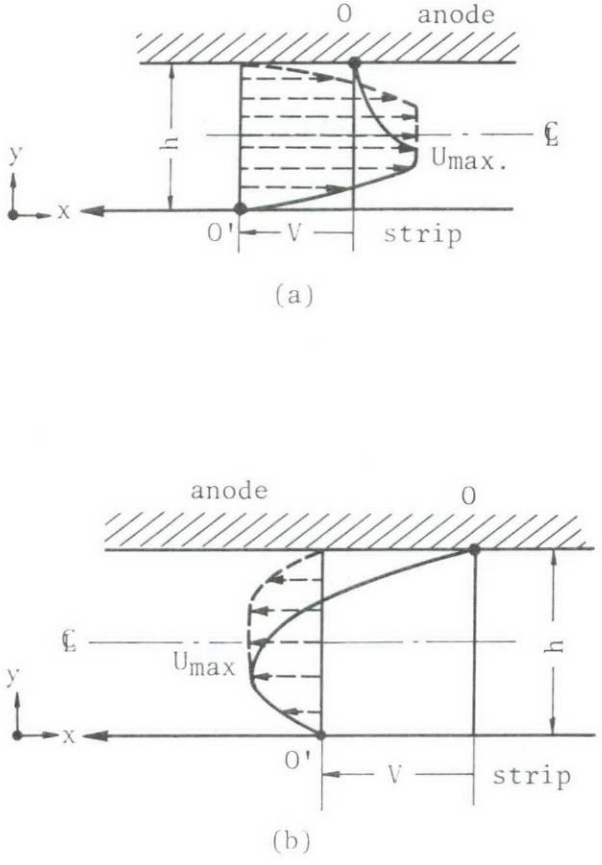


Fig. 7 Relative velocity, U, of electrolyte as a characteristic velocity for this system.
(a) Counter and/or wall jet flow injection
(b) Co-flow injection

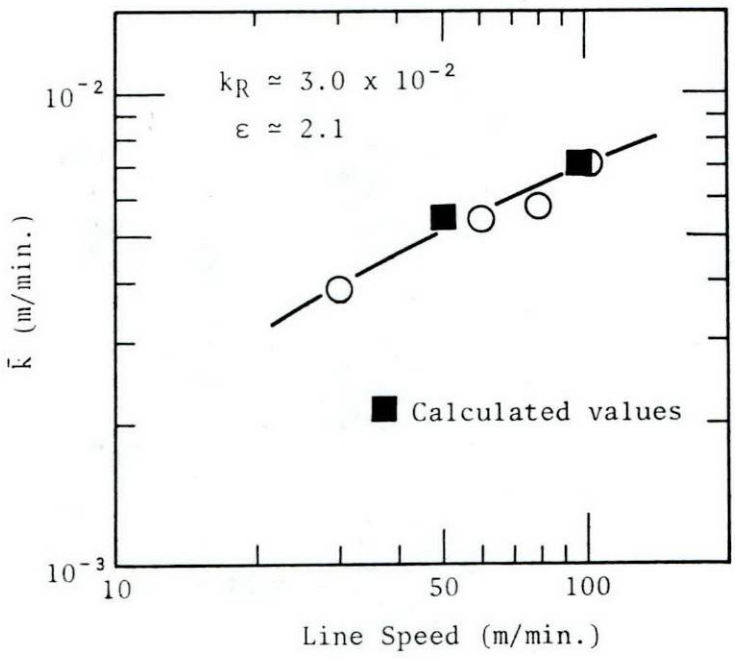


Fig. 8 Variation of the overall rate constant $\bar{k}$ for a tracer ion with the velocity of a moving strip.

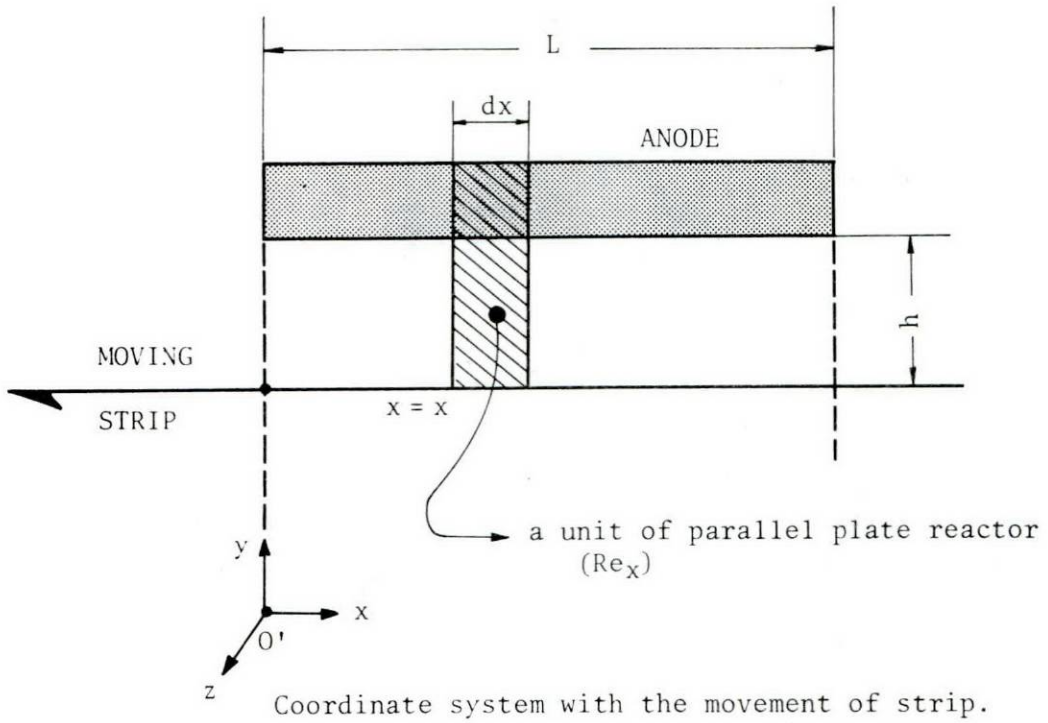


Fig. 9 Relaxation of model rules through geometric sectioning of a practical plating cell in the pilot line.


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