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Table of Contents

Research / Session A

Interdiffusion of Electrodeposits with Copper Substrates **A-1**
Suryanarayana Kaja, Dr. Howard W. Pickering and Dr. William Bitler
The Pennsylvania State University
University Park, PA

Deposition of Nickel Chromium Alloys **A-2**
Dr. David S. Lashmore
National Bureau of Standards
Washington, DC

Tensile Testing of Electrodeposits **A-3**
M. Parente and Dr. Rolf Weil
Stevens Institute of Technology
Hoboken, NJ

Hazardous Sludge Reduction **A-4**
Lt. James R. Aldrich, USAF
Tyndall AFB, FL
Charles G. Roberts and Edward D. Handel
Centec Corp.
Reston, VA

Influence of Magnetic Fields on the Electrodeposition of Chromium **A-5**
Dr. John Dash, Ru-Tsin Chen and K. Housen
Portland State University
Portland, OR

Plating on Titanium: Process and Applications **A-6**
Dr. Martin Thoma
MTU Motoren-und Turbinen Union
Munchen GmbH
Munchen, W. Germany

Management / Session B

Solving Alcohol and Drug Abuse Problems in the Work Place **B-1**
John R. Lewis
The Christ Hospital
Cincinnati, OH

Current Trends in Labor Relations **B-2**
Earl C. Leonhardt Jr.
Federal Mediation and Conciliation Service
Cincinnati, OH

Pricing: A Practical Approach **B-3**
John Thomas
Dayton Rust Proof
Dayton, OH

Personnel Techniques of a Job Shop Plater **B-4**
Milton F. Stevenson Sr.
Anoplate Corp.
Syracuse, NY

Tax Saving Tips for the Individual AES Member **B-5**
Daniel Leonhardt
Leonhardt Plating Co.
Cincinnati, OH

Environmental I / Session C

Process Modifications: The First Step in Wastewater Treatment **C-1**
Robert S. Capaccio, P.E.
Mabbett, Capaccio & Associates, Inc.
Cambridge, MA

What's New with Reverse Osmosis in Metal Finishing Waste Treatment **C-2**
Peter S. Cartwright
C_3 International
Minneapolis, MN

BPT to BAT **C-3**
Lawrence A. Greenberg
Post, Buckley, Schuh & Jernigan, Inc.
Orlando, FL

The Recovery and Treatment of Metals from Spent Electroless Processing Solutions **C-4**
Kevin Warheit
Lancy International, Inc.
Zelienople, PA

Electrochemical Removal of Heavy Metals from Wastewater **C-5**
Gregg Daniel Horner, P.E.
Wells Engineers, Inc.
Omaha, NE
Joseph G. Duffey, P.E.
Andco Environmental Processes, Inc.
Buffalo, NY

Copper Removal from Metal Finishing Waste Solutions **C-6**
John V. Peck and Dr. Rebecca M. Spearot
Udylite/Sel-Rex Plating Systems
Occidental Chemical Corp.
Warren, MI

Electronics I / Session D

Role of Cobalt in Acid Gold Plating **D-1**
Daniel Becker and Alan Blair
Engelhard Industries
East Newark, NJ

Engineering Grade Thermoplastics & Additive Plating **D-2**
David C. Frisch
PCK Technology Div.
Kollmorgen Corp.
Melville, NY

Tensile Testing of Printed Circuit Board Elements D-3
M. Parente and Dr. Rolf Weil
Stevens Institute of Technology
Hoboken, NJ
Dr. Milan Paunovic
PCK Technology Div.
Kollmorgen Corp.
Melville, NY

Automatic PCB Plating Machinery D-4
Joseph N. Simonin
International Automated Systems, Inc.
Corydon, IN

Gold Distribution on Printed Circuit Board Edge Connectors D-5
Dr. Paul Watson
Plessey Research (Caswell) Ltd
Towcester Northants, U.K.

New Procedures for Predicting Solderability Performance of Electroplated Tin Deposits D-6
William T. Hobson
Naval Avionics Center
Indianapolis, IN
Bance F. Hom
Indy Electronics Inc.
Manteca, CA

Environmental II / Session E

A New Industrial Wastewater Treatment Method for Removal of Multiple Contaminants E-1
Barbara Monick and Alexander Blake
Sweetwater Technologies Corp.
Smithtown, NY

Successful Electrodialysis Applications E-2
Richard J. Heller
The Lea Mfg. Co.
Waterbury, CT

Occupational Health and Safety Considerations for Electroplaters E-3
Arthur N. Mabbett, P.E.
Mabbett, Capaccio & Associates, Inc.
Cambridge, MA

Recovery Methods Which Will Meet Future Hazardous Waste Regulations E-4
Alfred B. Craig Jr.
U.S. EPA
Cincinnati, OH

Electronics II / Session F

A New Process for Recovering Gold as Potassium Gold Cyanide F-1
Dr. Henry H. Law and N. E. Gabriel
Bell Labs.
Murray Hill, NJ

Analysis of Organic Components in Copper Plating Baths by Liquid Chromatography F-2
David A. Zatko and Walter O. Freitag
Sperry Univac
Blue Bell, PA

Multi-Test Capability of Plating Parameters Using a Continuous Flow Analyzer F-3
Aldo Conetta and John DiLiddo
Technicon Industrial Systems
Tarrytown, NY

Analysis of Additives in Acid Copper Baths by Cyclic Voltammetry F-4
Walter O. Freitag and Michael Manning
Sperry Univac
Blue Bell, PA

Differential Pulse Polarography of Organic Additives in Acid Tin and Bright Tin-Lead Plating Baths F-5
Robert L. Summers
AMP Inc.
Winston-Salem, NC

The Use of Cyclic Voltammetric Stripping for Determination of Additive Concentration in Copper Plating Baths F-6
Gerry Bush
UPA Technology, Inc.
Syosset, NY

Organic & Chemical Pretreatment / Session G

Chemical Pretreatment of Steel for Water-Borne Coatings G-1
Joseph V. Otrhalek, P.E., Dr. S. M. Sokalski and J. J. McGovern
Detrex Chemical Industries, Inc.
Redford, MI

Ecological/Energy Impact on Phosphate Coatings G-2
Dr. James W. Davis
Amchem Products, Inc.
Ambler, PA

Compliance with Solvent Emission Regulations Without Change in Resins, Pigments or Basic Equipment G-3
Dr. George E. F. Brewer
Coating Consultants
Birmingham, MI

Considerations When Converting to Water-Borne Coatings for Dip, Flowcoat and Spray Applications G-4
C. E. Thomas
DeSoto Inc.
Des Plaines, IL

An Evaluation of Autodeposition G-5
Mary Jo P. Johnson
Delco Moraine Div., GMC
Dayton, OH

Automatic Control for Prepaint Systems G-6
David Boyd and William Roberts
Diversey Wyandotte Corp.
Wyandotte, MI

Electroless Plating / Session H

The Relationship Between Stress and Adhesion of Electroless Nickel-Phosphorus Deposits on Zincated Aluminum H-1
Glen O. Mallory
Allied-Kelite Div.
Witco Chemical Corp.
Los Angeles, CA

Performance of Electroless Deposits for EMI/RFI Shielding Applications H-2
Gerald Krulik and John Waggoner
Enthone, Inc.
Bridgeview, IL

Using Computer Technology in Electroless Nickel H-3
Phillip D. Stapleton
Stapleton Company
Long Beach, CA

Electroless Gold H-4
Dr. Raichur Narayan
TRW Connectors
Elk Grove Village, IL

Electroless Nickel for Stress Corrosion Protection in Power and Petrochemical Plants H-5
Gabrielle Salvago and D. Sinigaglia
Dipartimento di Chimica Fisica
Politecnico di Milano
Milano, Italy

Diverse Applications for Electroless Tin H-6
Jack Fellman
CuTech, Inc.
Hatfield, PA

General Interest / Session I

The Role of Boric Acid in Dilute Chromic Acid Plating Baths I-1
James P. Hoare
General Motors Corp.
Research Labs.
Warren, MI

Cleaning, Descaling, Passivation, and Inspection of Stainless Steels I-2
Lee H. Wilbur
Western Gear Corp.
Jamestown, ND

Trivalent Chromium: A Commercially Viable Alternative I-3
T. W. Tomaszewski and R. E. Fischer
Udylite/Sel-Rex Plating Systems
OCC
Warren, MI

Zinc/Graphite: A Potential Substitute for Anti-Galling Cadmium I-4
William A. Donakowski
Ford Motor Co.
Redford Township, MI
J. R. Morgan
Benchmark, Inc.
Wyandotte, MI

Analysis of Plating Baths by Differential Pulse Polarography I-5
Dr. John J. Reiss, Leon Ashley and Saroj K. Bohra
IBM Instruments Inc.
Danbury, CT

Rapid Analysis and Troubleshooting of Gold, Copper and Nickel Plating Bath Chemistry by Ion Chromatography .. I-6
Karen K. Haak and Gregory O. Franklin
Dionex Corp.
Sunnyvale, CA

Light Metal Finishing I / Session J

The Relationship of Electrolytic Coloring to Clear Anodizing Techniques J-1
Richard W. Mahn
Reynolds Aluminum International Services, Inc.
Richmond, VA

The Production and Properties of Cobalt-Based Electrolytic Finishes J-2
Peter G. Sheasby
Alcan International Ltd.
Banbury Labs.
Banbury, Oxon, UK
W. M. Kellerman
Alcan International Ltd.
Kingston, Ontario, Canada

Electrolytic Coloring of Anodized Aluminum Using Tin Electrolytes J-3
Dr. Hans J. Goehausen
Henkel KGaA
Dusseldorf, W. Germany
Glenn C. Schoener
Amchem Products, Inc.
Ambler, PA

Electro-Coloration of Anodized Aluminum: Evolution of these Processes J-4
Michel LeGrand
Cegedur Pechinery
Montreuil-Juigne, France

Non-Electrolytic Deposition Processes / Session K

Continous Cable Processing by the Physical Vapor Deposition Technique K-1
Gerald J. Hale
Bendix Corp.
Kansas City, MO

Vacuum Processes for Hard Surface Film Deposition ... K-2
Ted Van Vorous
Van Vorous Consultants
Boulder, CO

Magnetron Sputtering K-3
Donald R. Boys
Varian Industrial Equipment Div.
Santa Clara, CA

Thermal Outgassing Behavior of Electrodeposited Black Chromium K-4
Thomas G. Beat and Wendell K. Kelley
Lawrence Livermore
National Labs.
Livermore, CA

Light Metal Finishing II / Session L

Alkaline Corrosion of Anodized Aluminum: Cause and Cure L-1
Leon E. Cohen and John A. Hook
FMC Corp.
Princeton, NJ

How to Prevent Pitting on Color Anodized Parts when Using Titanium Anodizing Racks L-2
Fred Henschel
Vulcanium Corp.
Northbrook, IL

Chromate Conversion Coating Processes of the Conventional and Nonconventional Types for Nonferrous Metals L-3
W. J. Wittke
Oakite Products, Inc.
Berkeley Heights, NJ

Electroforming / Session M

Flexible Circuits Manufactured by an Electroforming Process M-1
Glenn R. Schaer
Batelle Columbus Labs.
Columbus, OH

Precious Metal Electroformed Reflectors M-2
David Epner
Cohan-Epner Co.
Brooklyn, NY

Electroformed Nickel, "The Modern Tool" M-3
Rich Edwards
Electroformed Nickel Products
Brea, CA

Electroformed Boiling Surfaces M-4
Clarence Albertson, George Nichols and John Rasmussen
Roy C. Ingersoll Research Center
Borg-Warner Corp.
Des Plaines, IL

Electroforming in Japan M-5
Osamu Nakamura and Kuniko Nishimura
The Eftech Co. Ltd.
Tokyo, Japan

A-1

Research Session A

Interdiffusion of Electrodeposits with Copper Substrates

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INTERDIFFUSION OF ELECTRODEPOSITS WITH COPPER SUBSTRATES

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This is a report on a portion of the research sponsored by AES under AES Reserach Project 50. Project 50 is concerned with those deposits of direct interest to the electronics industry i.e. principally gold and possible substitutes for gold.

Prior work under this project has concentrated on the effectiveness of various barrier materials in reducing the interdiffusion of gold with its substrate. At the conclusion of this paper some of the more recent results in this area will be reported. The major discussion, however, will center on our recent findings with regard to the interdiffusion of palladium with copper substrates. For your easy reference the palladium results will be continually compared with similar results for the nickel-copper system. Since nickel is frequently used as a barrier in the copper-gold system this will give some basis for comparing a copper palladium system with a copper-nickel barrier-gold system.

A blistering problem was encountered with the palladium electrodeposits most probably arising from hydrogen codeposited with the palladium. In view of this problem, conventional diffusion couples of wrought copper and wrought palladium were prepared and diffusion annealed at various temperatures ranging from 450°C to 900°C. The concentration profiles of these samples were determined from microprobe scans, Boltzmann-Matano analyzed and D_{chem} determined as a function of composition. An Arrhenius plot of the results showed linear behavior at low and high temperatures with the break occurring at about 750°C. See Figure 1. The composition dependence is consistent with what one would expect on the basis of the phase diagram i.e., the diffusivity decreases near the Pd rich end when the solidus temperature starts to rise appreciably.

Some qualitative observations with regard to the interdiffusion of the palladium electrodeposited on copper follow. Deposits of 1/2, 1 and 2 μm thick were diffusion annealed at temperatures ranging from 350°C to 750°C. At temperatures below 750°C the blistering of the thicker deposits, the 1 and 2 μm thick ones, was so severe that no diffusion results were obtainable Above 750°C the blistering problem disappeared. Below 750°C the thinnest samples, the 1/2 μm thick samples, were sufficiently adherent that diffusion behavior could be noted. These samples show very rapid interdiffusion. Three days at 350°C was sufficient to allow enough copper penetration of the palladium electrodeposit such that the naked eye could detect the color change in the palladium deposit. (No such color change could be detected on nickel deposits simultaneously diffusion annealed in the same capsule). Subsequent examination of the palladium electrodeposits by the transmission electro microscope (TEM) showed that the grain size of the palladium deposits was very small ∿100-500 A. Such small grain size and grain boundary diffusion

would explain the rapid penetration of copper through the palladium deposits. The effective diffusivity for these samples is much larger than the comparable data appearing in Figure 1 for wrought Pd-Cu couples.

Finally results on hexavalent chromium and semi-bright cobalt indicate that either of these would be a more effective diffusion barrier than nickel when used between copper and gold.

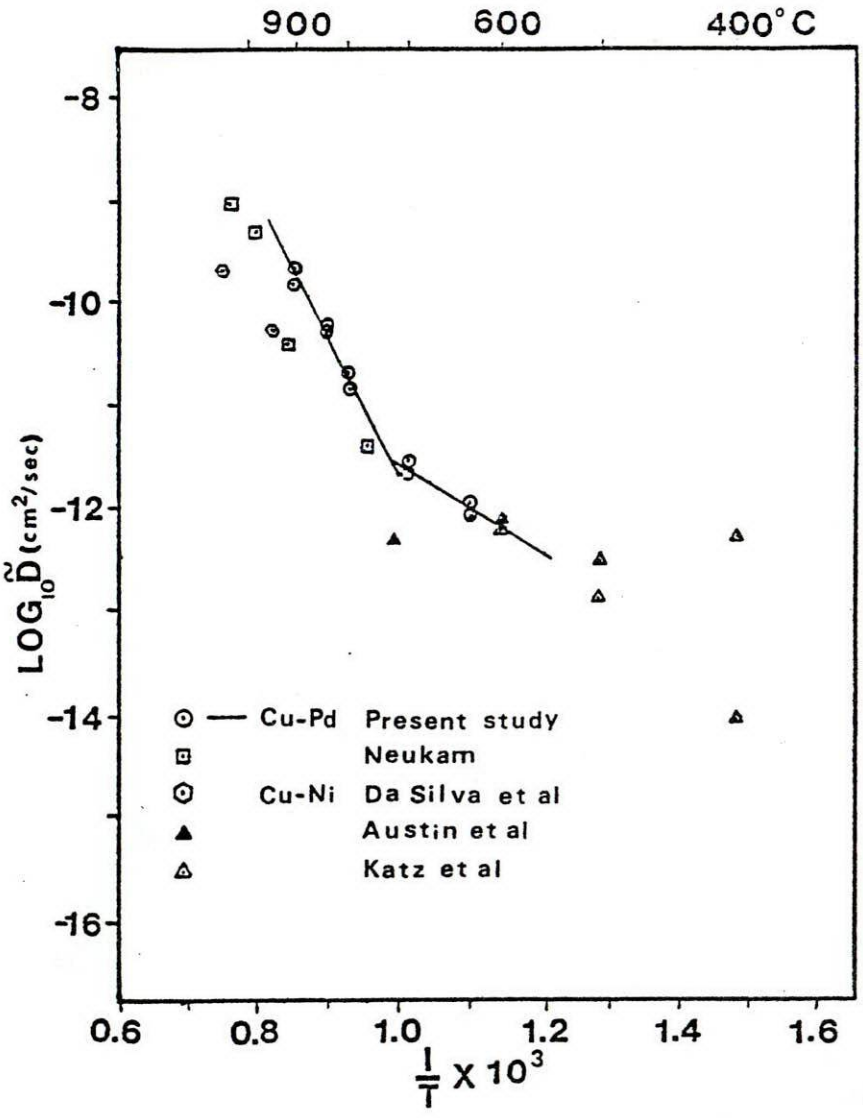

Figure 1.

Logarithm of Interdiffusivity vs. reciprocal temperature for Cu/Pd and Cu/Ni systems calculated at 50 atom percent copper, except Katz et al at 60 wt%.

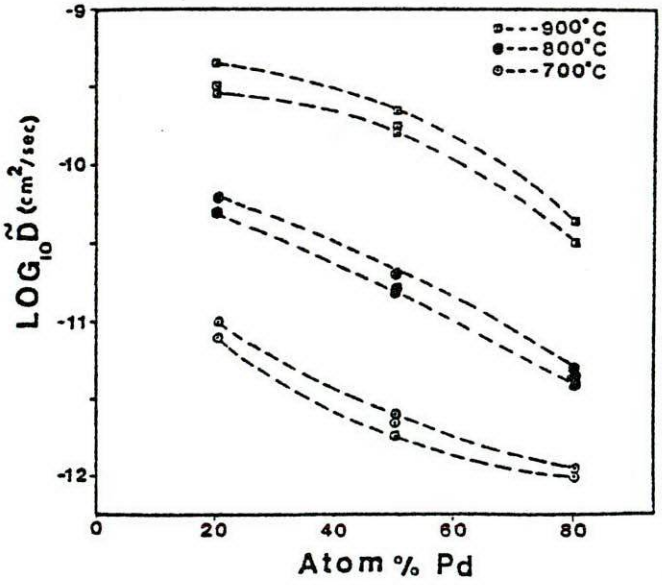

Figure 2.

Logarithm of Interdiffusivity vs. atom percent Pd for Cu/Pd system.

A-2

Research Session A

Deposition of Nickel Chromium Alloys

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DEPOSITION OF NICKEL CHROMIUM ALLOYS

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ABSTRACT

Nickel chromium alloys have been deposited from electrolytes containing the chloride salts of nickel and chromium. Coatings greater than 75 microns thick have been deposited with the chromium content controllable from about 0.1 Wt% to 60 Wt.% by appropriate choice of the deposition parameters. The surface morphology, corrosion performance and structure have been correlated with the deposition conditions. Applications of pulsed current deposition techniques have yielded improvements in surface morphology which is explained in terms of the changes in diffusion length occurring under pulsed conditions. Crystal phases were found in the coating deposited by direct current deposition which were different from those formed under pulsed current conditions. Preliminary potentiodynamic anodic polorization measurements of corrosion in both chloride and in 1 normal sulfuric acid indicate that these electrodeposited coatings may be significantly more corrosion resistant than comparable wrought alloys of similar chromium content. This unusual corrosion performance may be due to the presence of layers of strong chromium composition gradients.

INTRODUCTION

Electrodeposited coatings of nickel chromium alloys have a number of properties which would be likely to attract wide commercial interest if an appropriate deposition process existed. It has been reported by Kruger and McBee (1) for materials with chromium contents greater than about 20 Wt. % that the surface would be covered with an amorphous passive film that would be unusually resistant to corrosion. This finding has been observed for a number of stainless steels and has been discussed in depth by Revesz and Kruger (2). The wear performance especially at higher temperatures might also be expected to be comparable to other commonly used coatings such as hard chromium (3) and because the coating can be applied using electrodeposition techniques, the adhesion between the coating and the substrate can be comparable to the cohesive strength of the substrate, with the additional advantage that the coatings can be applied to the interior surfaces of very small parts. Protective wear and corrosion resistant coatings are becoming increasingly important to alleviate the dependence of the United States on strategic materials particularly important among these are chromium and cobalt. The United States imports almost 100% of its chromium and 97% of its cobalt from countries that can not be relied upon (4). Since chromium is used mainly for its corrosion properties, a surface phenomena, coatings containing chromium offer an important means of dealing with the critical materials problem. By using corrosion *resistent coatings the entire part no longer has to contain large quantities of the strategic material.

There have been numerous attempts to electrodeposit alloys of nickel with chromium and nickel with molybdenum. Many of these attempts were reviewed by Chisom (5) who concluded that there is presently no commercial process capable of depositing the alloy. Typical of the problems encountered by the earlier investigators were (a) the inability to build up a coating of thickness greater than 25 microns, (b) inability to incorporate significant amounts of chromium into the deposit and (c) poor morphology, that is coatings which are highly stressed or dendritic. More recent studies of Stromatt (6) and Hayashi (7,8) seem to have been more successful. Hayashi's study was of an iron nickel chromium process which made use of electrolytes containing trivalent forms of chromium and various complexing agents. Pulsed electrodeposition of the ternary iron nickel chromium alloys were reported by Hayashi (8) who found that direct current coatings exhibited structures much different from those observed for pulsed deposited coatings.

PROCESSES DEVELOPMENT

A process was formulated using trivalent chromium which was chosen because it is far less oxidizing in solution than the hexavalent form of the ion and so is more tolerant of organic complexing agents. This is rather important as, based on the results of previous investigators organic, complexing agents would seem to be required for the successful deposition of the alloy. It should also be noted that the trivalent ion requires less energy to reduce to the metal than the hexavalent. Trivalent

ions are also far easier to treat when present in electroplating wastes that are hexavalent ions. Hexavalent electrolytes have been reported to be successful for the deposition of nickel chromium alloys by Shluger and Kazakov (9) and more recently for cobalt chromium alloys by Gilshinski and Yahalom (1Ø). Experience in our laboratory has shown us that thick coatings of a nickel chromium alloy are very difficult to obtain from hexavalent electrolytes under normal conditions.

In deposition from trivalent chromium electrolytes, formation of the hexavalent chromium ion at the anode should be avoided both to avoid oxidizing the complexing agents as well as to maximize the current efficiency. To help accomplish this in the process described here ammonium bromide was added to the solution as the bromide oxidizes at a lower potential than does the trivalent chromium. Probably an iodine salt also could be used. This of course results in the liberation of some bromine at the anode. Further to aid in the reduction of any hexavalent chromium which may be formed, formic acid was added to the solution. Formic acid is a known catalyst (11) for the reduction of chromium from hexavalent solutions. It should not be overlooked that the formic acid may play a role in the reduction of the trivalent ion. A number of complexing agents for both nickel and chromium were investigated, the most successful was found to be glycolic acid. Glycine was also found to be successful but its instability under long term use made it unacceptable. Boric acid was found to be essential and may act to minimize hydrolysis reactions or to act as a buffer through some mechanism which is not clear.

mount of chromium in the electrolyte was optimized by first fixing the concentration of nickel hexahydrate at 30 g/L and varying the chromium chloride hexahydrate from 0 to 130 g/L. Measurements of chromium content of the coating were made by X-ray fluorescence using the procedure described by Rasberry and Heinrich (12). It was found that the chromium content of the deposit exhibited a peak at a solution content of 100 g/L of chromium hexahydride as is shown in Fig. 1a. The solubility of glycolic acid is very large and much more has been added to the solution than is necessary to complex the chromium and the nickel. No effect on chromium content of the deposit was observed by varying the amount of glycolic acid in the solution.

The amount of chromium in the electrolyte was then fixed at 100 g/L and the nickel content varied. The chromium content in the coating was found to peak at 30 g/L nickel, as shown in Fig. 1b which was then fixed for future experiments. The maximum chromium current efficiency for the deposition of chromium was found to be around 14.4 percent. This value compares with the the current efficiency of typical hexavalent chromium plating solutions which is usually around 13%.

The dependence of the current efficiency for chromium deposition on the current density is shown in Fig. 2. At about 20 A/dm^2 direct current deposition yields coatings of about 18 Wt. % chromium.

The amount of chromium in the alloy was measured as a function of temperature and pH of the electrolyte and the results are shown in Fig. 3. As the temperature increases, the amount of

mium in the alloy gradually decreases. This result may indicate that the diffusion of chromium ions to the cathode is less than nickel and most probably the activation energy for diffusion of chromium is less than that for nickel.

In order to determine the effect of pH on the amount of chromium in the alloy, a number of coatings were made at various pH values and their chromium contents were measured using the X-ray fluorescence technique discussed above. The results are shown in Fig. 4 where the current efficiency for chromium deposition is plotted as a function of pH and a function of temperature. The efficiency goes through a minimum at around 55 ^{o}C and at a pH of 2. At a temperature of 30 ^{o}C deposits containing over 18 Wt.% chromium were produced by direct current deposition. Significant improvements in deposit morphology were obtained by pulsed electrodeposition and are discussed below.

The overall current efficiency was measured as a function of temperature for three values of pH. These results are shown in Fig. 5 . The cross-over of the curve for pHl indicates that the deposition of hydrogen is favored at higher temperatures. The appearance of the coating at pH 2 is also better.

Based on these studies along with Hull cell measurements, which will not be discussed here, an electrolyte formulation was developed and is given below:

::

NiCl2 6H2O	3Ø g/L
CrCl3 6H2O	1ØØ
Formic acid	35 ml/L
Glycolic acid	5Ø g/L
NH4Br	8Ø g/L
Boric Acid	4Ø
Temperature	3Ø oC
pH	2.Ø

::

PULSED CURRENT DEPOSITION

Pulsed current deposition using the waveform shown in Fig. 6 was undertaken in order to determine the effect on coating morphology and composition. Duty cycle in the following discussion is defined as time on divided by the sum of time on and time off as:

$$(1)\quad \text{Duty Cycle} = \frac{\text{Time On}}{\text{Time On} + \text{Time Off}}$$

Current density is the value during the On Time. The effects of pulsing the current in the above manner were discussed by Ibl(13,14) and Che(15,16) and a number of investigators have found important effects on both morphology and composition (17,18). During the On time, the concentration of both nickel and chromium ions is reduced within a certain diffusion distance. This diffusion layer pulsates with the same frequency as the applied current as described by Ibl (14). Its magnitude is also

elated to the peak current density but reaches a limiting value governed by the diffusion coefficient of the ions involved. During the off time the concentration of the reactants build up again and if enough time is allocated will reach the equilibrium concentration of the bulk electrolyte. Typically for frequencies of several hundred cycles a second this diffusion distance is rather less than the corresponding diffusion distance for direct current deposition therefore it can be expected that the resulting morphologies of coatings under direct current deposition will be more dendritic or nodular than coatings formed under pulsed conditions. This is only a general description and a rigorous treatment of the problem would have to take into account the diffusion parameters of each ion separately as well as the mass transport conditions. If this diffusion distance is comparable to the dimension of the surface roughness then the asperities of the surface which protrude into the diffusion layer will be exposed to a concentration of the reactants which is higher than the average surface and therefore will experience a higher deposition rate. During pulsing however the average diffusion distance is usually small compared to the surface roughness so that the surface sees an uniform concentration of ions at even its rough places, then the deposition rate is everywhere about the same. It is for this reason that for pulsed current deposition a smoothing effect is often realized and dendrite formation is suppressed.

The effects of pulsed galvanostatic deposition on chromium content were determined as a function of current density for various duty cycles and are plotted in Fig. 7, for a fixed off

time of 2 ms. Generally as the current density increases so does the chromium content for all duty cycles from 20 to 90%. However the higher the duty cycle the higher the chromium content.There is a significant difference in the surface morphology of deposits produced by different waveforms as might be expected from Ibl's explanation of the deposition process. In Fig. 8a and 8b a comparison is made of surface morphology, using scanning electron microscopy, between a typical direct currrent deposit and a coating produced by pulsed current deposition. The surface of the direct deposit is clearly much rougher. The duty cycle also effects the surface roughness as is shown in Fig. 9a and Fig. 9b which illustrate two pulsed coatings produced under identical conditions except for duty cycle. As a general trend the smoother deposits are produced at lower duty cycles. The effect of on time for the same duty cycle is shown in Fig 10a and Fig. 10b, again the lower On time provides the smoother coating.

Cross section of a typical coating show that the deposit grows in a layered structure with the layers exhibiting marked chromium concentration gradients. The scanning electron micrograph shown in Fig. 11 is of a coating produced at a 33% duty cycle at 50 A/dm^2 and an On time of 0.2 ms. It was deposited on copper coated brass and etched in aqua regia.

PROPERTIES

Microhardness measurements have been made on several coatings as a function of duty cycles and are shown in Fig. 12, for current densities of 25 A/dm^2 and 50 a/dm^2. Both current density values result in a minimum microhardness at around 50%

duty cycle. As is shown below the chromium content generally increases with the duty cycles so that higher hardness alloys are also high in chromium content.

Data on corrosion performance can be obtained in a number of ways such as salt spray, potentiodynamic anodic polarization, current staircase, potentiostatic scratch, and other electrochemical test along with actual exposure to a corrosive environment for an extended time. For the time being the corrosion performance is being evaluated using the technique of potentiodynamic anodic polarization. This technique is covered by ASTM G5-78 (19) and is quite widely used by industry. Samples for the corrosion tests reported here were prepared on a rotating disc electrode made of brass which was plated with gold. We have also found that a nickel strike can form an excellent undercoat for the nickel chromium coatings. Corrosion results will only be reported for one alloy composition namely 18% Cr 82% Ni (Wt. %). This alloy composition is formed at Ø.1 ms On time and Ø.2 ms Off time at 5Ø A/dm^2 at 5ØØ rpm. The samples were about 1 cm. diameter. Results are given for both 1 N sulfuric acid and 3% sodium chloride electrolytes.

The corrosion data shown in Fig. 13, in sulfuric acid for nickel chromium is compared with data taken under similar conditions for 43Ø SS stainless steel. Note that the passive region extends to almost 1 volt SCE. When compared to 43ØSS stainless steel shown in Fig. 14, whose passive range is somewhat less it seems clear that this coating has a very strong tendency to passivate. In chloride environments the corrosion performance

is degraded significantly as shown in Fig. 15, compared with the performance of 430 stainless shown in Fig. 16.

The passive region is now only a few hundred millivolts however, the strong tendency of the current to drop upon reversal of the potential reveals an extreme resistance to pitting. A possible explanation for this excellent corrosion behavior lies in the particular microstructure of the coating. As in most binary alloys electrodeposited coatings, the second constituent is not uniformly distributed. Typically layers are formed that are rich in one of the constituents. This microstructure is typical for different coatings plated under the same conditions as was shown above. Clearly there are strong chromium concentration gradients present. It would seem reasonable to assume that corrosion would proceed into the coating until one of these layers was encountered and then spreads laterally until the outer layer was dissolved so that pitting is eliminated. Since the layer spacing is on the the order of 1 micron, in a 50 micron engineering coating more than 75 layers would have to be uniformly dissolved before that substrate could be attacked. This mechanism occurs in the duplex and triplex nickel systems used on automobile bumpers.

Two samples of nickel chromium coatings were studied by X-ray diffraction. The first is a direct current deposit designed to produce a 20% chromium content and the second is a pulsed deposit designed to produce a 6% chromium content. Neither of the coatings were examined directly for chromium content so that these studies need to be expanded upon. In the pulsed deposit

the Cr_3Ni and the CrNi phase were detected which for the direct current deposit only the Cr_3Ni phase seemed to be present. Both coatings contained metallic nickel. However, in the direct current deposit the nickel was extremely fine grained.

CONCLUSIONS

1. A process has been developed that is capable of producing thick coatings of nickel chromium alloy whose chromium content can be controlled through the deposition parameters in a range from about Ø.1 Wt. % chromium up to 6Ø Wt. % chromium.
2. The resultant coatings exhibit unusual corrosion resistant in both chloride and sulfuric acid environments. This behavior is thought to be a result of their unusual layered structure.
3. Microhardness measurements imply that the wear performance of these coatings should be excellent.
4. Distinct differences in surface morphology and in the types of crystal phases present has been observed between coatings produced by direct current deposition and by pulsed current deposition. The differences in surface morphology or roughness can be accounted for by Ibls theory describing the pulsating diffusion layer.

ACKNOWLEDGEMENTS

The author gratefully acknowledges the financial support of the American Electroplaters Society and Center for Materials Science of the National Bureau of Standards. The following students have worked on this project: Carlos Beauchamp, Ann Perry, and JoAnne Weinroth and their assistance along with that of Dr. Ilan Weisshaus has contributed a great deal to the success of this project.

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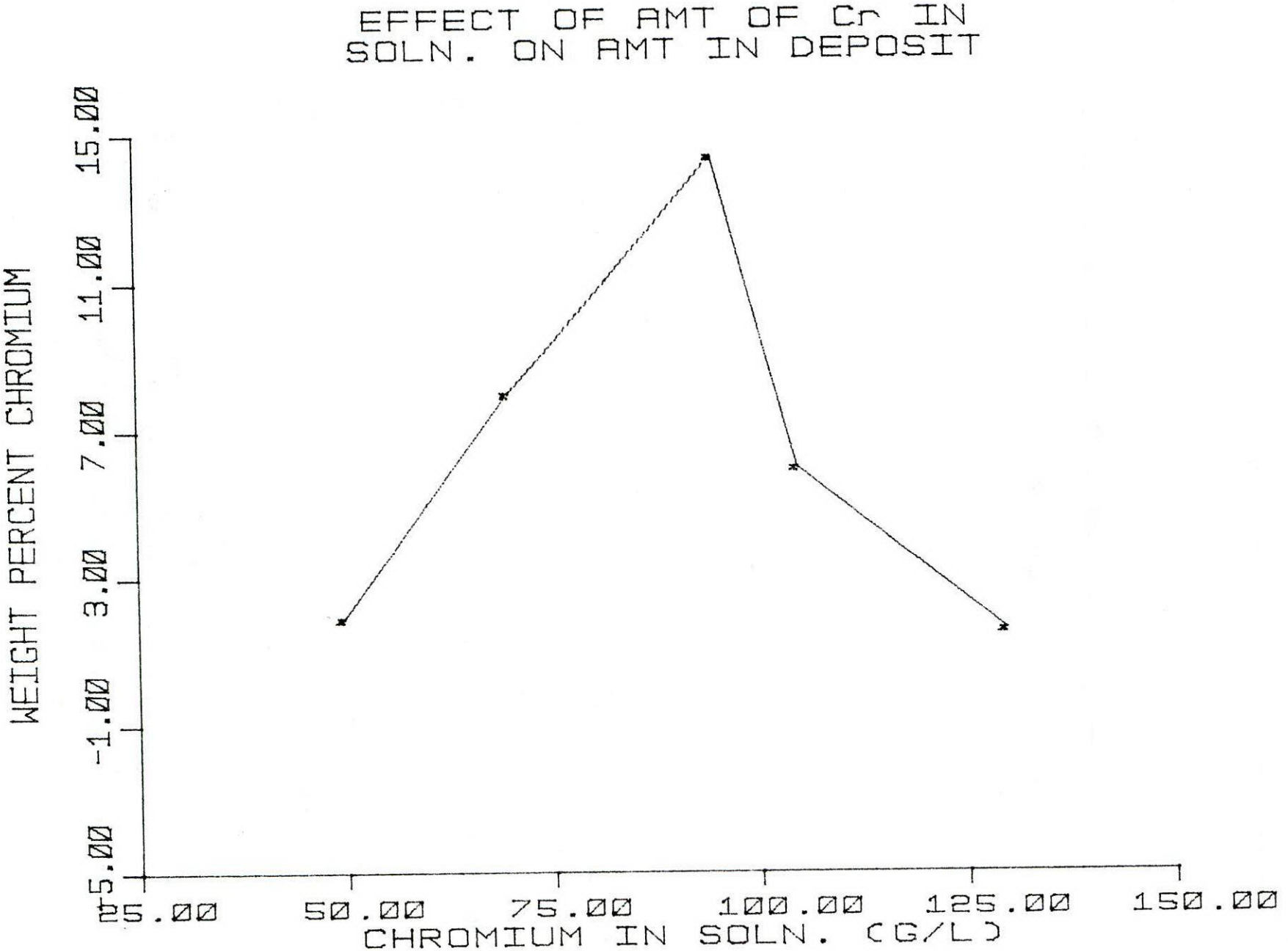


Fig. 1a. Variation of the Chromium content in the coating with chromium hexahydrate in the electrolyte.

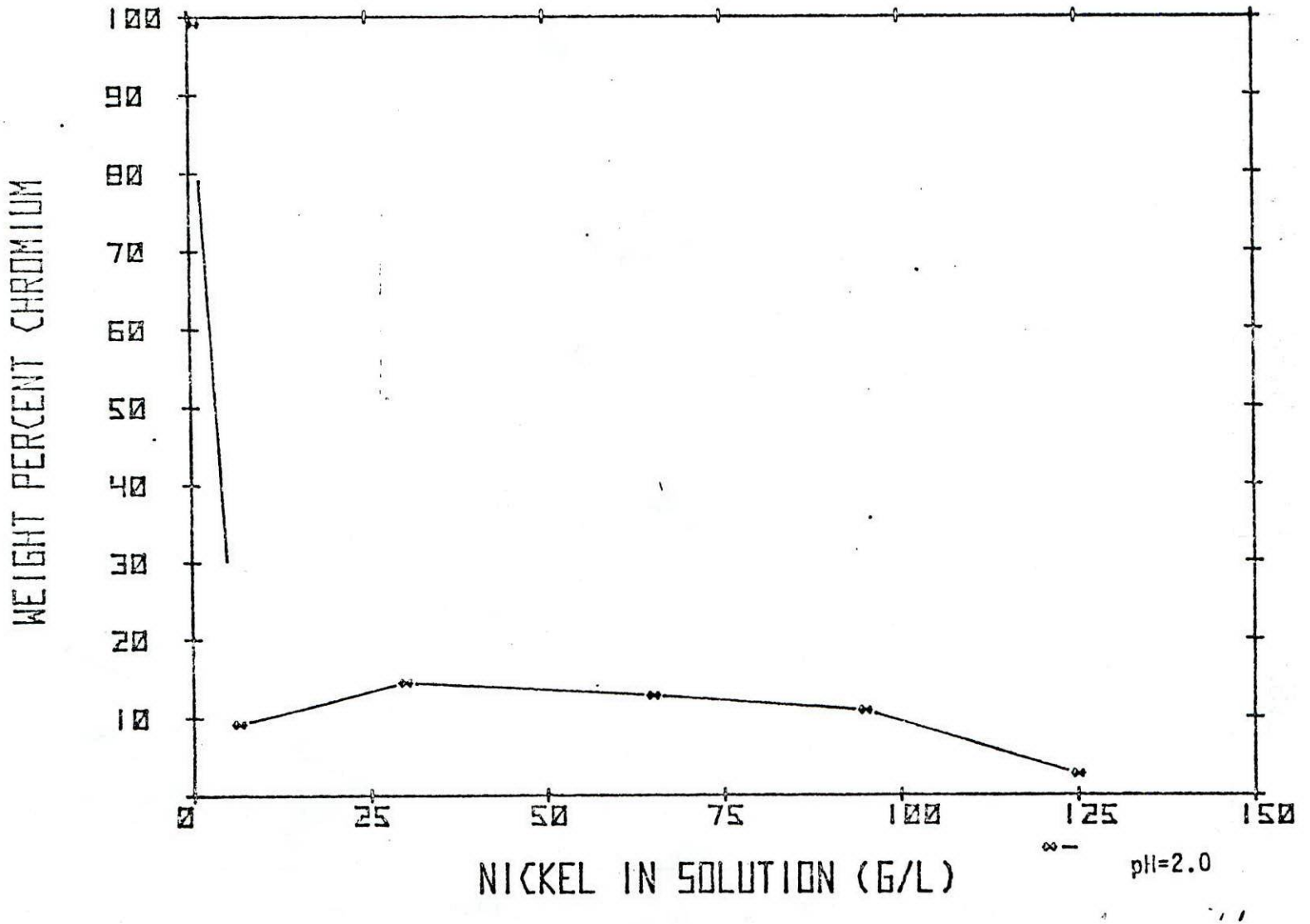


Fig. 1b. Variation of Chromium content in the coating with nickel hexahydrate in the electrolyte. (pH=2.0)

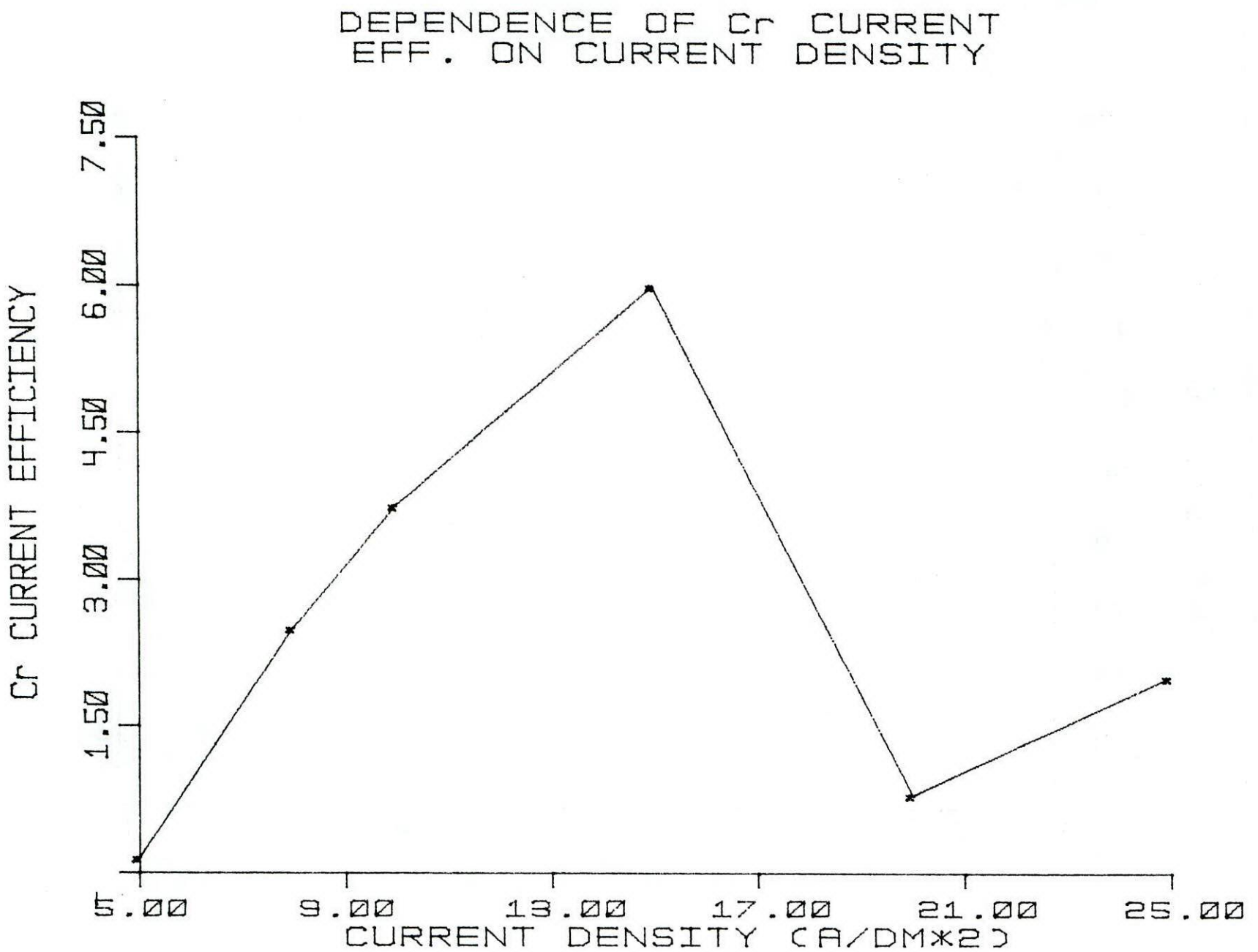


Fig. 2. Dependence of the current efficiency on the current density for the deposition of chromium only. (based on wt.% Cr. in alloy)

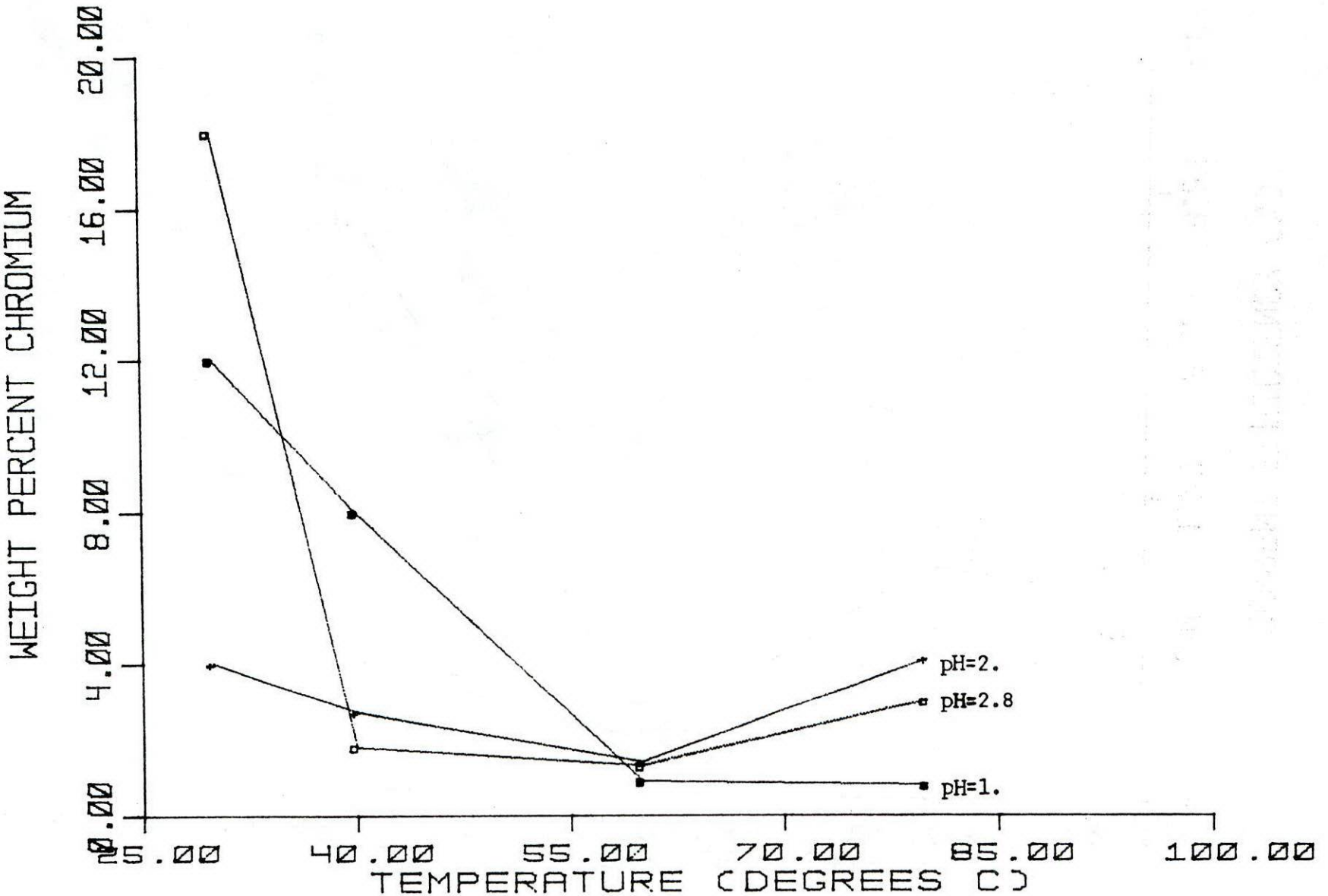


Fig. 3. Dependence of the chromium content of the alloy on the temperature and pH.

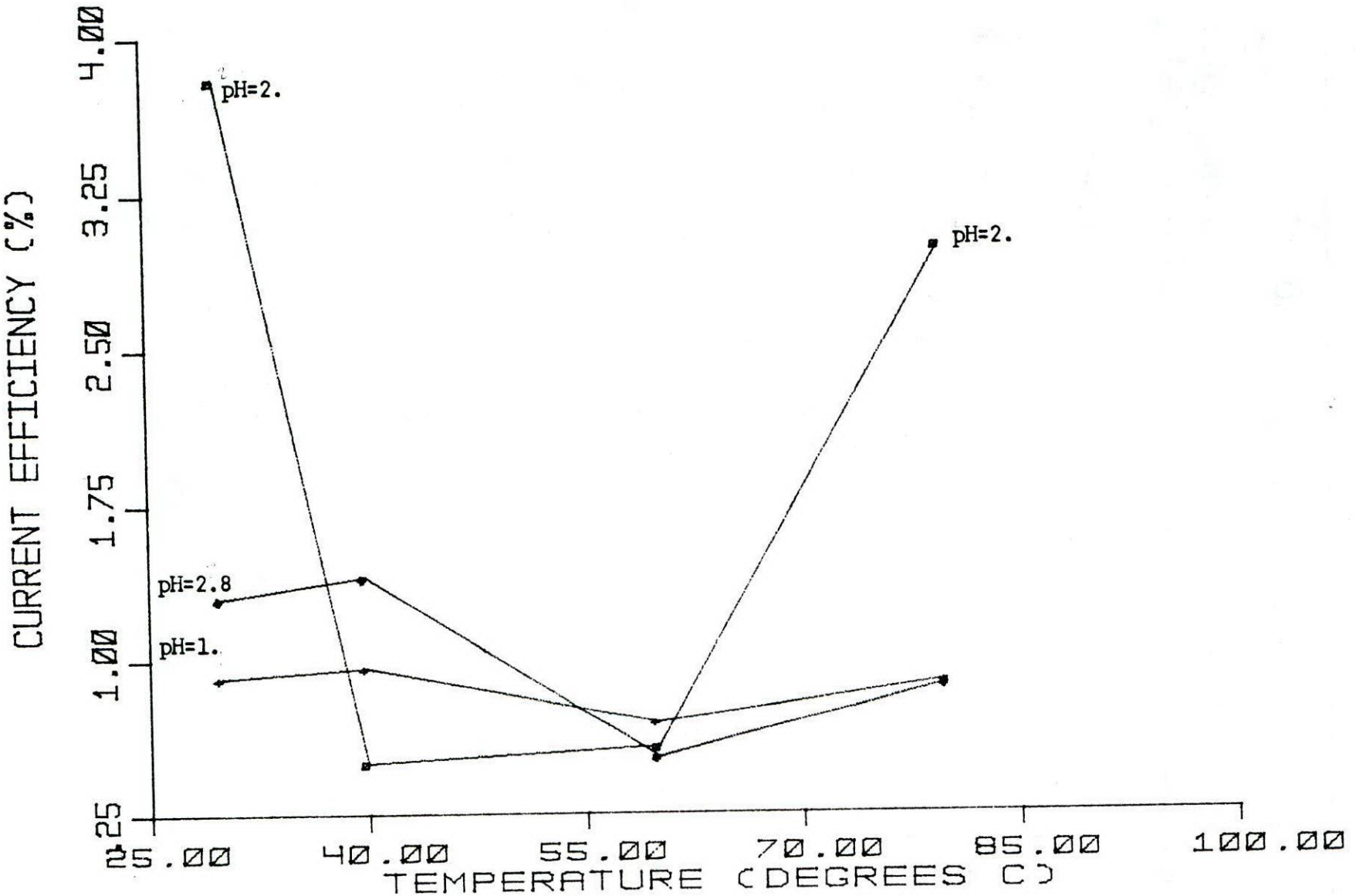


Fig. 4. Dependence of the chromium current efficiency on temperature of the electrolyte and on pH.

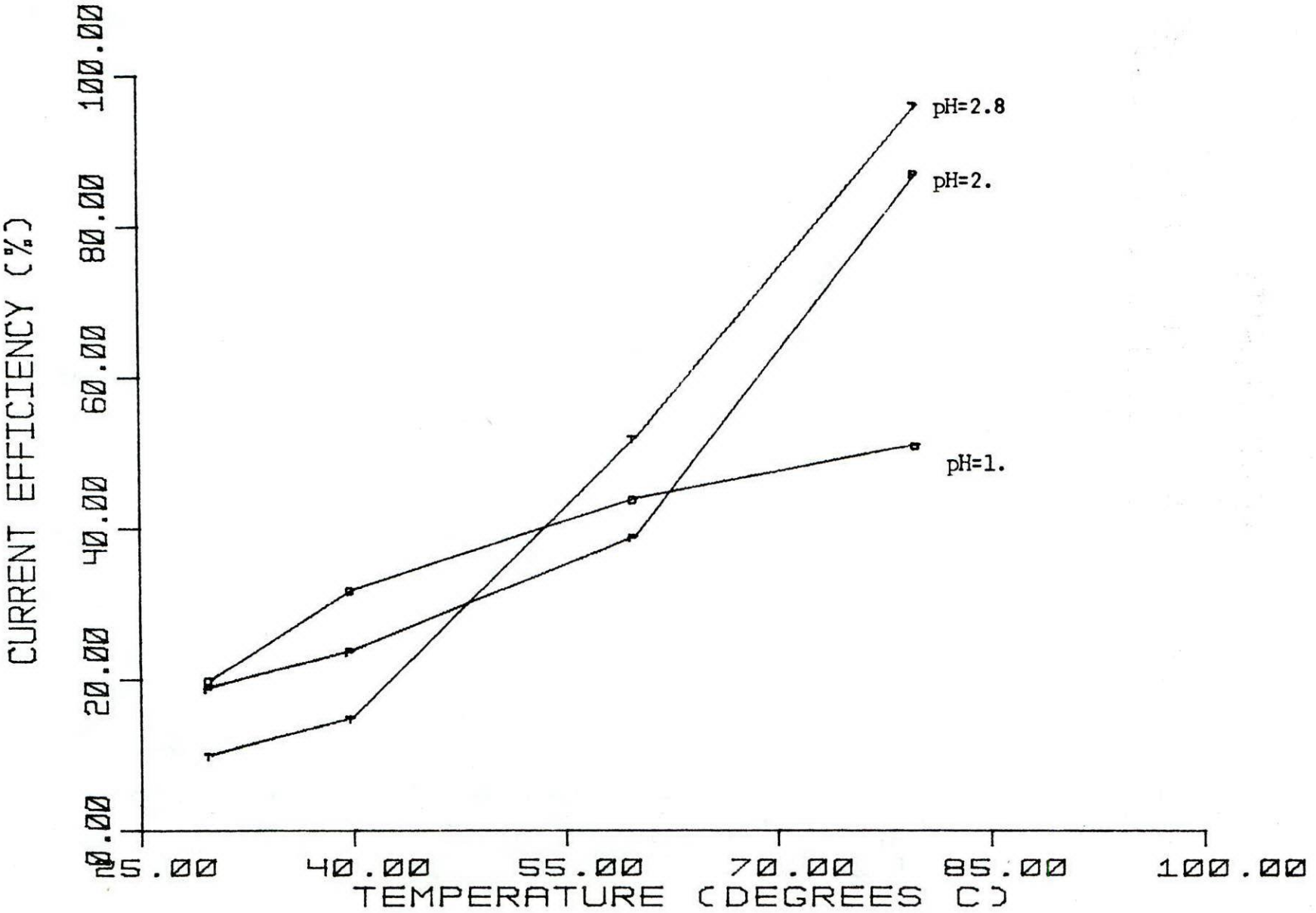


Fig. 5. The overall current efficiency as a function of temperature of the electrolyte and as a function of pH.

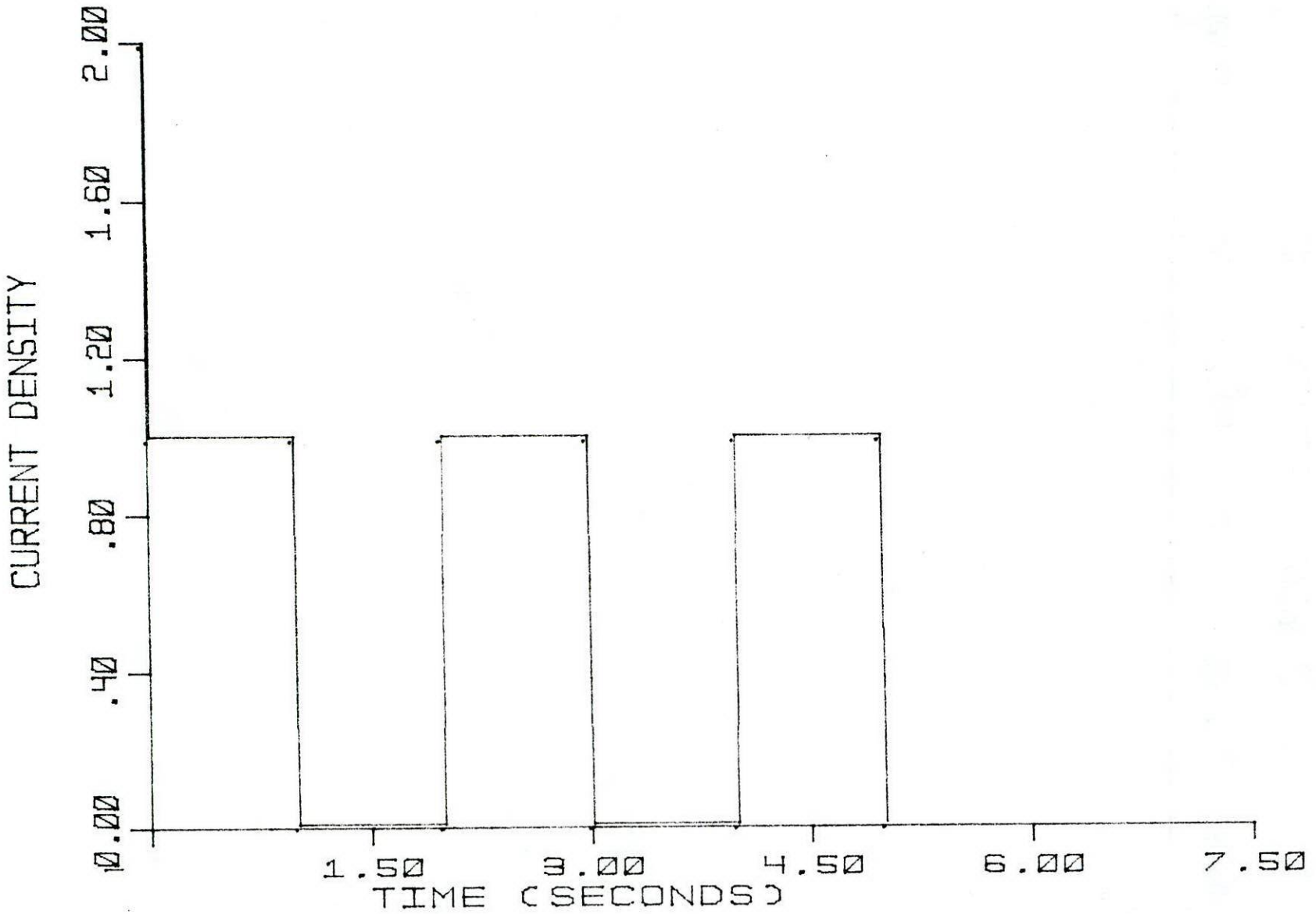


Fig. 6. Waveform of pulses used in galvanostatic deposition(arbitrary time scale)

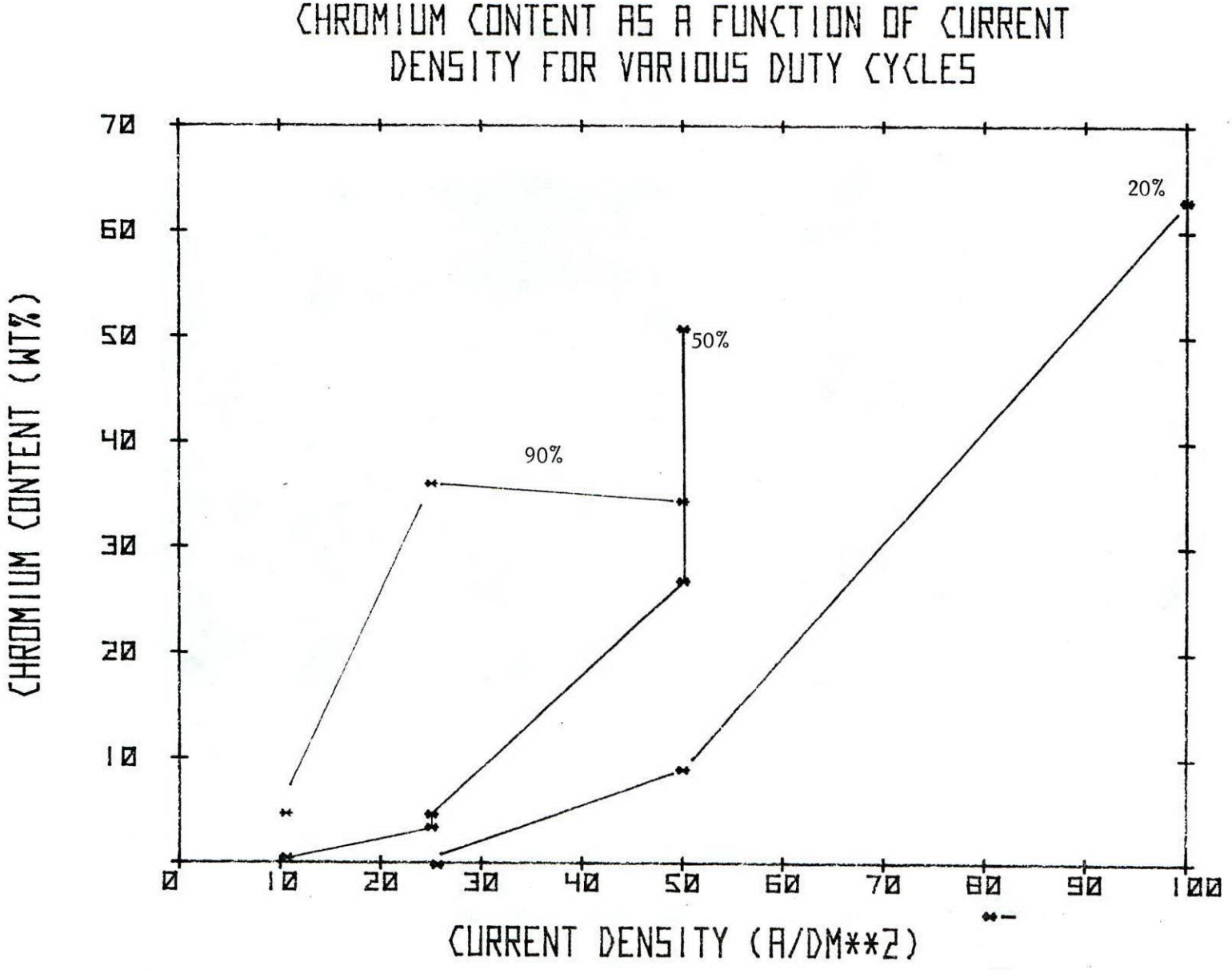


Fig. 7. Chromium content of the alloy as a function of duty cycle and as a function of current density

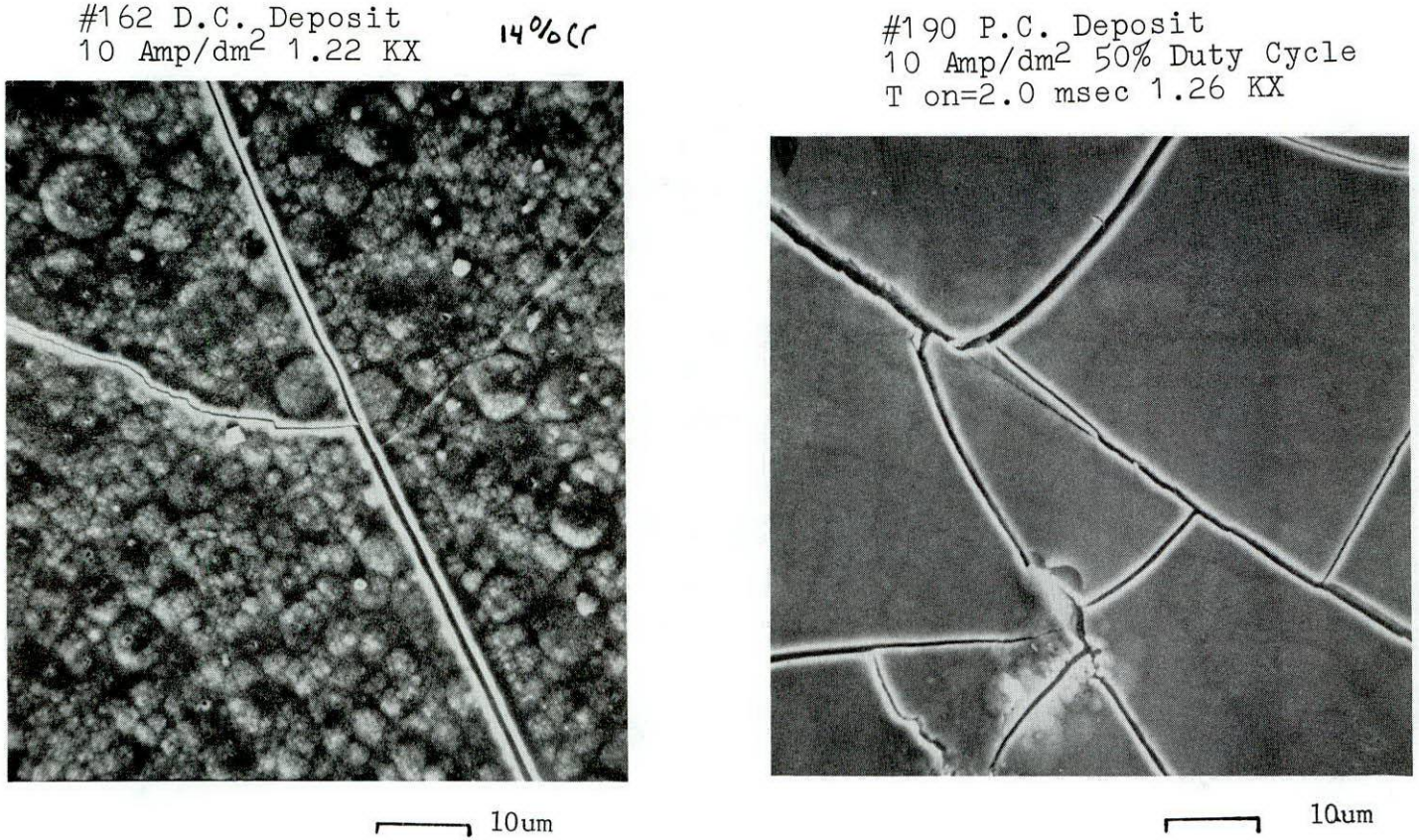


Figure 8. A comparison between direct current deposited alloy and pulsed deposited alloy under the same current density.

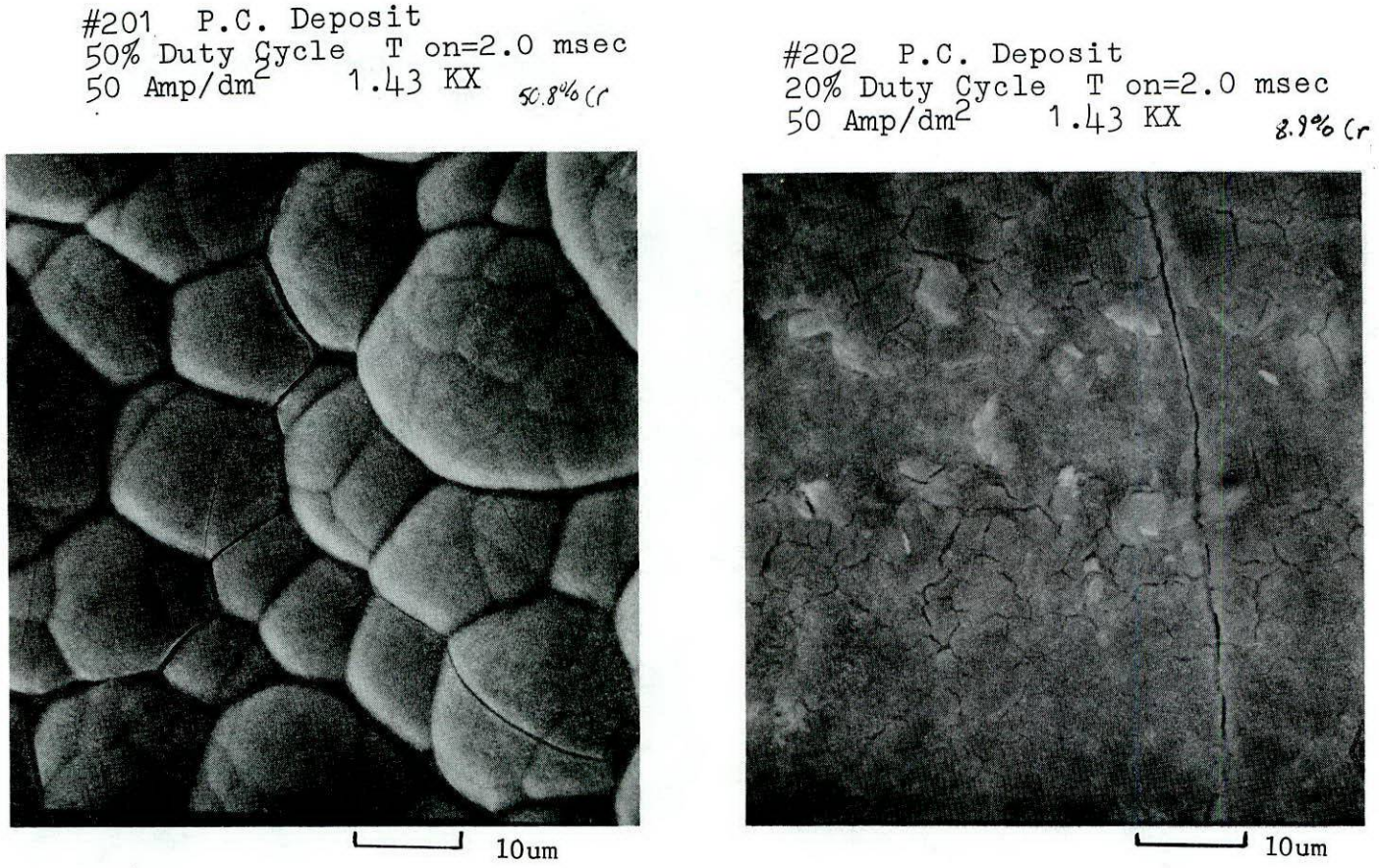
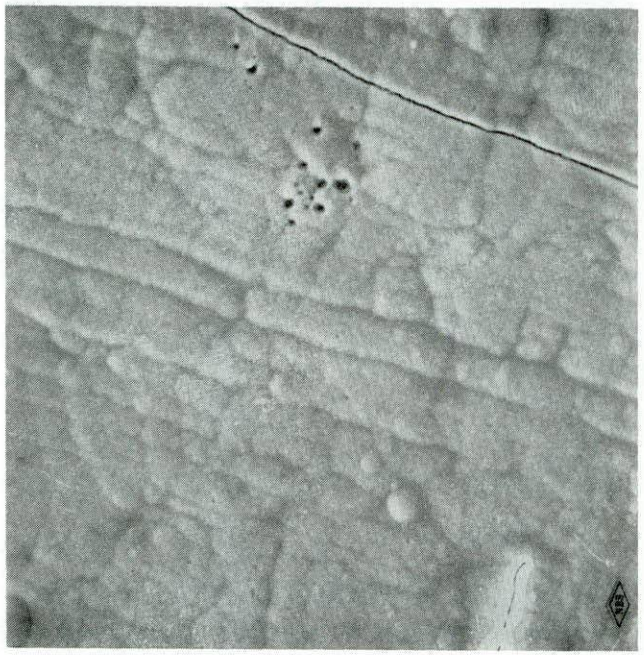


Fig. 9. The effect of duty cycle on morphology.

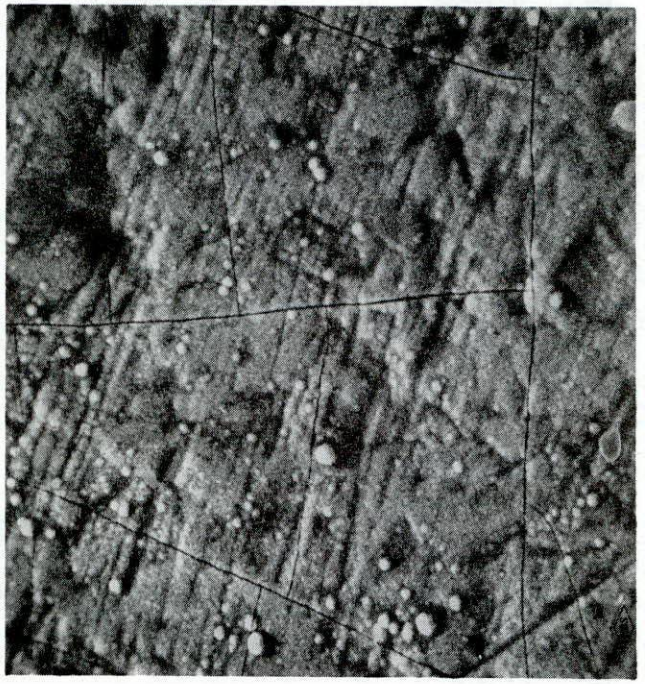
#199 P.C. Deposit
25 Amp/dm^2 20% Duty Cycle
T on=2.0 msec 1.4 KX 1.9%Cr



10um

(a)

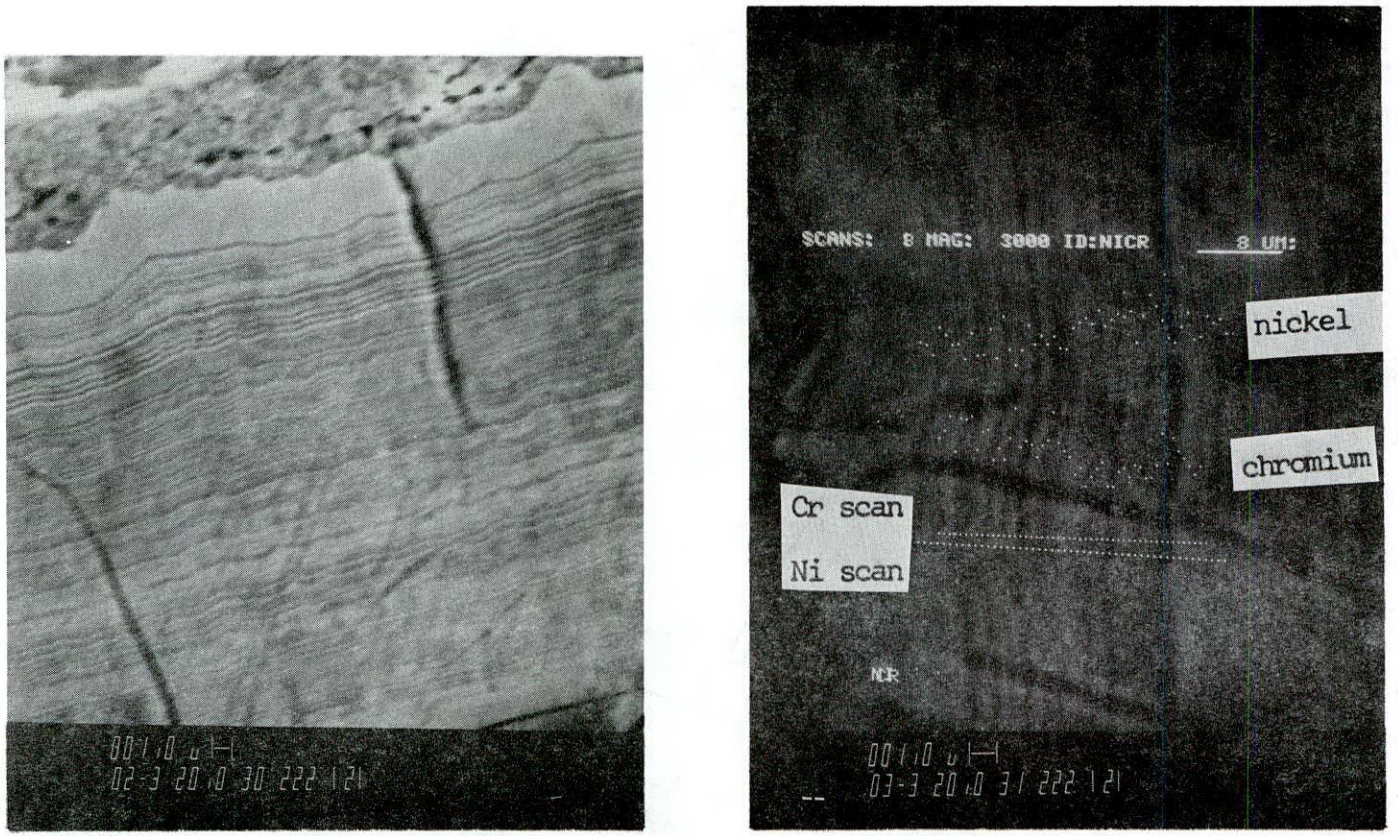
#210 P.C. Deposit
20% Duty Cycle T on=1.0 msec
25 Amp/dm^2 1.38 KX



10um

(b)

Fig. 10. The effect on On time on the coating morphology. The duty cycle has been kept constant.



(a) (b)

Fig. 11. (a) SEM micrograph illustrating the laminated structure of a typical nickel-chromium alloy coating, (b) An X-ray line scan using Cr radiation illustrating that the periodic layer structure is a result of strong chromium concentration gradients. (sample etched in aqua regia)

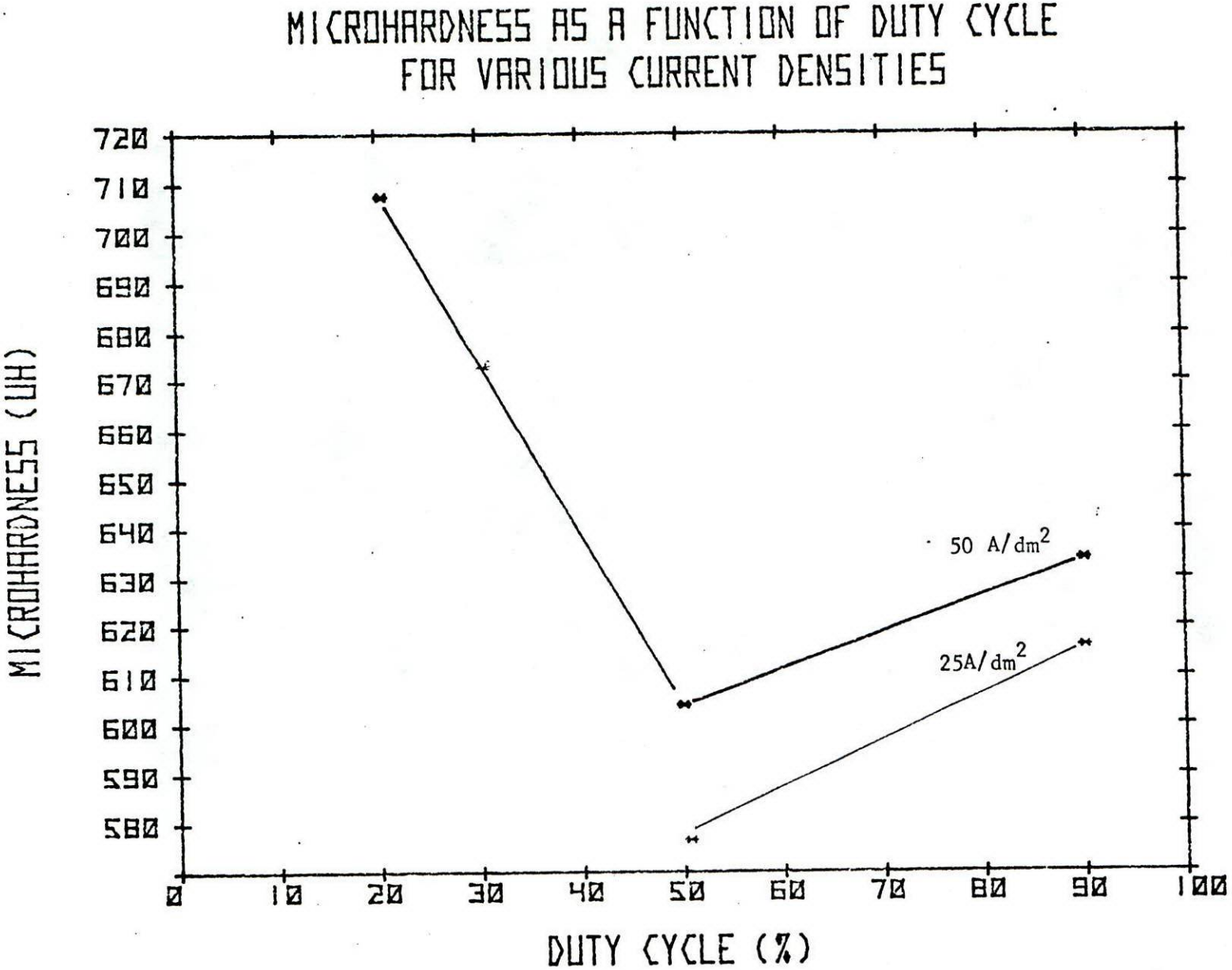


Fig. 12. Microhardness as a function of duty cycle for two different current densities.

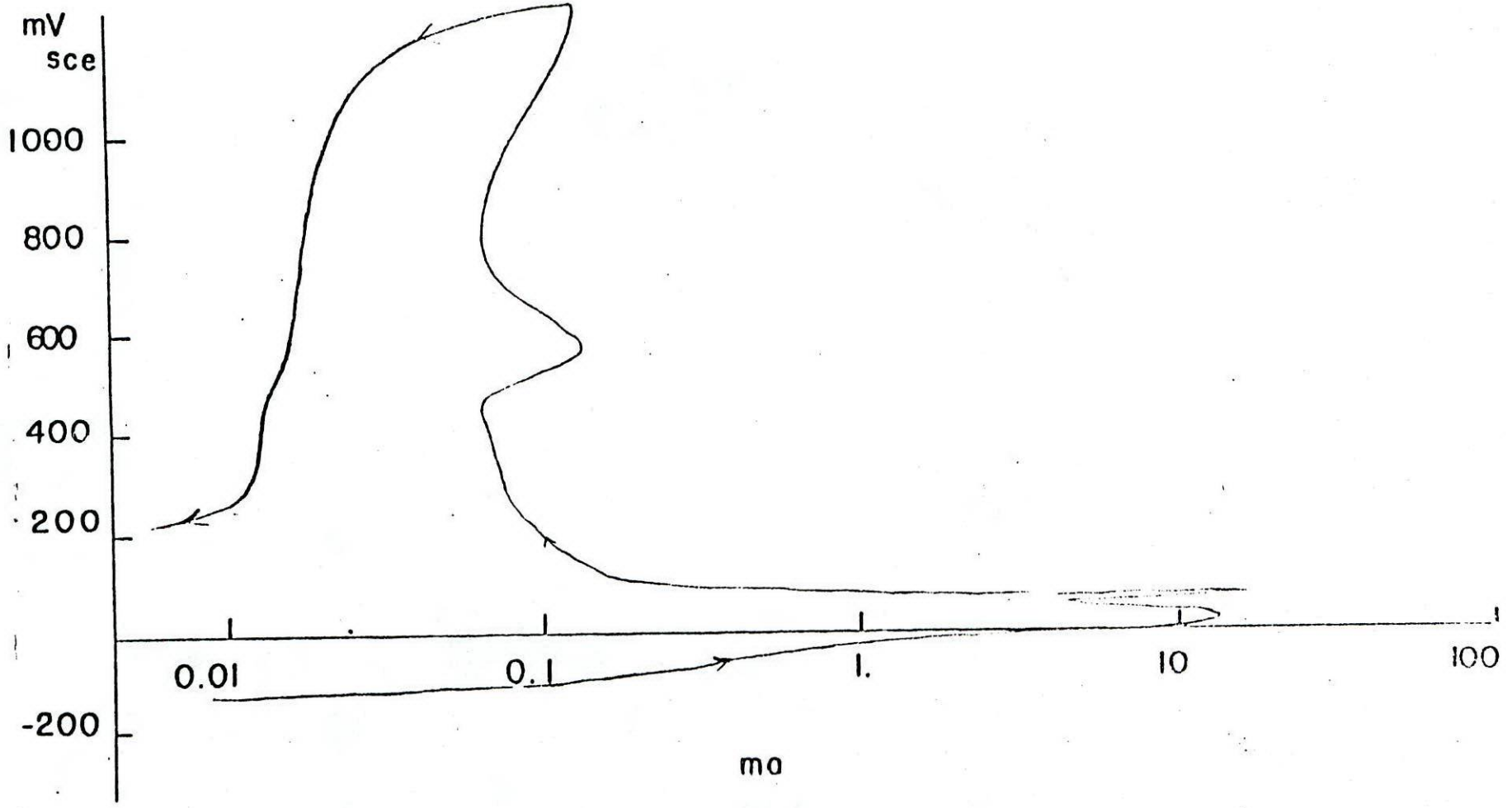


Fig. 13. Potentiodynamic anodic polarization data for a NiCr alloy (20% wt. Cr. nominal) in a 1N sulfuric acid electrolyte

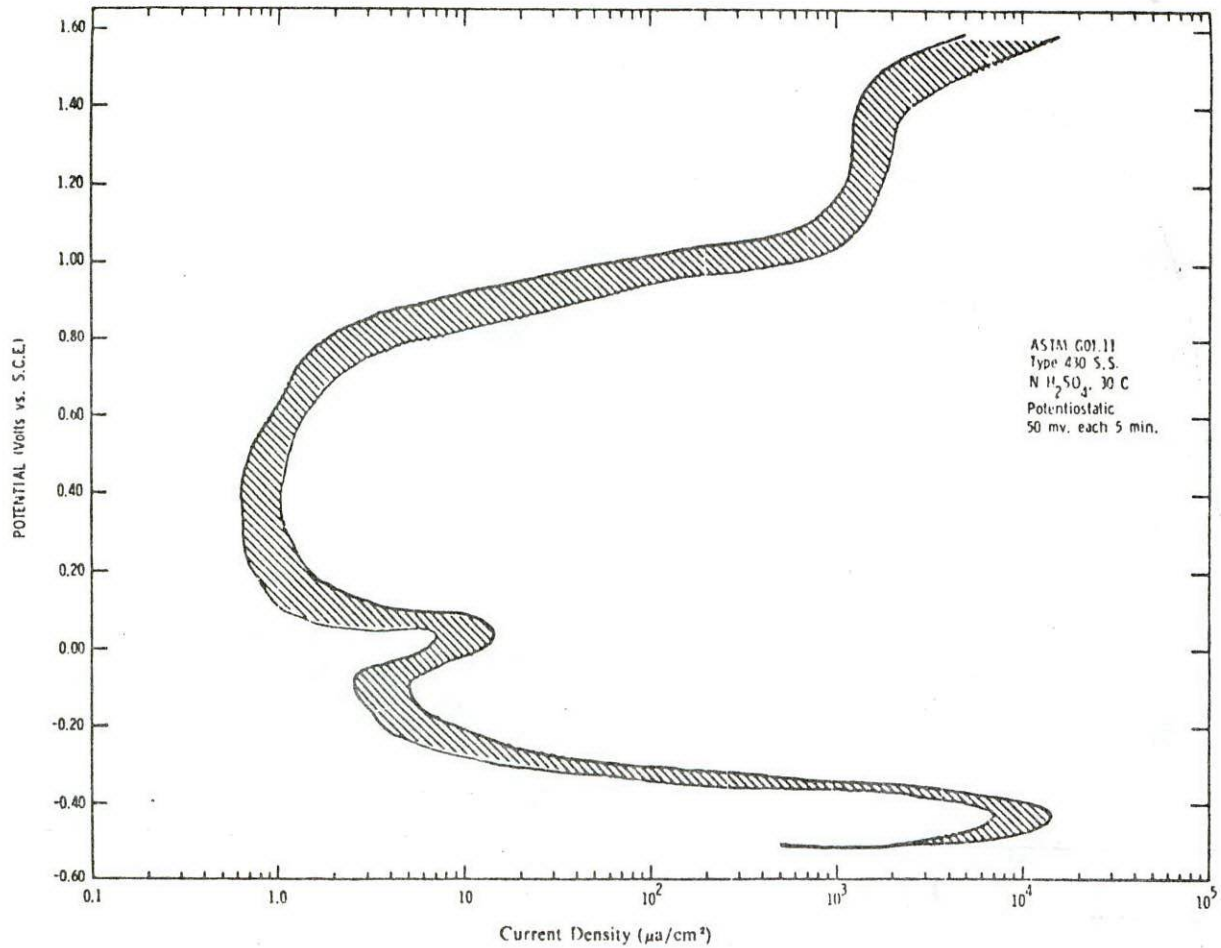


Fig. 14. Potentiodynamic anodic polarization data for 430 SS stainless steel (compare with Fig. 13 for NiCr)

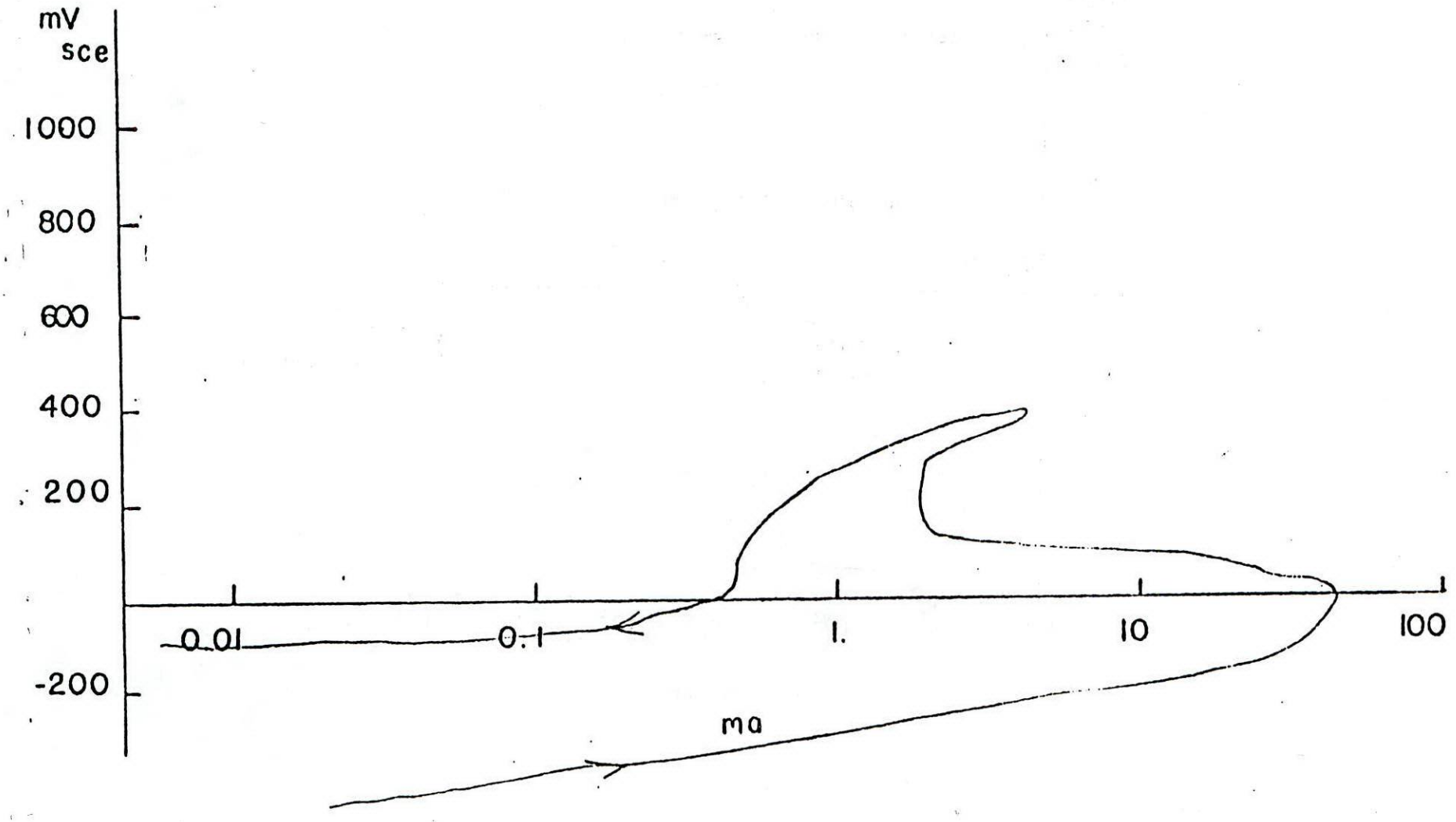


Fig. 15. Potentiodynamic anodic polarization data for a NiCr alloy coating (20 wt. % Cr nominal) in a 3 Wt. % sodium chloride electrolyte.

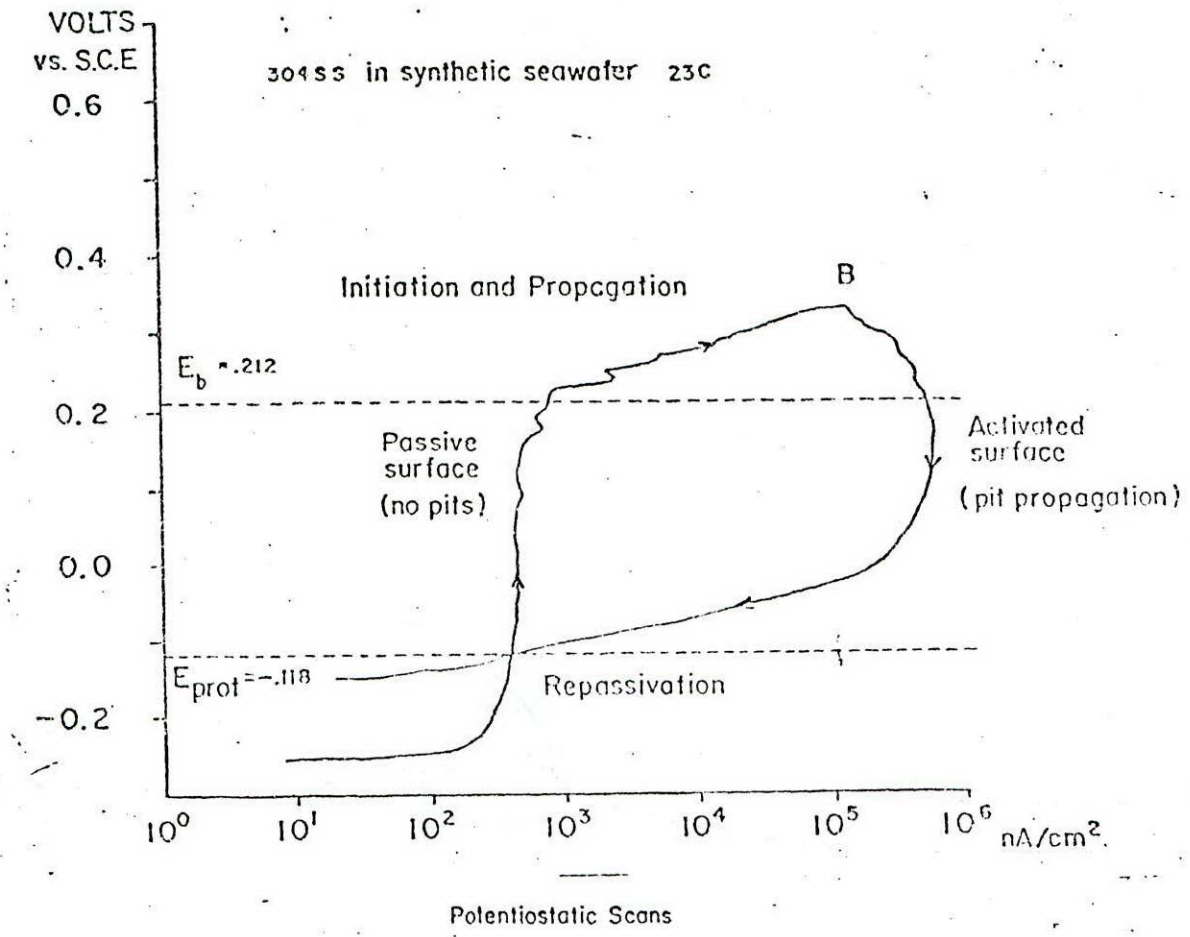


Fig. 16. Potentiodynamic anodic polarization data for 304 stainless steel in a 3 wt. % sodium chloride electrolyte.

A-3

Research Session A

Tensile Testing of Electrodeposits

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Stevens Institute of Technology
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AES Project 38

ABOUT TENSILE TESTING OF ELECTRODEPOSITS

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It has been difficult to obtain accurate and reproducible mechanical-property data from tensile tests especially for thin electrodeposits. Defects introduced by specimen preparation and from mounting in the tensile machine as well as porosity which developed during plating can result in premature fracture and therefore lower tensile strengths and ductilities. These difficulties are most serious in the conventional uniaxial tensile testing where also even slight misalignment of the specimen leads to erroneous results. Bulge testing has been used to overcome some of the difficulties, but it also has some drawbacks.

In order to attain the objective of Project 38; namely, to understand the reasons why the mechanical properties of electrodeposits differ from those of materials formed by other means and particularly the effects of additives in the plating solutions, it was necessary to develop a tensile-testing machine which yields accurate and reproducible data for deposits as thin as 200 nm (50 millionth of an inch). After the construction and modification of several models, such a machine has been built. It is shown in Figure 1.

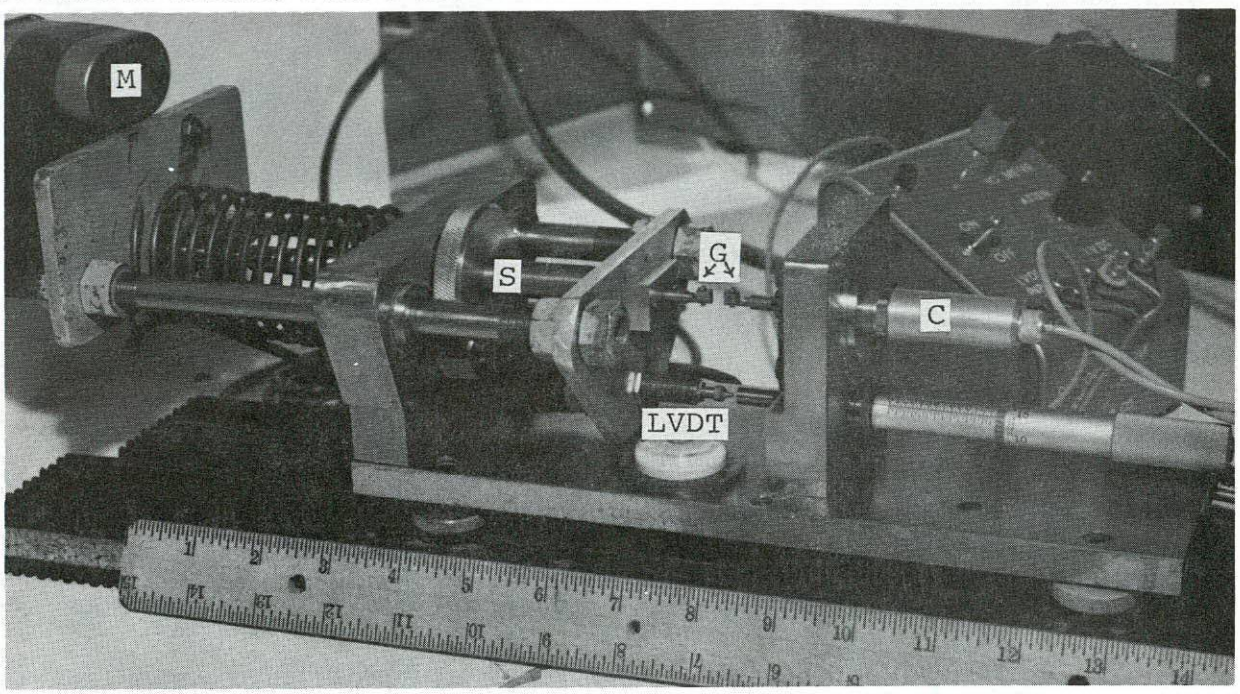
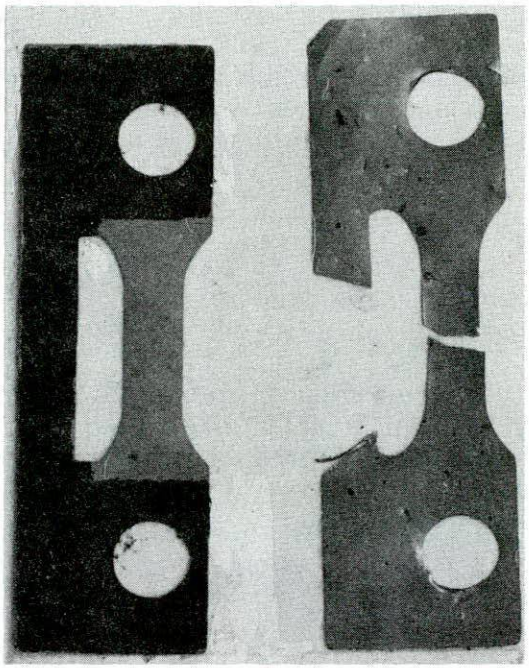


Figure 1 Tensile Testing Machine

This machine is small and compact. The load is applied by means of very fine-threaded screws (S) turned by a small motor (M). A load cell (C) measures the force applied to the specimen and its output is recorded on a

strip chart. The tensile specimen, which is not shown, is held between screw grips (G). The separation of the grips, one of which is fixed and is also the one attached to the load cell, is measured by a linear variable differential transformer (LVDT). The output of the LVDT is also recorded on the strip chart. The strain rate can be varied by changing the motor speed and/or the specimen gage length.

As already mentioned, the preparation and mounting of the tensile specimen is very important for reliable results. Figure 2 shows the tensile specimen and the supporting frame, which serves to prevent deformation during mounting. Figure 2 is an enlargement. The actual specimen is only 1.3 cm long. Specimen preparation begins by placing a mask in the shape of the specimen and the supporting frame on the substrate. Using photoresist, the areas on the substrate not covered by the mask are insulated. The deposit thus will have the shape of the mask. For testing thin deposits, the supporting frame has to be strengthened. To accomplish the strengthening, the specimen gage length is covered with an insulating lacquer. After the proper activating treatment, a much heavier deposit is plated on the supporting frame and on the ends of the specimen where it will be gripped. The area plated with this reinforcing deposit was painted black for illustrative purposes and therefore appears darker in Figure 2A. Prior to testing, the substrate is dissolved. After mounting in the tensile machine, the frame is carefully cut. Figure 2B shows the specimen after testing and illustrates the absence of the supporting frame.



A B

Figure 2 Tensile Specimen

Some results have been obtained for nickel plated in an additive-free, all-sulfate solution on single-crystal and cube-textured copper substrates. A typical stress-strain graph, drawn by computer, is shown in Figure 3. The stress reaches a maximum value and then decreases again before fracture. This phenomenon, which is known as necking, results when there is a large decrease in the cross-sectional area over only a very small portion of the gage length. The actual strain in the necked region is quite large as evidenced by the reduction in the cross-sectional area at the fracture which was about 20% for the deposit depicted in Figure 3. The thickness of the deposit at the fracture, which is used to calculate the reduction in area, was determined by interferometry. All nickel deposits exhibited necking.

The significance of necking in practical plating lies in the application of the tensile-test results, which are obtained when the deposit is not attached to the substrate, to plated work pieces. Two conditions have to be

considered. One is the case when the whole piece, i.e., deposit and substrate, is subjected to the same load. The second case is when the stresses in the deposit and in the substrate are of opposite sign. The second case is encountered when the plated work piece is heated and then cooled and the deposit has a different coefficient of expansion from that of the substrate. This case is also found when the deposit is under internal stress as was discussed last year[1]. In the first case, a deposit showing the behavior depicted in Figure 3 would behave in a much more ductile fashion than the nominal tensile-test results indicate provided the substrate is also ductile. As the strain before fracture can approach the same value as the reduction in area, which as already indicated is quite large and probably greater than the elongation of the substrate, the deposit is unlikely to crack prematurely. In the second case, the large localized strain measured in the tensile test cannot be realized in the deposit. The substrate, which would deform only slightly, would not permit the deposit to deform appreciably either. However, in this case, it still would require a greater stress than the tensile strength to fracture the deposit.

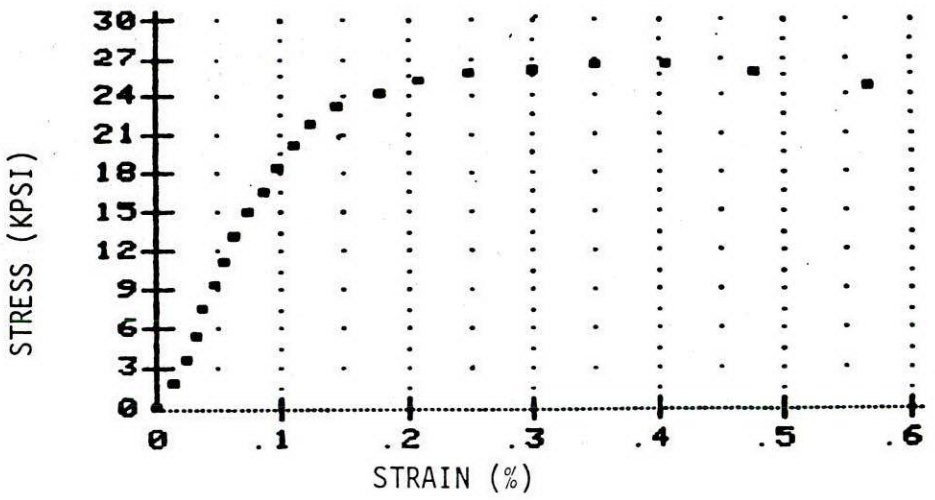


Figure 3 Computer-Drawn Stress-Strain Graph

It was also found that nickel plated epitaxially (i.e., it copies the substrate grain size and orientation) on cube-textured copper substrates had lower tensile strengths and elongations than those which were single crystals. The deposit the properties of which are depicted in Figure 3 was a single crystal and had a tensile strength of 184 MPa (∿27,000 psi). Epitaxial deposits on a cube-textured substrate have tensile strengths of about 136 MPa (∿20,000 psi). The difference can be attributed to a previously observed result[2] that the thickness of the deposit varies with grain orientation. The thickness of the single-crystal deposit is therefore more uniform while that of the one plated on the cube-textured substrate varies. The variation results because while most of the grains in a cube-textured substrate have the {100} crystal plane parallel to the surface, there are a number of grains with different orientations. In the case of nickel plated in an additive-free, all-sulfate solution, the thickest deposits grow on {100}-oriented substrate grains. On grains of other orientations, the deposit is thinner. This thickness variation can result in a deviation from a true uniaxial state of stress and a lower strength. When the deposit plated on cube-textured copper became nonepitaxial, i.e., it no longer copied the grain size and orientation of the substrate, a substantial strength increase resulted. A typical tensile-strength value was

306 MPa (~45,000 psi). The finer grain size and more uniform thickness are probably responsible for the higher strength.

The new tensile testing machine was also applied for the testing of electroless copper deposits used for printed-circuit boards. The widths and thicknesses of deposits on such boards are much smaller than those of the specimen which are generally tested to determine the mechanical properties. In the range of dimensions involved, there is a considerable effect of specimen size on the mechanical properties. With the new tensile machine it is possible to test specimens having the same dimensions as the deposits on printed-circuit boards. A paper dealing with this subject is being presented in the Electronics Session at this Conference.

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A-4

Research Session A

Hazardous Sludge Reduction

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HAZARDOUS SLUDGE REDUCTION

by

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FOREWORD

Stated simply, the Air Force Mission is to "Fly and Fight." As a result, we have over 70 different types of aircraft, ranging from the huge C-5A Galaxy to the relatively small T-33 trainers. These aircraft all have one common factor--they all need preventive maintenance. An integral part of this maintenance is the periodic rework of components, engines, air frames, landing gear, etc. To accomplish this mission, the Air Force has five major Air Logistic Centers (AFLCs) under the Air Force Logistics Command. These maintenance centers, located in Texas, Georgia, California, Oklahoma, and Utah, split the major maintenance duties by both geographic location of the aircraft homebase and by specific maintenance operation. All maintenance centers, however, have extensive electroplating capabilities for chromium, cadmium, nickel, and copper. Although some precious metal plating is also done, in comparison to the above metals, it is insignificant.

Under the Resource Conservation and Recovery Act (RCRA) Hazardous Waste and Consolidated Permit Regulations, the wastes generated by these electroplating facilities are classified as hazardous. Because wastes from these shops are channeled through Industrial Waste Treatment Plants (IWTPs) the resulting sludges also become hazardous and require special handling and disposal methods. Presently, most hazardous sludge is disposed

of in landfills; however, the costs have risen from $8 to $15 per ton before RCRA to $100 per ton and they are expected to rise even further.

Given the present configuration of the treatment facilities, available funding, and the lead time required for major construction, an interim solution to the problems of sludge volume and disposal costs had to be found. This is not to say that the Air Force is not keenly aware of its public responsibility in the hazardous waste area. Indeed, other research projects are aimed specifically at eliminating waste through reuse and recycling. The fact remains that hazardous sludge is a problem today and, under present constraints, an intermediate or "tide-us-over" step had to be taken.

With that in mind, a research project was begun with three objectives as follows:

1. Reduce the volume of hazardous sludge generated at the Air Force IWTPs.

2. Make the resulting sludge "non-hazardous" under the Environmental Protection Agency's criteria.

3. Accomplish the above with a minimum of changes in equipment and procedures at the plating shops and the IWTPs.

Meeting these three objectives could save the Air Force a considerable sum of money, get the treatment equipment on line quickly, and buy the time needed for the long-term recycling research.

The following report contains the results of the testing procedures and a summary of the reseach results.

OVERVIEW

The hazardous constituents in the treatment sludges often leach when exposed to the aqueous, acidic environment common to many sanitary landfills. To determine the leachability of hazardous wastes, EPA has adopted a test procedure that simulates this acidic condition. The test is referred to as the Extraction Procedure (EP). A measured sample of the sludge is placed in distilled water, a fixed amount of acid is added, and the mixture is agitated for 24 hours. The aqueous portion of the mixture is then analyzed for the presence of toxic constituents to determine to what extent they leached from the sludge. By comparing the results of the analysis to the maximum allowable concentrations, shown in Table 1, a level of toxicity can be determined. If the EP test results show that a given sludge consistently leaches less than the EPA standards, with a reasonable margin of safety, the sludge may be reclassified as nonhazardous. This reclassification would allow the generator to dispose of the waste by less expensive nonhazardous waste methods. EPA has established a "delisting" procedure for generators of hazardous sludges to petition for the reclassified status.

TABLE 1

EPA STANDARDS FOR LEACHABILITY

OF SLUDGES UNDER THE EP TEST[a]

Contaminant	Maximum Concentration (mg/liter)
Arsenic	5.0
Barium	100.0
Cadmium	1.0
Chromium	5.0
Lead	5.0
Mercury	0.2
Selenium	1.0
Silver	5.0

[a]U.S. Environmental Protection Agency, Federal Register, V. 45, No. 98:33122, May 14, 1980.

The results from the leaching tests on electroplating sludges are highly variable, depending on the types and concentrations of metals in the sludge, the amount of free and interstitial wastewater present in the sludge, and the final pH of the aqueous solution. Some electroplating treatment sludges readily pass the EP test while others fail due to high leaching of one or more metals. The sludge samples from the ALCs have shown a tendency to fail the leaching test for chromium and cadmium making their delisting impossible at this time.

This experimental research project was designed specifically to help the Air Force reduce the quantities of hazardous sludge produced by treatment of their mixed metal wastewaters, then treat the toxic metal sludges to allow delisting and ultimate disposal via methods approved for nonhazardous wastes. Because disposal costs are often a function of waste volume, the goal of minimizing the sludge volume could greatly reduce the overall cost of waste treatment.

This project consisted of five tasks and was conducted over a 2-year period. While this paper focuses on the two experimental phases, all five tasks are described briefly to illustrate the scope of the project.

Task I: A comprehensive literature search was conducted to establish the current state of technology for the removal of dissolved metals from industrial wastestreams and for the separation of heavy metals from mixed-metal sludges.

Task II: The EP test was used to characterize sludges generated at Air Force IWTPs to obtain baseline data on the hazardous nature of these sludges.

Task III: This experimental oriented task involved laboratory-scale testing of selected processes designed to reduce the dry weight of solids generated during the metal precipitation process.

Task IV: This task, also experimental in nature, involved the development of sludge treatment techniques to reduce the leachability of toxic metals to a level that would qualify the sludges for delisting. In addition, an effort was made to investigate methods of metal separation and recovery.

Task V: Basic design and cost data are currently being developed for a prototype system employing the most promising techniques from Tasks III and IV.

As developed, completion of these tasks would fulfill three objectives. First, as previously mentioned, the main focus was placed on end-of-pipe treatment processes that would be simpler

and quicker to put on line. Next, the criteria for selection of the final treatment process were to include capital costs, operating costs, metal removal efficiency, and complexity of operation, with the greatest emphasis on the dry weight of both hazardous and nonhazardous sludges. Finally, the sludge produced would be required to leach less than one-third the level deemed hazardous by EPA. This constraint was selected because delisting petitions are decided on a case-by-case basis. Previous contact with EPA had revealed that a sludge would generally have to demonstrate this low level of leaching to receive approval for delisting.

Experimental Study of Metal Removal Technologies

Hydroxide precipitation using lime for pH adjustment was identified in Task I as the "conventional treatment technology" to remove metals from mixed metal wastestreams. This treatment method was therefore selected as the control for evaluation of all other tested technologies. Metal removal processes identified in the literature search with the potential for producing a reduced quantity of sludge were selected for screening tests. The potential processes were evaluated using a computerized worth assessment model designed to provide an objective ranking based on a list of input characteristics. The following processes were selected for the Task III experimental screening studies:

1. Lime treatment - To provide baseline data.

2. Caustic treatment - Hydroxide precipitation using caustic in place of lime for pH adjustment to study the effect of pH reagent on sludge generation.

3. Water softening - Since water hardness varies by location, the effect of water softening on sludge generation was investigated.

4. Segretated treatment of hexavalent chromium - This treatment step was studied to determine the effect of segregated treatment on sludge generation.

5. Treatment chemicals for the reduction of hexavalent chromium - Since ferrous sulfate and sodium bisulfite are commonly used, a comparison of sludge generation was done.

6. Combined oxide precipitation and cyanide oxidation - This treatment technology uses a strong oxidizing agent such as ozone to treat cyanide and produce a sludge mixture of metal oxides and metal hydroxides. Although ozone was reportedly used to condition the precipitate following the pH adjustment of mixed metal wastewaters

with lime in the Ozodyne process, the use of a strong oxidizing agent to carry out the actual precipitation had not been performed.

7. Sodium borohydride (SBH) treatment - Although the literature indicated SBH could precipitate single or dual metal waste streams, treatment of complex metal waste streams and sludge generation were investigated.

The screening tests demonstrated that lime treatment produced 945 mg of sludge per liter of contrived wastewater.[1] The composition of all the contrived wastewaters used in this project are presented in Tables 2 through 5. This sludge was observed to settle well.

TABLE 2

COMPOSITION OF CONTRIVED WASTEWATER #1 (WW#1)

For Task III Screening Tests

Constituent	Concentration, mg/l	Chemical Used
Cr^{+6}	15	CrO_3
Cr^{+3}	30	$Cr(NO_3)_3 \cdot 9H_2O$
Cd^{+2}	1	$Cd(NO_3)_2 \cdot 4H_2O$
Cu^{+2}	25	$CuSO_4 \cdot 5H_2O$
Ni^{+2}	10	$NiCl_2 \cdot 6H_2O$
Fe^{+2}	20	$FeSO_4 \cdot 7H_2O$
$CaCO_2$	80	$CaCO_3$
Mg^{+2}	40	$MgCl_2$
Na_2CO_3	0	Na_2CO_3
Na_2SO_4	100	Na_2SO_4

[1] All sludge concentrations (volumes) are on dry weight basis and comparisons between methods were on a mg/l basis.

TABLE 3

COMPOSITION OF CONTRIVED WASTEWATER #2 (WW#2)

For Task III Screening Tests

Constituent	Concentration, mg/l	Chemical Used
Cr^{+6}	15	CrO_3
Cr^{+3}	30	$Cr(NO_3)_3 \cdot 9H_2O$
Cd^{+2}	1	$Cd(NO_3)_2 \cdot 4H_2O$
Cu^{+2}	25	$CuSO_4 \cdot 5H_2O$
Ni^{+2}	10	$NiCl_2 \cdot 6H_2O$
Fe^{+2}	20	$FeSO_4 \cdot 7H_2O$
$CaCO_2$	240	$CaCO_3$
$Mg^{+2}{}_2$	120	$MgCl_2$
Na_2CO_3	0	Na_2CO_3
Na_2SO_4	100	Na_2SO_4

TABLE 4

COMPOSITION OF CONTRIVED WASTEWATER #3 (WW#3)

For Task III Screening Tests

Constituent	Concentration, mg/l	Chemical Used
Cr^{+6}	15	CrO_3
Cr^{+3}	30	$Cr(NO_3)_3 \cdot 9H_2O$
Cd^{+2}	1	$Cd(NO_3)_2 \cdot 4H_2O$
Cu^{+2}	25	$CuSO_4 \cdot 5H_2O$
Ni^{+2}	10	$NiCl_2 \cdot 6H_2O$
Fe^{+2}	20	$FeSO_4 \cdot 7H_2O$
$CaCO_2$	0	$CaCO_3$
$Mg^{+2}{}_2$	0	$MgCl_2$
Na_2CO_3	381	Na_2CO_3
Na_2SO_4	100	Na_2SO_4

TABLE 5

COMPOSITION OF CONTRIVED WASTEWATER FOR TASK III COMPREHENSIVE STUDIES AND TASK IV

Constituent	Concentration, mg/l	Chemical Used
Cr^{+6}	56.8	CrO_3
Cr^{+3}	18.8	$Cr(NO_3)_3 \cdot 9H_2O$
Cd^{+2}	1.3	$Cd(NO_3)_2 \cdot 4H_2O$
Cu^{+2}	1.7	$CuSO_4 \cdot 5H_2O$
Ni^{+2}	1.0	$NiCl_2 \cdot 6H_2O$
Fe^{+2}	20.0	$FeSO_4 \cdot 7H_2O$
CN	10.0	KCN
$CaCO_3$	80	$CaCO_3$
Mg^{+2}	40	$MgCl_2$
Na_2CO_3	0	Na_2CO_3
Na_2SO_4	100	Na_2SO_4

Treatment of the wastewater using caustic in place of lime demonstrated the potential for reducing the sludge volume by as much as 60 to 75 percent; however, the sludge was characterized as having poor settling and handling characteristics.

While neither water softening nor segregated treatment of hexavalent chromium were found to have an appreciable effect on solids generation, chromium reduction using ferrous sulfate had greatly increased production of sludge. The results, presented in Table 6, show that the use of ferrous sulfate instead of sodium bisulfite resulted in 31 times more sludge. Further, the reduction reaction proceeded more slowly with ferrous sulfate as evidenced by the slow change in oxidation-reduction potential (ORP) during the treatment process. This slow reaction is likely to lead to the overaddition of ferrous sulfate, which would increase sludge generation even further.

Oxide precipitation and simultaneous cyanide oxidation using hydrogen peroxide demonstrated the potential for significantly reducing the dry weight of sludge produced during treatment. The sludge volume was comparable to that achieved by caustic treatment and the sludge exhibited superior settling and handling characteristics. Cyanide was found to be effectively destroyed simultaneously with precipitation, thus reducing the number of separate process steps required.

TABLE 6

EFFECT OF FERROUS SULFATE ON GENERATION OF SOLIDS[a]

Wastewater #	Treatment	pH	Settleable Solids, ml/l	Total Suspended Solids, mg/l
1	Combined $NaHSO_3$	2.5	37	1370
1	Combined $NaHSO_3$	2.5	39	--
1	Combined $NaHSO_3$	2.5	--	1145
1	Combined $NaHSO_3$	2.5	--	1215
1	Combined $FeSO_4$	3.3	160	29800
1	Combined $FeSO_4$	3.3	133	25400
1	Segregated $NaHSO_3$	2.5	35	1210
1	Segregated $NaHSO_3$	2.5	33	1190
1	Segregated $FeSO_4$	3.3	290	38000
1	Segregated $FeSO_4$	3.3	250	29000
2	Combined $NaHSO_3$	2.5	17	845
2	Combined $NaHSO_3$	2.5	17	832
2	Combined $FeSO_4$	3.3	135	42200
2	Combined $FeSO_4$	3.3	152	43000

[a]Combined treatment indicates that the entire wastewater solution containing all the metals was mixed prior to treatment for chromium reduction. Segregated treatment indicates treatment for chromium reduction of the wastewater containing only chromium prior to mixing with the other wastewaters. In both cases, the mixed wastewaters were treated with lime to precipitate metal hydroxides following chromium reduction.

Sodium borohydride treatment of the mixed metal wastewater also reduced the sludge volume to the level achieved by caustic treatment and oxide precipitation. In addition to chromium reduction, SBH treatment simultaneously reduces other metal ions to base metal.

The technologies tested in the screening study were then evaluated using the worth assessment model comparing 16 different characteristics of each process to the lime treatment baseline.

The two highest ranking technologies (sodium borohydride treatment and oxide precipitation) were selected for further testing. This second round of tests was more comprehensive and designed to provide statistically significant data to quantify their characteristics in terms of sludge produced.

In the second phase of testing, ozone was used as the oxidizing agent for oxide precipitation. The tests revealed, however, that ozone was so powerful an agent it caused trivalent chromium to reoxidize to the hexavalent state. Therefore, hydrogen peroxide was used for the remainder of oxide precipitation tests.

The quality of the effluent produced by oxide precipitation was very good. The sludge produced by oxide precipitation fell within 295.9 to 345.4 mg/liter of wastewater treated (95 percent confidence limits) with an average of 321 mg/liter. The weight difference of this sludge, as compared with that from lime treatment (985 mg/l) was determined to be significant with nearly 100 percent statistical confidence. However, the oxide sludge leached hazardous amounts of cadmium and chromium when subjected to the EP test and the sludge was unstable. After a sample of the wastewater containing sludge was allowed to stand overnight, it exhibited the yellow color characteristic of hexavalent chromium. Thus, even though hydrogen peroxide is a weaker oxidizer than ozone, it also is too strong an oxidizing reagent. This factor rendered simultaneous oxidation/precipitation unsuitable for practical application.

Analysis of the filtered SBH effluent showed that the process was capable of consistently producing effluent with metal concentrations below detection limits. The effluent, when decanted following clarification rather than filtered, was still of very good quality. Effluent data for the SBH treatment tests are presented in Table 7. These concentrations compare favorably to the EPA's effluent limits presented in Table 8.

The sludge produced by the SBH process fell within 293.7 to 323.6 mg/liter of wastewater treated (95 percent confidence limits), with an average of 309 mg/liter.

Again, the weight difference of this sludge, as compared with that from lime treatment (985 mg/l) determined to be significant with nearly 100 percent statistical confidence. However, as shown in Table 9, the sludge produced by SBH treatment leached hazardous amounts of both cadmium and chromium.

TABLE 7

EFFLUENT DATA FROM SODIUM BOROHYDRIDE TREATMENT TESTS

Sodium Borohydride Treatment Wastewater[a]

Run	TSS mg/l	TDS mg/l	Metals (mg/l)					
			Cr^{+6}	Cr Total	Cd	Cu	Ni	CN
1	314	2930	<0.05	<0.05	<0.01	<0.01	<0.1	<0.05
2	310	2370	<0.05	<0.05	<0.01	<0.01	<0.1	<0.05
3	286	2930	<0.05	<0.05	<0.01	<0.01	<0.1	<0.05
4	330	2380	<0.05	<0.05	<0.01	<0.01	<0.1	<0.05
5	306	2220	<0.05	<0.05	<0.01	<0.01	<0.1	<0.05
6	306	2670	<0.05	<0.05	<0.01	<0.01	<0.1	<0.05
7	-	-	-	0.44	0.01	0.02	0.1	-

[a]Runs 1-6 were treated with sodium borohydride and filtered using industrial filter media. Run 7 was unfiltered.

TABLE 8

U.S ENVIRONMENTAL PROTECTION AGENCY POINT SOURCE EFFLUENT LIMITATIONS[a]

Constituent	Daily Maximum, mg/l	Maximum 30 Day Average, mg/l
Chromium (total)	2.87	0.80
Cadmium (total)	1.29	0.27
Copper (total)	3.72	1.09
Lead (total)	0.67	0.23
Nickel (total)	3.51	1.26
Silver (total)	0.44	0.13
Zinc (total)	2.64	0.80
Cyanide (total)	1.30	0.28
Total Toxic Organics	0.58	--

[a]U.S. Environmental Protection Agency, Federal Register, V. 77, No. 169:38477, August 31, 1982.

TABLE 9

ANALYSIS OF SLUDGE PRODUCED BY SODIUM BOROHYDRIDE TREATMENT

Moisture Content and Leachability Study

Run[a]	Moisture (weight %)	EP Toxicity (mg/l) Cr	Cd	Cu	Ni
1,2	85.3	28.3	12.5	0.74	13.2
3,4	85.4	16.7	12.5	1.20	14.5
5,6	85.8	10.3	9.84	1.21	9.46

[a]Sludges from two runs were analyzed together to provide a sufficient amount of sludge for proper analysis.

Hydrogen gas is evolved during treatment with SBH and it is likely to be a function of the pH of the wastewater. Even though it could be eliminated with optimization of the treatment process, it nevertheless should remain a design consideration.

The oxide precipitation and SBH treatment technologies were again evaluated using these latest test results by another worth assessment model. Based on the stipulated criteria, SBH treatment was selected as the preferred technology. Although the cost of SBH is very high (currently in the range of $14.60/lb.to $17.00/lb. on a 100 percent basis for a stabilized water solution of 12 percent SBH), the reduced quantity of sludge (68 percent less) reduces hauling and disposal costs. A study of treatment system costs indicated that the economics of using SBH treatment are highly site-specific. Factors such as the type and efficiency of dewatering equipment and transportation and disposal costs must be considered. Detailed cost comparisons of SBH treatment and existing systems at the Air Force IWTPs indicate SBH treatment could not be economically applied at all five AF major maintenance centers. However, if the quantity of SBH required can be reduced by optimization studies, or if sludge transportation and disposal costs continue to increase or if present disposal sites close, the economics of SBH application could change. Thus, it is evident that to properly evaluate the SBH treatment technology, a site-specific assessment of current treatment system economics must be accomplished continuously as treatment system costs escalate.

Experimental Study of Methods For Rendering Sludge Nonhazardous

Many liabilities, as well as costs, are associated with the generation and disposal of hazardous sludge. Thus, the

advantage not only lies in minimizing the volume of hazardous sludge, but also in treating the sludges produced to render it nonhazardous. This is the aim of Task 4.

Since SBH treatment may or may not be economical at any given site, the following three sludge types are being tested under this task (still in progress): lime treatment, caustic treatment, and SBH treatment. Thus, the results of this task may be applied to sites using any of these three treatment processes whether or not SBH would be economical. The application of results from this task may, however, affect the economics of employing SBH treatment because delisting a sludge would reduce the total treatment costs.

Potential processes were selected for screening tests based upon information gathered from literature. Five processes were tested initially and these are described briefly below:

1. Solidification: The sludge produced is solidified by combination with a mixture of Portland cement and fly ash.

2. Heat treatment: The sludge is treated by heating and drying under controlled conditions of time and temperature.

3. Leaching: The sludge is treated to selectively leach components for recovery.

4. Barium compound addition: The wastewater is treated with barium-based compounds to stabilize the sludge based on similar process applications identified in existing patents.

5. Sludge aging: The sludge is allowed to age exposed to a sheltered environment.

Data and observations from the screening tests were used in another worth assessment model and three technologies were selected for further testing. Further, a fourth technology was identified at this time and added to the list as follows:

- Barium compound addition
- Heat treatment
- Solidification
- Sludge washing

While barium compound addition did not fare well in the initial screening tests, it was selected due to its simplicity of application. Optimization studies showed the addition of barium acetate could reduce the level of chromium that leached, but the sludge still remained hazardous. Use of barium carbonate increased the leachability of the sludge.

Heat treatment was investigated as a method of reducing both the volume and toxicity of the sludge. The volume reduction that occurs is primarily a result of water loss, whereas a reduction in toxicity would be a result of physical and/or chemical changes in the sludge. These physical/chemical changes, considered to be mainly a collapse of the gelatenous structure of the sludge, were observed during sludge drying in a previous project (AES/EPA Cooperative Agreement). It was hypothesized that this process could be accelerated by the application of heat.

Results of the heat treatment studies indicate that temperature has a significant effect on the leaching of metals, particularly chromium and nickel. Over a specific time, if temperature is increased, the metals leaching from the sludge decrease to very the leachability increased, as shown graphically in Figure 1. While complete sample drying at 120°C took approximately 2 hours, the leaching was minimized after one hour of treatment.

The results of these tests show that heat treatment may be a viable means of rendering sludge nonhazardous, but this depends on the sludge composition. A high degree of process control would be required to ensure that the treated sludge would be nonhazardous. Although this technology would require some energy input, it could be provided by a low level waste heat source. In addition to "detoxification," the sludge volume decrease would further reduce transportation and disposal costs.

To date, solidification has made two types of sludges nonhazardous: lime and SBH. Solidification tests using caustic sludge are currently underway.

In evaluating the solidification experiments, the solidified samples were first subjected to the EPA integrity test. This impact test breaks the solidified sludge and then the pieces are run through the EP test.

Tests to date have indicated that up to 18.2 percent SBH sludge and 47.7 percent lime sludge can be mixed with Portland cement and fly ash and be rendered nonhazardous. The higher sludge percentage for lime mixtures can be attributed to the good bonding characteristics of the lime sludge, cement, and fly ash.

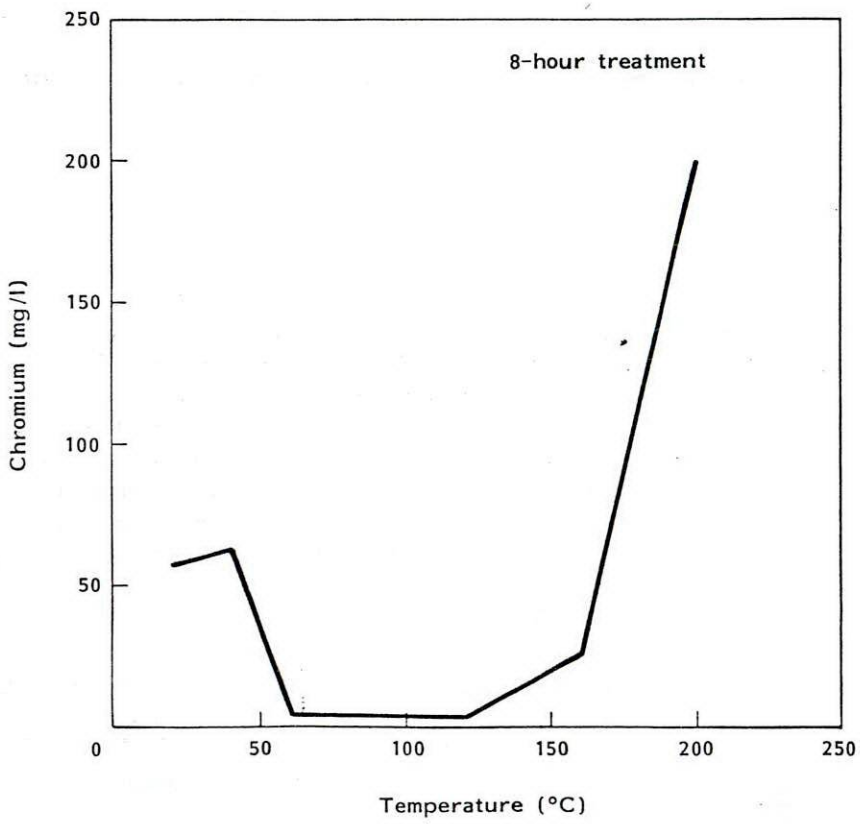

Figure 1. Heat Treatment Temperature Study - EP Results for Chromium

As with SBH, the economics of employing solidification are highly site specific. A detailed economic evaluation of transportation and disposal costs and a subjective evaluation of liability would be required to assess the applicability of this technology. Liability would be particularly important if the sludge were disposed of in a landfill owned or operated by the plater.

Sludge washing is also being tested. Initially, it was hypothesized that washing the sludge with a dilute ammonium chloride solution would cause collapse of the gelatinous structure of the sludge and reduce its leachability. Tests to date, however, have indicated that although the leachability of the sludge is not reduced, its dewaterability is enhanced by the washing

process and the wash solution does not require treatment following the process. Additional tests using water for washing are currently being performed. Preliminary results indicate that this procedure may also be effective in improving the dewaterability of the sludge. This is particularly significant in that the volume of sludge for disposal could easily and inexpensively be reduced if the procedure proves to be effective in repeated tests.

Conclusions and Summary of Results

The results from this project indicate that innovative technologies may be economically applied to both reduce the volume of mixed metal electroplating treatment sludges and render these resulting sludges nonhazardous. However, the economics associated with employing these technologies are highly dependent on site-specific factors and warrant a detailed study of total treatment costs before application. Further, with increasing treatment and/or disposal costs, reevaluation of these technologies is warranted. The more important results obtained from studies performed to date under this project are as follows:

1. The use of ferrous sulfate, rather than sodium bisulfite, for the reduction of hexavalent chromium results in a dramatic increase in sludge generation. The increase from ferrous sulfate was 31 times the amount of sludge produced by the bisulfite process.

2. The use of caustic in place of lime for the precipitation of metals as hydroxides results in a reduced quantity of sludge. The sludge, however, without additional treatment, does not settle as well as the lime sludge and is perceived to be more difficult to handle because of the delicate nature of the floc.

3. Oxide precipitation and simultaneous cyanide oxidation using hydrogen peroxide or ozone should produce an effluent of good quality when applied to non-chromium mixed metal wastewaters; however, if chromium is present, it will reoxidize to the hexavalent state.

4. Sodium borohydride treatment of mixed metal wastewaters is capable of producing a high quality effluent without filtration, or an effluent with metal concentrations below detection limits when filtered with industrial filter media.

5. Substitution of SBH treatment for lime treatment of mixed metal wastewaters can result in a 68 percent sludge reduction. This is illustrated graphically in Figure 2. The economics of employing the SBH treatment technology are highly dependent on site specific factors. Economic applicability of the technology must therefore be evaluated on a case-by-case basis.

6. Heat treatment was determined to be a viable process for rendering SBH sludge nonhazardous if subjected to strict control.

7. Solidification was determined to be effective in rendering both lime treatment and SBH sludges nonhazardous. The maximum aggregate substitution for each sludge on a dry weight basis, was determined to be 47.7 percent lime sludge and 18.2 percent SBH sludge.

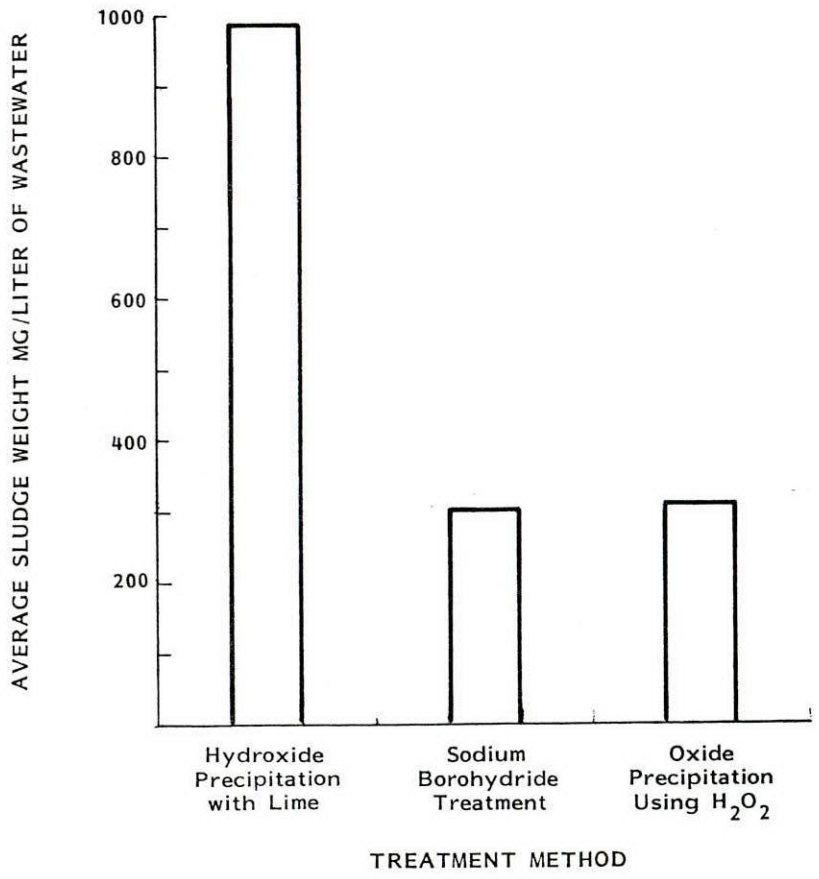

Figure 2. Comparison of Dry Weights of Sludge Produced by Treatment Methods Tested, Average Sludge Weight mg/liter of Wastewater Treated vs. Treatment Method.

A-5

Research Session A

Influence of Magnetic Fields on the Electrodeposition of Chromium

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INFLUENCE OF MAGNETIC FIELDS ON THE ELECTRODEPOSITION OF CHROMIUM

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Abstract

It is shown that magnetic fields increase the current efficiency of chromium deposition, and reduce the volume of hydrogen gas produced. These effects are attributed to the Lorentz force on ions which causes visible convection in the electrolyte. This convection apparently lowers the cathode temperature sufficiently to account for the observed increase in chromium deposited and reduction in hydrogen evolved.

Introduction

In recent years, a number of investigators have reported that magnetic fields applied during electrolysis produce very significant effects on various aqueous electrolytic processes. Laforgue-Kantzer concluded that a Hall effect occurs in aqueous electrolytes (1). This effect was attributed to the Lorentz force on protons which were postulated to have a finite lifetime in the un-hydrated state. The basis for the explanation of her results was that the un-hydrated proton has a velocity which is about 10^5 times as large as the drift velocity. In her model, the drift velocity of the proton is represented as a composite of the relatively slow velocity in the hydrated state and the extremely high velocity in the un-hydrated state. Virlan and Parsadanjan reported that iron deposited electrolytically in the presence of a magnetic field has very significantly increased hardness and reduced porosity (2). They attributed these effects to magnetohydrodynamic sweeping of H_2 molecules off of the deposit.

A report by Perakh shows that nickel and iron-nickel films deposited in a magnetic field have greatly different macrostresses compared with films deposited without a magnetic field (3). This report hypothesizes that changes in the macrostress level may be caused by changes in the amount of hydrogen gas produced during electrodeposition, although the author stated that it was unclear why a magnetic field changes the amount of hydrogen co-deposited with the metal. The results of references (2) and (3) are consistent with Laforgue-Kantzer's work, i.e., they can be understood if protons are preferentially deflected away from the cathode by a magnetic field.

Dash et.al. showed that magnetic fields improve the uniformity of electrolytic thinning in the preparation of specimens for electron microscopy (4). In a later report Dash and King reported that magnetic fields improve the uniformity of copper deposits and simultaneously reduce the resistance of the copper deposition cell (5). These authors also determined the effect of magnetic field orientation on the profiles produced by anodic thinning and by cathodic deposition. Gak and Rokhinson found that a magnetic field of 4 kG doubles the limiting current for deposition from 0.1 N $CuSO_4$, 0.1 N $CuCl_2$, and 0.1 N $NiSO_4$ (6). They also determined that the current density above which powder-type deposition occurs increases continuously with magnetic field strength in the range zero to 12 kG. As an example, a field of 4 kG allows deposition of compact copper at 40 percent higher current density than

zero applied field. In studies of flow cells, Mohanta and Fahidy found that the imposition of a uniform magnetic field can prevent the existence of limiting currents at moderate Reynolds numbers (7).

As originally observed by Frary (8), magnetic fields cause circulation of electrolytes during electrolysis due to the force on moving charged particles. The electrolyte circulates around the magnetic flux lines, as expected from the Lorentz force (equation 1 below). This circulation is analogous to mechanical stirring, and it therefore should reduce the concentration overpotential and increase the limiting current. An important difference compared with mechanical stirring is that magnetic stirring persists through the double layer until the moment when ionic discharge occurs or it begins at the moment when an ion is formed on the surface of an electrode. In comparison, mechanical stirring is not effective within the adsorbed layers of liquid on the electrodes. Thus, it should be expected that, if the magnetic force is significant compared with the electrical force on ions, then there must be significant effects on electrode processes (including adsorption and surface diffusion) in the presence of an applied magnetic field.

In the presence of electric and magnetic fields, the Lorentz force on an individual ion in the electrolyte is given by (1):

$$\vec{F} = q\,(\vec{E} + \vec{v} \times \vec{B}) \qquad (1),$$

where $\vec{F}$ = Lorentz force on an ion,

q = ion charge,

$\vec{E}$ = electric field,

$\vec{v}$ = ion velocity, and

$\vec{B}$ = magnetic field.

If only an electric field is present, an ion moves in the direction of the electric field. When a magnetic field is superimposed, the magnetic component of the Lorentz force causes the ion to circulate around the direction of the magnetic field. Positive ions and negative ions move in opposite directions in the electric field. Because their motion and their charges are opposite, the magnetic force on them is in the same direction. This produces circulation of the electrolyte (8).

An estimate of the magnitude of the magnetic force acting on the bulk electrolyte to produce circulation can be made as follows. In an electrolyte the total moving charge per unit volume is given by

$$\frac{q}{V} = \frac{i_1}{v_1} + \frac{i_2}{v_2} + \ldots + \frac{i_n}{v_n} \qquad (2),$$

where q is the charge (C), V is the volume (cm^3), i_1, i_2, . . . i_n are the individual ionic current densities at an electrode (A/cm^2), and v_1, v_2, . . . v_n are the magnitudes of the individual ionic velocities (cm/sec).

Assuming B normal to v_1, v_2, . . . v_n, the magnitude of force per unit volume of electrolyte is

$$\frac{F}{V} = \left(\frac{i_1 v_1}{v_1} + \frac{i_2 v_2}{v_2} + \ldots \frac{i_n v_n}{v_n}\right) B$$

$$= (i_1 + i_2 + \ldots + i_n)\, B$$

$$= iB \qquad (3),$$

where B is the magnitude of the magnetic field and i is the total current density at the electrode.

For $i = 10^{-1}$ A/cm^2 and $B = 10^4$ gauss, $\frac{F}{V} = 100$ dynes/cm^3.

This force is opposed by frictional forces, so the rate of bulk circulation depends on the viscosity of the electrolyte.

Even in the absence of bulk circulation of the electrolyte, magnetic fields produce significant effects on electroysis (9,10). For example, in five similar experiments with applied magnetic field of 3.3 kG, a total of 30 Leclanché cells in the magnetic field produced 24 per cent more energy than 30 similar cells discharged under the same conditions with no applied magnetic field. The power for the cells in the magnetic field was continuously greater for the first 100 minutes of discharge in all five of these experiments (10). Here, circulation is absent, due to the high viscosity of the electrolyte. According to accepted theory (11), the rate-limiting reaction depends on proton motion to the cathode and the subsequent polarization produced by the reaction products. If proton motion to the cathode is inhibited by magnetic fields, then some other (as yet undetermined) reaction must become rate-limiting.

The results in references (1,2,3,9,10) are all consistent with the hypothesis that magnetic fields preferentially inhibit proton motion to the cathode in a wide variety of electrolytic cells. In the present work, another system was chosen in which hydrogen co-deposits with a metal, namely, electro deposition of chromium from aqueous CrO_3 solutions. Measurements were made of the quantity of chromium deposited and of hydrogen gas produced as a function of the applied magnetic field strength.

Experimental

Figure 1 shows a diagram of the circuit used for electrolysis. All experiments were performed at constant current, with the cell in the magnetic field connected in series to the cell outside the field. Thus, the current through both cells was exactly the same in each experiment. The potential difference across each cell was recorded continuously for all experiments. The cell used for current efficiency experiments is illustrated in Figure 2, and Figure 3 shows the cell used to measure hydrogen evolution. Table 1 gives other experimental conditions for both types of experiments.

Magnetic fields greater than one kG were applied with an electromagnet (Varian Model V4004), and fields below one kG were applied with either a Variflux permanent magnet (Laboratory for Science Model 2) or with the electromagnet. The magnitude of the magnetic field was determined for each experiment with a Bell Model 620 gaussmeter (accuracy $\pm$ 1.5 percent). The variation of the field within the gap is included in Table 4.

Some temperature data were taken with a thermometer and some were taken with a thermocouple, both of which were calibrated.

The standard chromic acid electrolyte, containing 250 gm CrO_3 per liter and a ratio of CrO_3 to sulphate ion of 100:1, was used in all experiments. The electrolyte was changed after each nine-hour deposition experiment and after four hydrogen evolution experiments.

The cathodes were all cut from 25 μm-thick nickel (0.9999 Ni). These

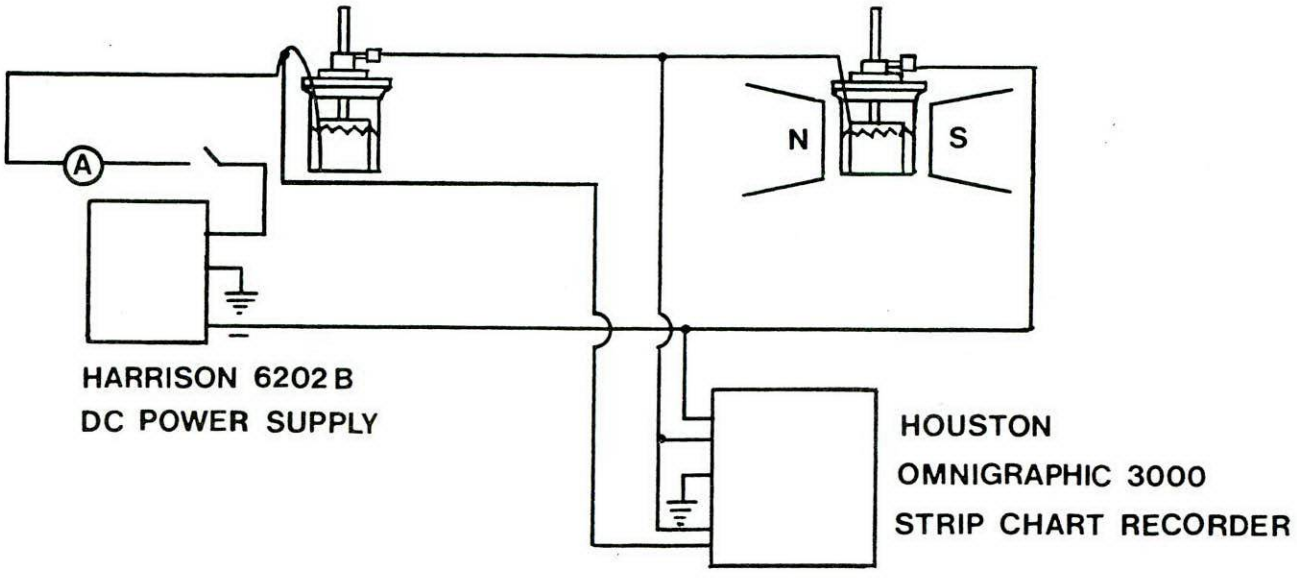

Figure 1
Diagram of the circuit used for both the current efficiency and the hydrogen evolution experiments.

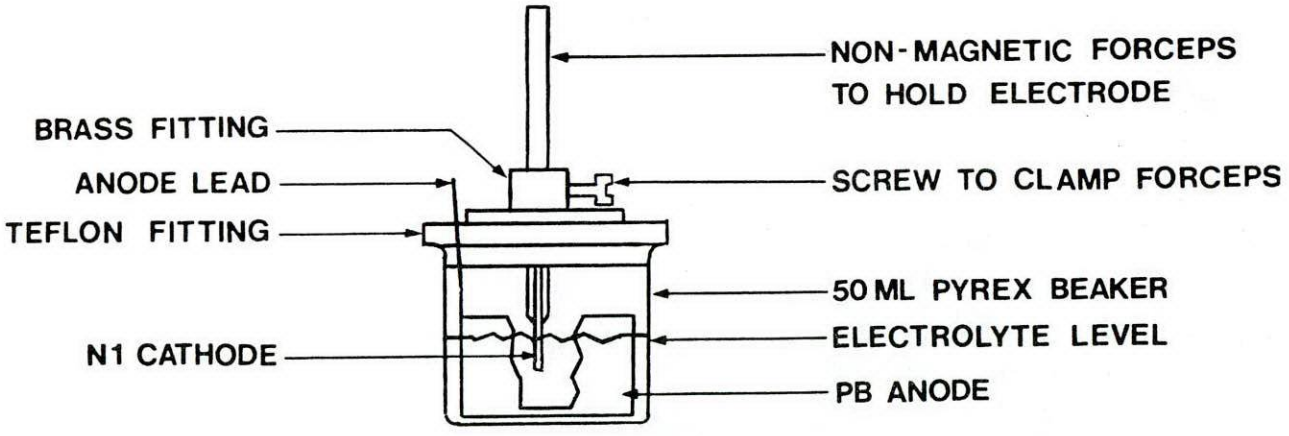

Figure 2
Diagram of the cell used for experiments on the current efficiency of chromium deposition.

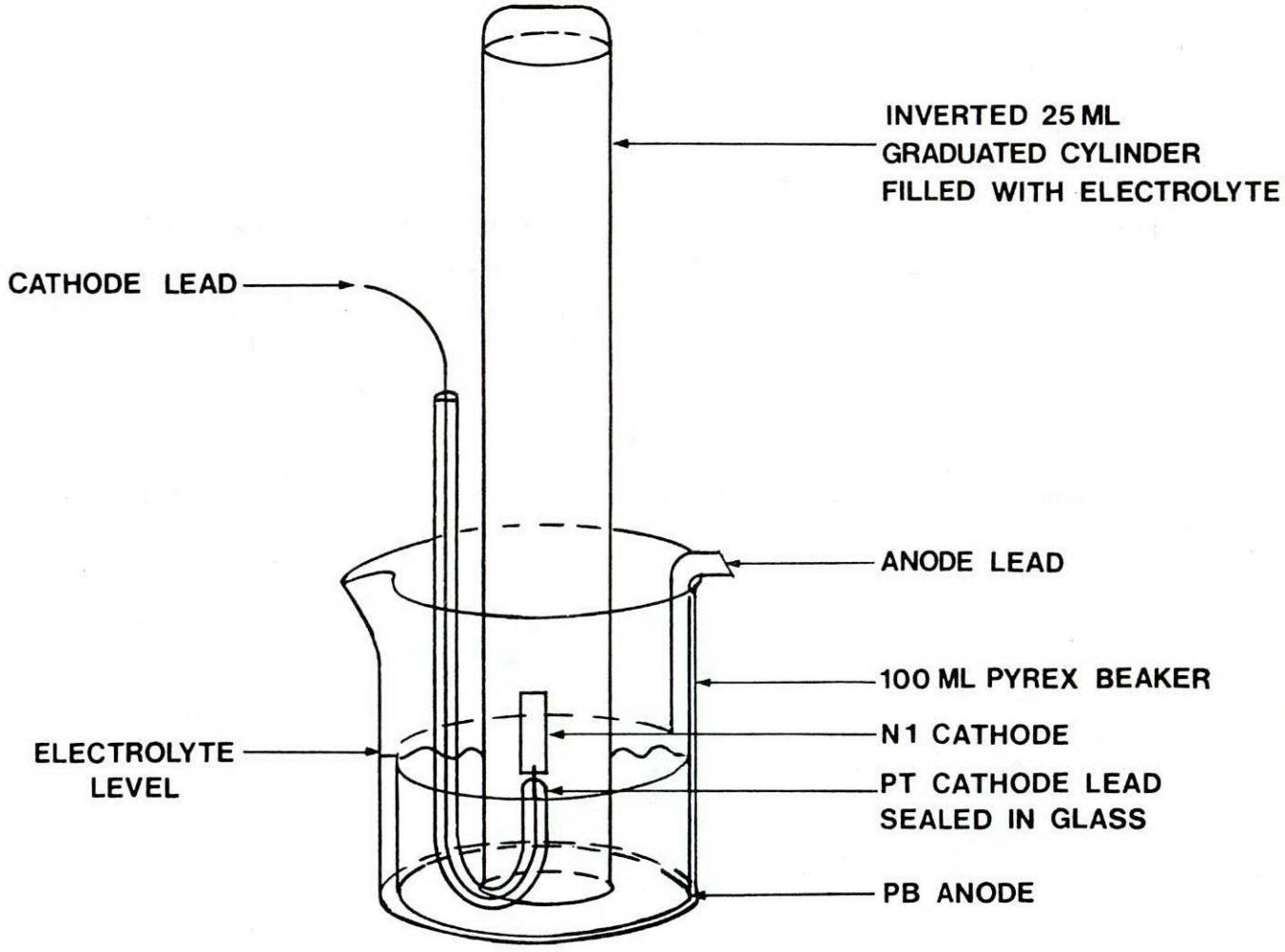

Figure 3
Diagram of the cell used for experiments on hydrogen evolution during chromium deposition. The nickel cathode is spotwelded to the platinum lead wire.

EXPERIMENTAL CONDITIONS	TYPE OF EXPERIMENT	
	Current Efficiency	Hydrogen Evolution
Current (ma, $\pm$ 0.5)	180	270
Surface Area of Cathode Immersed in Electrolyte (cm^2 $\pm$ 0.05)	0.3	0.45
Approximate Current Density at Cathode (amp/cm^2)	0.3	0.3
Time	9 hours $\pm$ 0.01	25 minutes $\pm$ 0.1
Size of Lead Anode	Diameter 3.3 cm Height 3.8 cm	Diameter 3.7 cm Height 2.15 cm

Table 1

Conditions used for current efficiency and hydrogen evolution experiments.

were cleaned ultrasonically with a detergent, rinsed with distilled water, and air-dried. The cylindrical lead anode (0.99999 Pb) was chemically polished after each experiment by immersing in a solution of 20 percent H_2O_2 (30 percent) and 80 percent glacial acetic acid for ten seconds, rinsing in distilled water, and air-drying. New cathodes were used for each experiment.

Hardness tests were made on cross sections of cathodes from the current efficiency experiments with a Tukon hardness tester using a Knoop indenter under a load of one kG. The electrodes were first mounted in epoxy and heated for 69 hours at 96 C in an effort to reduce the amount of hydrogen present in the deposits and possibly develop porosity. After this heat treatment, the mount was ground and polished to produce a smooth, plane surface.

Results

1. Current efficiency experiments. The results for six experiments are given in Table 2. Because the current efficiency for chromium deposition decreases rapidly with increasing electrolyte temperature (12), it is essential to refer data for deposition in and outside a magnetic field to the same electrolyte temperature. In all experiments, the electrolyte temperature at the start was closely the same for the cell in the field and the cell outside the field. For experiments one and two, in which the permanent magnet was used, the final electrolyte temperature for the cell in the field was about 0.8 C lower than for the cell outside the field, due in part to the magnet polepieces. In experiments three to five, this effect is more pronounced because the field was applied with a water-cooled electromagnetic and the polepieces were below room temperature. In experiment six, the effect of the polepieces is less because the higher magnet current required for the eight kG field warmed the cooling water to room temperature or higher.

A plot of the current effeciency versus temperature data for B = 0 is given in Figure 4. Using the line in this plot, which was determined by the method of least squares, the data for each experiment were corrected, and the averaged results are given in Table 3. This shows that magnetic fields in the range 0.8 to eight kG significantly increase the current efficiency for chromium deposition.

Except for the first two minutes, the cell potentials decreased linearly with time. The total decrease in each experiment was about 0.05 v. The average potential given in Table 2 ignores the spike (about 0.3 v high) which was present at the beginning of every experiment for both cells. The lack of dependence of cell potential on the magnitude of the applied magnetic field in these results is in contrast to the case of copper deposition at similar current densities, where concentration overpotential is large (5). This suggests that concentration overpotential is absent in chromium deposition due to convection induced by the formation and dispersion of gas at the electrodes, as noted previously in the case of nickel electrowinning (13).

The main difference in appearance of the deposits made in a magnetic field compared with those produced without a field is that the former have more uniform color from top to bottom of the deposits. All deposits (except that made with B = 8 kG, experiment 6) have a light gray color at the top of the electrode and a dark gray color at the bottom. The extent of the light gray zone decreases with increasing magnetic field strength until it disappears at 8 kG (Figure 5). This effect is caused by motion of the electrolyte induced by the Lorentz force on ions, as described above.

The results of hardness tests on the electrodes shown in Figure 5 are

EXPT.	FIELD (kG)	AVERAGE CELL POTENTIAL (v ± 0.005)	MASS OF CHROMIUM DEPOSIT (gm ± 0.0001)	ELECTROLYTE TEMP. (C ± 0.1) Initial	Mean	Final	CURRENT EFFICIENCY (gm/coulomb ± 0.002 X 10^{-5})
1	0	3.07	0.1931	21.4	22.7	23.9	3.31 X 10^{-5}
	0.763	3.07	0.1957	21.5	22.3	23.1	3.36
2	0	3.07	0.1894	22.8	24.3	25.9	3.25
	0.763	3.07	0.1921	22.6	23.8	25.0	3.29
3	0	3.06	0.1779	23.5	25.2	27.0	3.04
	2	3.05	0.1912	23.5	24.1	24.7	3.27
4	0	3.01	0.1694	23.0	25.3	27.5	2.91
	2	3.05	0.1914	23.0	23.5	24.0	3.28
5	0	3.02	0.1741	25.5	26.3	27.0	2.99
	2	3.08	0.1928	25.0	25.0	25.0	3.30
6	0	3.03	0.1787	25.4	25.7	26.0	3.06
	*8.0	3.07	0.1944	24.7	25.1	25.5	3.33

Table 2

Effect of a magnetic field on the current efficiency of chromium deposition. The field was normal to the cathode surface in experiment 1 and parallel to the cathode surface in all other experiments.

* In this experiment the field in the magnet gap ranged from 8.00 to 8.45.

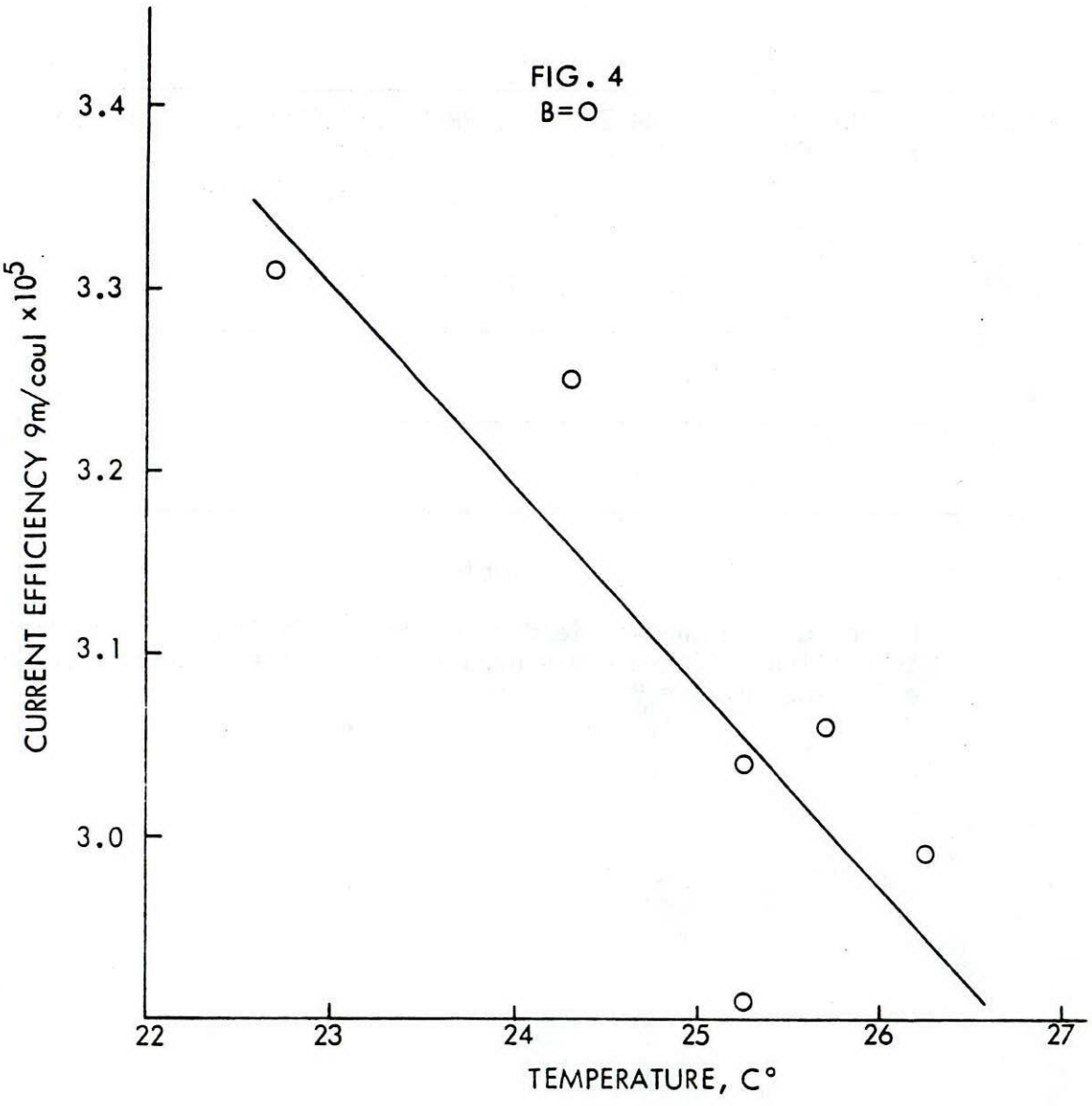

Figure 4

Current efficiency of chromium deposition versus temperature for the cell outside the magnetic field. The line in the figure was calculated by the method of least squares.

FIELD (kG)	NUMBER OF EXPERIMENTS	AVERAGE TEMP °C	CURRENT EFFICIENCY gm/coulomb		INCREASE DUE TO B %
			In Field	Outside Field	
0.763	2	23.1	3.33×10^{-5}	3.29×10^{-5}	1.2
2.0	3	24.2	3.28	3.17	3.5
8.0	1	25.1	3.33	3.07	8.5

Table 3

Effect of a magnetic field on current efficiency of chromium deposition. Figure 4 was used to obtain the data for current efficiency at B = 0.

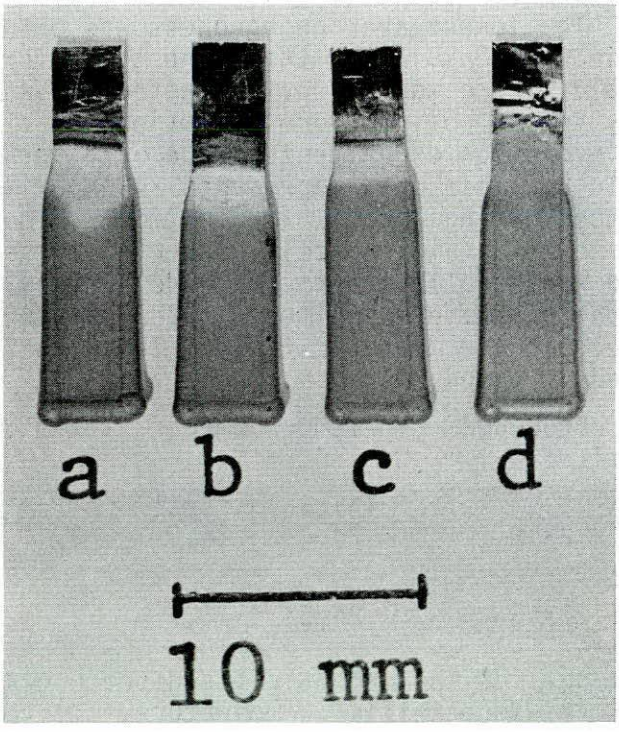

Figure 5

Effect of a magnetic field on the appearance of chromium deposits: (a) B = 0; (b) B = 0.8 kG; (c) B = 2 kG; (d) B = 8 kG.

given in Table 4. These data indicate that a magnetic field has only a small effect on the average hardness, but it significantly improves the uniformity of hardness. For example, hardness ranged from 633 to 670 KHN for electrode b (deposited in a field of 0.8 kG) compared with 621 to 706 KHN for electrode a (no magnetic field during deposition). These two deposits have the same average hardness. The lowest average hardness was obtained for electrode d, (deposited in a field of 8 kG), and the highest was for electrode c (deposited in a field of 2 kG). There was no obvious effect of a magnetic field on the amount or porosity in the polished cross sections.

2. Hydrogen evolution experiments. The data for these experiments is summarized in Table 5. This data represents 24 experiments, in each of which the hydrogen produced during chromium deposition was measured for one cell in a magnetic field and for a similar cell connected in series outside the field. The magnetic field was parallel to the cathode surface in all of these experiments. In only one of these experiments was a greater volume of hydrogen produced by the cell in the magnetic field. The data for the experiment in which this occurred is given below:

B kG, ± 0.005	H_2 Produced ml, ± 0.1	Temperature °C, ± 0.1 initial	final	Time min., ± 0.1	Source of Field
0	23.2	24.4	26.5	25	-
0.25	23.6	24.5	26.7	25	permanent magnet

For the cells outside the magnetic field the electrolyte temperatures ranged from 22.8°C (minimum initial temperature, T_i) to 28.2°C (maximum final temperature, T_f). The average temperature for all experiments outside the field $\left(\frac{\text{av. } T_i + \text{av. } T_f}{2}\right)$ was 25.3°C. The temperature range for all experiments in the field was 22.8 C to 27.6°C, and the average temperature was 24.7°C.

The volume of hydrogen produced by cells outside the field ranged from 23.2 ml to 24.4 ml, and the average for all experiments outside the field was 23.9 ml. For cells in the field, the range was 20.1 ml (at 7 kG) to 23.7 ml (at 0.25 kG), and the average for all experiments in the field was 22.4 ml. In these results there is no regular increase in volume of hydrogen produced with increasing temperature. For example, the group 3, no field experiments (Table 5) at an average temperature of 26.2°C produced less hydrogen than the group 4, no field experiments at an average temperature of 24.9°C. However, there is a definite decrease in volume of hydrogen produced with increasing magnetic field strength, as shown in Figure 6.

Discussion of Results

Our measurements show that a magnetic field slightly increases the current efficiency of chromium electrodeposition. The convection of the electrolyte caused by the magnetic field enhances heat dissipation from the electrodes (14). Thus, the electrodes in the cell located in the magnetic field tend to run approximately 1°C cooler than the electrodes in the cell outside the magnetic field. This should enhance chromium deposition efficiency, because of its strong temperature dependence, Fig. 4. For example, the data

Specimen	Trans. KHN		Long. KHN		Av. KHN (Long and Trans) / 2
	Av.	Range	Av.	Range	
a (B=0)	666	641-706	645	621-670	656
b (B=0.8kG)	662	649-670	649	633-666	656
c (B=2kG)	670	645-702	662	645-684	666
d (B=8kG)	658	645-688	645	633-684	652

Table 4

Hardness of electrodes shown in Fig. 5. Knoop hardness numbers (KHN) were determined with a Tukon hardness tester, using a one kG load. Twenty readings were taken in a cross section of each electrode approximately eight mm from the top. Ten were parallel and ten were perpendicular to the plane of the electrodes.

GROUP	B(kG)	H_2 PRODUCED (ml ± 0.1)			AVERAGE ELECTROLYTE TEMPERATURE (C ± 0.1)		
		Ave.	range Min.	Max.	Initial	Mean	Final
1	0	23.7	23.2	23.9	25.0	25.8	26.5
	0.25 ± 0.005	23.5	23.3	23.7	24.5	25.6	26.7
2+	0	23.8	23.4	24.2	24.9	25.7	26.5
	0.5 ± 0.02	23.3	23.0	23.5	24.8	25.7	26.5
3	0	23.9	23.9	24.2	25.6	26.2	26.8
	0.5 ± 0.02	23.0	22.8	23.4	25.3	25.5	25.6
4	0	24.1	23.8	24.2	23.8	24.9	26.0
	1.0 ± 0.03	22.9	22.4	23.1	23.7	24.3	24.8
5	0	23.7	23.3	24.0	22.4	23.6	24.7
	1.75 ± 0.05	21.9	21.8	22.0	22.2	22.8	23.3
6	0	24.2	23.9	24.4	25.3	26.1	26.8
	3.50 ± 0.08	21.0	20.4	21.6	24.5	25.2	25.8
7+	0	23.5	23.4	23.5	23.4	24.3	25.1
	7.0 ± 0.1	20.5	20.1	20.8	22.8	23.5	24.1

Table 5

Effect of a magnetic field on the volume of hydrogen co-deposited with chromium. Group 1 and 2 experiments were performed with the permanent magnet and all others were performed with the electromagnet. The averages are for four experiments, except for groups 2 and 7 (+) in which only two experiments were performed.

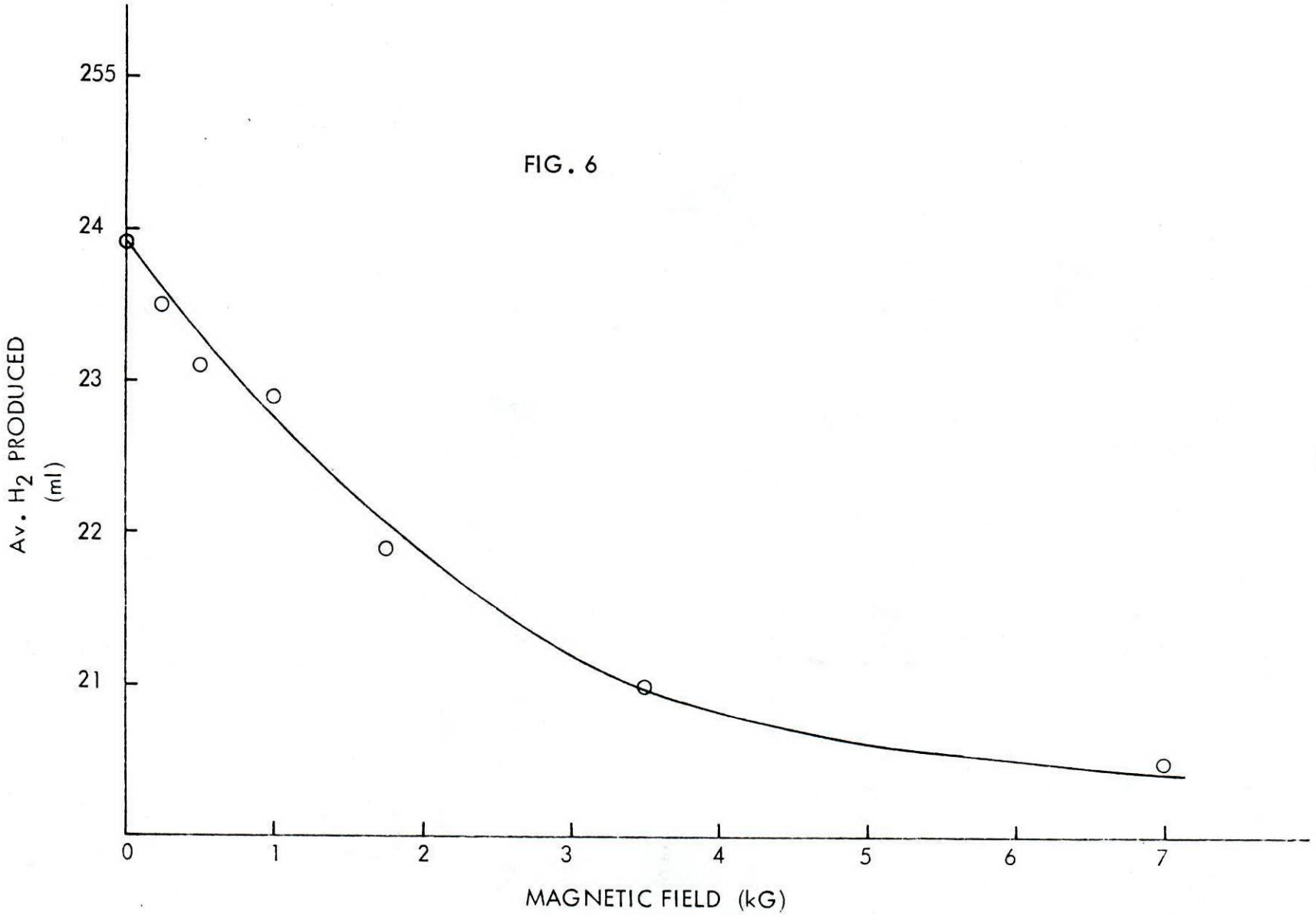

Figure 6. Effect of a magnetic field on the volume of hydrogen produced during deposition of chromium.

in Table 3 at 2 kG show that the average current efficiency obtained for the cell in the magnetic field was 0.11 X 10^{-5} g/C greater than for the cell outside the magnetic field. From Fig. 4, it is apparent that this increase in current efficiency can be obtained by a decrease in electrolyte temperature of 1°C. We suggest that the effect of convection caused by the applied magnetic field is to lower the temperature of the cathode by approximately 1°C compared with the cathode temperature in the cell outside the magnetic field, even though the bulk electrolyte in both cells is at the same temperature.

Fig. 6 indicates that a magnetic field of 2 kG reduces the amount of hydrogen gas collected by about 2 ml (after passage of 405 coulombs). The magnetic field causes visible swirling of the gas bubbles in the electrolyte, resulting in dissolution of some of the gas and passage outside the collection tube of some of it. These latter two effects probably reduce the volume of hydrogen gas collected by about 0.2 ml (14). The current consumed by the enhanced deposition of chromium accounts for about one-third of the reduced hydrogen volume. It is possible that the remainder of the current resulting from reduced hydrogen formation may have been consumed in enhancing the formation of Cr (III) at the cathode, but we did not measure Cr (III).

A recent study concluded that a magnetic field promotes the discharge of molecular hydrogen during cathodic charging and inhibits the diffusion of atomic hydrogen into steel (15). These effects occur in the absence of competing cathode reactions. In our experiments, competing cathode reactions are favored by reduced temperature. Convection of the electrolyte induced by the magnetic field reduces cathode temperature, thus enhancing chromium deposition and inhibiting discharge of molecular hydrogen. We have no information on the hydrogen content of the deposits, but the long deposition time probably permitted saturation of all deposits with hydrogen.

Acknowledgements

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A-6

Research Session A

Plating on Titanium: Process and Applications

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PLATING ON TITANIUM - PROCESS AND APPLICATION

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INTRODUCTION

Electroplating on titanium and titanium alloys with good adhesion of the platings to the substrate has been made possible by special activation of the titanium alloys (1). The process is simple to be carried out and it is reproducible. Hence, this method can be used for the application of functional electroplatings to titanium and titanium alloys.
Applications required are the following ones:
Salvaging of components/Restoring of dimensions required
Protection against wear
Tribological coatings
Protection against stress corrosion cracking
Protection against oxidation at elevated temperatures.

PLATING PROCESS

Experimental procedure

The titanium alloys used for testing are Ti6Al4V, Ti2Cu, IMI 685, Ti6Al2Sn4Zr2Mo and pure titanium (Table 1).
The platings were deposited using common electroless and electroplating baths.

The plating process requires the following operation sequences: Vapour degreasing, Blasting, Pickling, Activating and Plating. The process parameters are shown in Table 2.

An advantage of the process is, in contrast to conventional processes, that plating must not be carried out immediately after activation. This type of activation guarantees a properly bonded deposit without the need for an intermediate layer. Pickling and activation processes are combined with stock loss. Pickling removes material at the rate of approximately 3 µm per area, and activation at approximately 3 µm per area, i. e. total stock loss of about 6 µm.

The different steps of the process result in special surface conditions clearly to be recognized by visual inspection. A uniform, stainless medium-grey colour indicates the effective activation of titanium alloys. In addition to this grey colour, Ti2Cu shows a characteristic longitudinal grain-flow.

Mechanism

The activation of titanium materials prior to plating is made possible by the selective dissolution/passivation activity of the activation solution.

With titanium alloys this selectivity means that:

The baser phase is dissolved

The surface topography generated by activation depends on the alloy and on its heat-treatment condition.

SALVAGE OF COMPONENTS

Adhesion

Plated parts withstand bend tests that deform the metal, machining and thermal shock. Quantitatively, the adhesion of deposits - determined by different adhesion tests (Figs. 1, 2) - ranges from 70-120 N/mm^2.

Application

Several engine parts out of dimension have been nickel plated or electroless nickel plated to salvage these components. Some examples are shown in Figs. 3-5. Thickness of nickel plating ranges from 0.1 to 0.6 mm (= 0.004-0.024 inch). Platings have been finished to dimensional shape by turning, milling or grinding.

Additionally to these machining operations, being good adhesion tests, plated test sheets have been prepared for determination of the adhesive strength.

TRIBOLOGY

The tribological characteristics of titanium in conjunction with electroplatings were investigated using a pin on disc apparatus and an oscillating wear tester (Figs. 6, 7).

Coefficient of friction

The coefficients of friction of electroplatings in conjunction with Ti6Al4V, determined in the pin on disc test, are shown in Table 3. If the coefficients of friction are compared with that of the Ti6Al4V-Ti6Al4V combination, it is revealed that the coefficient of friction of cobalt and cadmium in association with Ti6Al4V is lower than that of the Ti6Al4V combination, and the coefficient of friction of all the other combinations is higher than that of the combination Ti6Al4V-Ti6Al4V (μ = 0.45).

The tribological characteristics at room temperature can be changed at elevated temperature. Table 3 shows that at a temperature of 300 ^{o}C the coefficient of friction of the chromium - Ti6Al4V combination falls to 0.45 (30 ^{o}C μ = 0.65), while the coefficient of friction of the other combinations at 300 ^{o}C remain virtually unaffected.

Under the conditions of the oscillating test, the characteristics are somewhat different from those under sliding conditions. The major difference here being the rise in the coefficient of friction in relation to the number of cycles. This is particularly noticeable with the combination cobalt - Ti6Al4V, where the coefficient of friction increases from 0.3 to 0.85. The coefficient of friction is raised to 0.7-1.0 for all combinations.

Wear

Under sliding conditions, the wear characteristics of the Ti6Al4V pin against electroplatings differ according to the material of the countersurface. The wear is minimal against silver, copper and cobalt, moderate against electroless nickel and nickel, and maximal against chromium.

These wear characteristics of titanium at room temperature, in principle, do not change at a test temperature of 300 ^{o}C.

The wear of the Ti6Al4V under oscillating conditions is minimal against silver, slight against cobalt, moderate against copper, nickel and electroless nickel, high against chromium, and maximal against nickel composite coatings.

BEHAVIOUR AT ELEVATED TEMPERATURES

Adhesion

Adhesion of nickel platings can be improved by a heat treatment.

Heat treatment at 480 °C for 2 hours increases the adhesion of nickel on Ti6Al4V to 300 N/mm^2 and on Ti2Cu to 165 N/mm^2.

To improve adhesion of chromium on titanium temperatures of more than 750 °C are required.

Interdiffusion

The effects of heat treating the plating - titanium couples were examined after prolonged annealing at different temperatures. The results of interdiffusion were evaluated by light microscopy, and electron microprobe scans. In addition, phase determinations by these two techniques were confirmed by x-ray diffraction analysis. Depending on the plating and temperature, different effects can be observed.

Nickel or electroless nickel on titanium form Ti_2Ni and $TiNi_3$ by diffusion of nickel atoms into the base metal (Fig. 8). These compounds form two intermediate layers, which are inserted between the nickel coating and the titanium base metal in the order of nickel-$TiNi_3$-Ti_2Ni-titanium alloy. The formation of the third intermetallic compound, TiNi, theoretically possible according to the phase equilibrium diagram (2), has not been detected.

The diffusivity of nickel in titanium is remarkably high. In a 24 h treatment at 600 °C the diffusion distance, $\sqrt{4\,Dt}$ is 8 μm. This interdiffusion reaction starts already at temperatures of about 450 °C. As consequence of the high nickel diffusivity, Kirkendall voids are formed at the $TiNi_3$-Ni interface.

Cobalt or copper form a Ti_2Co or Ti_2Cu intermediate layer within an acceptable time at temperatures of 600 °C.

Chromium diffuses "normally" into titanium at temperatures of $\geq$750 °C.

CONCLUSION

Titanium alloys can be plated reaching good adhesion. Engine components made in titanium materials can be salvaged by plating.

The tests show that the combination of cobalt or cadmium with titanium results in favourable coefficients of friction. The wear of titanium alloys can be kept low, if a soft plating is used as the partner. Silver, cadmium, cobalt and copper are particularly favourable. As cadmium and silver can lead to solid embrittlement of titanium (3), operating temperature of the components to be plated are to be considered when using plating in these materials. Unfavourable tribological combinations are titanium with nickel or chromium.

Nickel plating on titanium alloys exposed to temperatures above 450 ^{o}C give rise to the formation of layers of intermetallic phases. Layers will be formed with cobalt or copper plated titanium alloys at temperatures above 600 ^{o}C. Chromium - titanium diffusion starts above 750 ^{o}C.

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Alloy	Alloying Constituents Al	Cu	Sn	Mo	V	Zr	Alloy Type
Ti6Al4V	6	-	-	-	4	-	α , β
Ti2Cu	-	2	-	-	-	-	α
Ti6Al2Sn4Zr2Mo	6	-	2	2	-	4	α , β
IMI 685	6	-	-	0.8	-	5	α , β

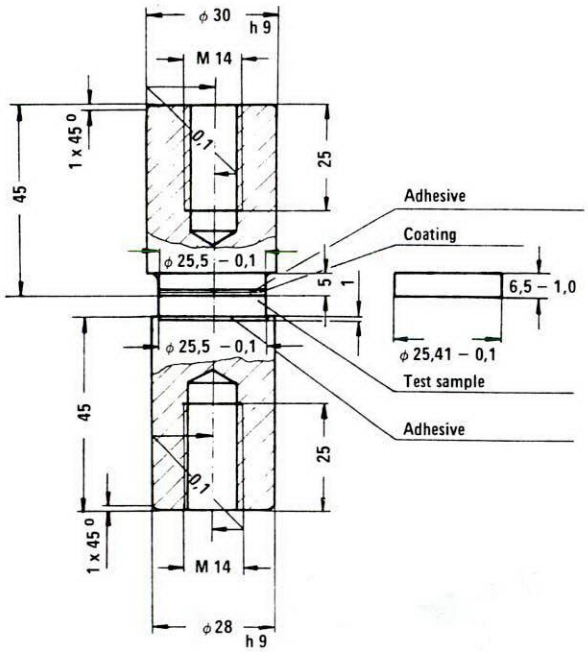
Table 1 Titanium alloys

Step	Time (min)	Components	Temp. °C
Vapour degreasing	5	CCl_2 = CHCl (stab)	87
Blasting	-	Al_2O_3/270 mesh 4 bar	-
Pickling	15	HNO_3/HF	25
Activating	30	CrO_3/As_2O_3/HF	50
Plating	/um	Co/Cr/Cu/Ni/Ni-P	50

Table 2 Plating process

Coating	POD 30°C	POD 300°C	SRV 20°C
Ag	0.70	0.65	0.70 - 1.05
Cd	0.34	-	-
Co	0.30	0.27	0.2 - 0.85
Cr	0.65	0.43	0.6 - 0.7
Cu	0.8	0.63	0.6 - 0.7
Ni	0.85	0.75	0.65 - 0.75
Ni/P	0.46	0.43	0.55 - 0.8
Ni/P(400°C/1h)	0.59	0.57	0.6 - 0.65

Table 3 Coefficient of friction



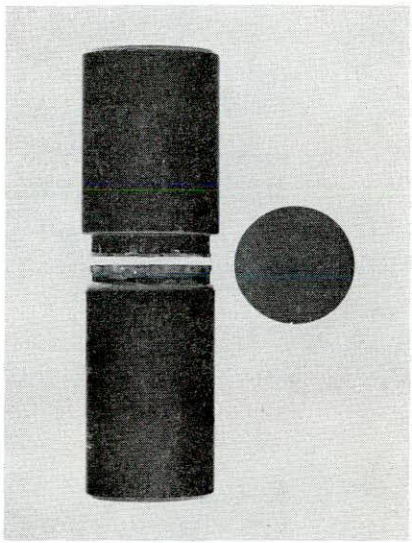
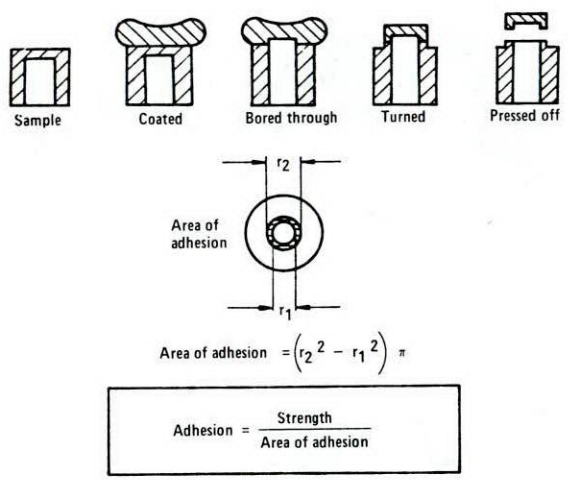


Fig. 1 Face-tensile test/sample



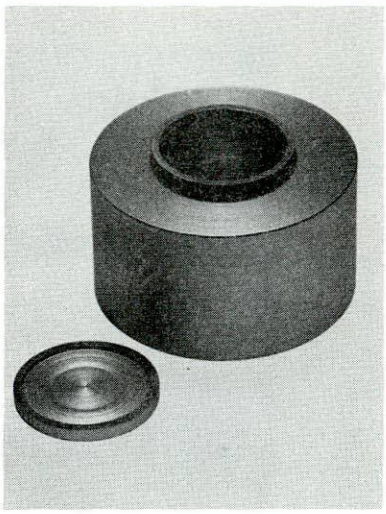


Fig. 2 Adhesion test by pressure/sample

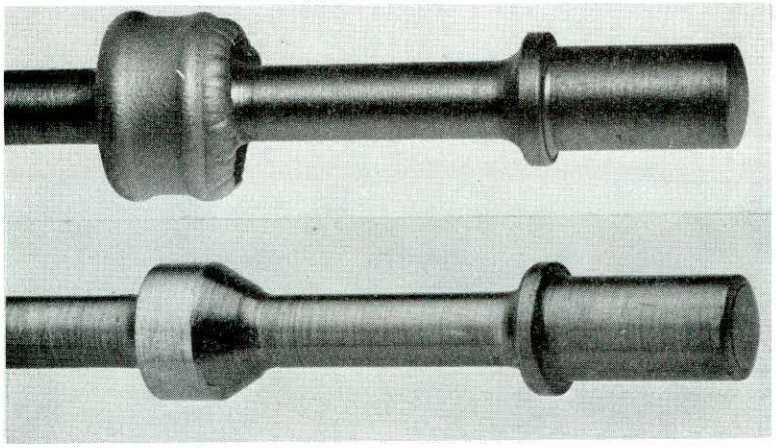


Fig. 3 0.1 mm Ni on Ti6Al4V, turned and ground

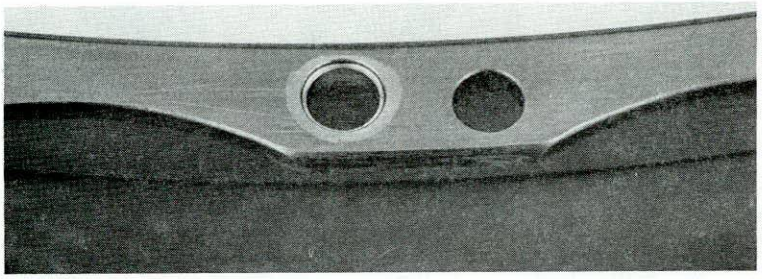


Fig. 4 0.15 mm Ni on Ti6Al4V, milled and bored

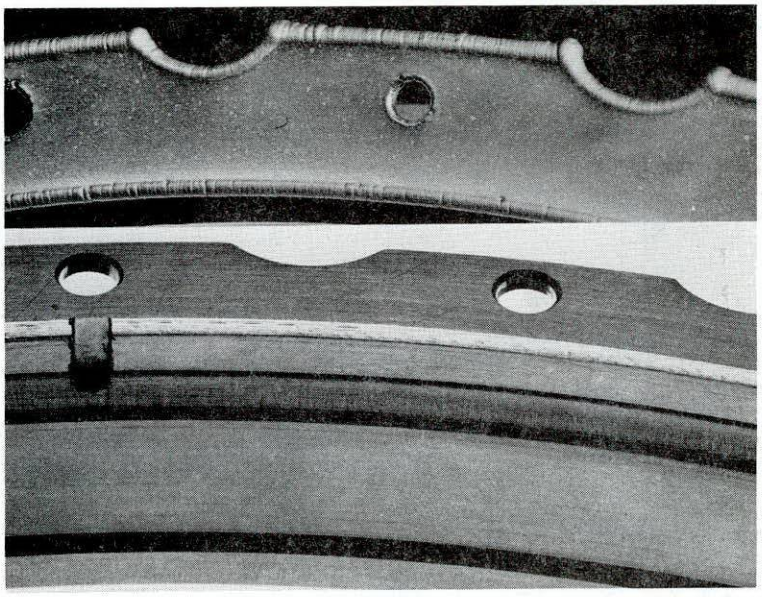


Fig. 5 Ni on IMI 685, turned

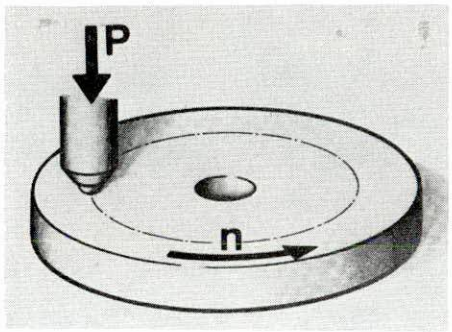


Fig. 6 Pin on disc

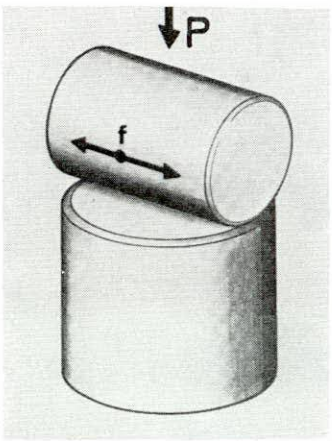


Fig. 7 Oscillating wear test

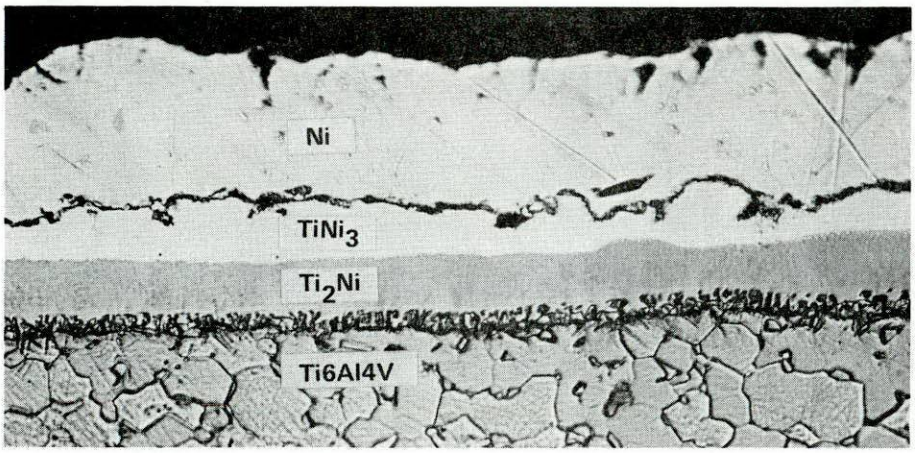


Fig. 8 Ni on Ti6Al4V, heat treatment 600 ^{o}C/100 h (x1000)

B-1

Management Session B

Solving Alcohol and Drug Abuse Problems in the Work Place

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SOLVING ALCOHOL AND DRUG ABUSE PROBLEMS IN THE WORKPLACE

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It has been reported that half the Fortune 1000 companies have instituted some type of program to help employees solve personal problems. Heading the list are employee alcohol and drug abuse programs. The reason: alcohol and drug abuse effect, conservatively, 6% of a company's work force. Because of the prevalence of the problem and the associated economic costs, "alcohol and drug abuse represent greater losses to business than all other illnesses combined.

Underlying this claim is a data base that has been developing since the 1960's, with much of the data generated ultimately by business and industry itself. Studies have shown, for example, that the chemically dependent (C.D.) employee is absent two to eight times as frequently as the average employee, has two to three times the risk of being involved in an industrial accident, and three times the medical claims. The resulting loss to the employer has been calculated at 25% of the C.D. employee's annual salary, with some experts placing the figure nearer to 50%.

While more and more companies are beginning to recognize the scope of the problem, many remain uncertain about what their role should be. This is particularly true for the small employer who lacks the resources of the larger corporation.

Traditionally, employers believed they had two options: tolerate the problem, or terminate the employee. Never very effective, these options are even less satisfactory today. Ten years ago many companies were able to pass on their inefficiencies to the consumer, covering their losses due to toleration. Few companies find themselves in that position today. Yet a a number of recent arbitration cases demonstrate, it is no longer acceptable to terminate C. D. employees without first offering help.

What are concerned employers to do when they have problem employees and reason to believe that work-related problems may be due to alcohol or drug abuse? The answer is, "confront the troubled employee." Because that often appears like a difficult task for the employer or supervisor, it may be useful to outline a few simple "how to's.." As you will see, the process is one the average employer can do and do

successfully. Any extra time and energy spent in the short run should be more than compensated for by the long range benefits to the company and the employee. Above all, the process works.

The first step involves documenting the problem. Identify key work-related issues and document any incidents that provide support. The primary focus should be on work performance. Document separately data that points to alcohol or drug abuse as a part of the problem.

The next step is for the employer to get some assistance. Alcoholism has been recognized as a disease by the American Medical Association since 1955, and most companies today have a chemical dependency treatment program in a hospital that is within a reasonable distance. Use it just as you would use a supplier if you had a problem on a specific electroplating job and needed technical assistance -- for example, in finding the right balance of chemicals for a solution. Because the supplier wants your company's business, he willingly provides consultation on technical matters.

A chemical dependency program supplies treatment. To merit your business, it should be willing to provide technical assistance at little or no cost. The more effective treatment programs today have this service orientation. They recognize that the employer who wants to confront a troubled employee is acting in the employee's best interest. The program should want to help.

Describe the problem to your "consultant," who may be able to offer some useful suggestions in how to approach the specific situation. Include any information that seems to point to alcohol or drug abuse as a key factor. Than arrange for the program to professionally evaluate the employee for chemical dependency. All of this can be accomplished without mentioning the employee's name at this point, so that appropriate confidentially is maintained.

In management terms, the planning phase has been completed. Now is the time to implement the plan and confront the troubled employee. During the confrontation, focus initially only on work-related issues (for example, excessive absenteeism or tardiness). Use documentation to support your concerns. Mention alcohol or drug abuse only if you have documented on-the-job incidents. Finally specify what step in the disciplinary process you are entitled to take (written warning, suspension, termination, etc.)

The first part of the confrontation defines the problem and specifies the potential consequences for the employee. Here the employer is the expert. Only after completing this phase should the focus shift to the alcohol or drug abuse issue. Do not diagnose. Leave that to the professionals. Identify alcohol or drug use as one possible cause of the work-related problems. Indicate that help is available if alcohol or drugs were the problem. Then encourage the employee to call the treatment program to arrange for a professional evaluation. Finally, indicate that a decision on the employee's part to receive professional evaluation, and treatment if appropriate, would be weighed postively in making a final decision about disciplinary action.

If the employee chooses to accept the invitation of help, the employer can count on the treatment program professionals to give an expert assessment. Be sure to provide the treatment professionals with whatever data you have; this can be invaluable to them in the evaluation process. If the employee does have a chemical dependence problem, treatment is the next step toward a solution. Cost will not be a factor in most cases becuse the cost of treatment will be paid for by the employee's health insurance.

While the solution should not create any additional costs, it should save the company money at the same time it helps the employee regain a healthy and productive life. And these cost savings can be dramatic. Employees who are successfully treated for their chemical dependency return to normal levels of absenteeism, accidents and medical claims utilization. Everyone wins.

Before the employee leaves treatment, request an exit interview. The exit interview will provide an opportunity for you to show support. Some employees may also want to review there aftercare plans. Since chemical dependency is a chronic illness, like diabetis, follow-up on their part is essential. A realistic aftercare plan should build in Aftercare sessions as well as Alcoholics Anonymous meetings. Indicate to employee that it is their responsibility to follow through on their plan. Finally, the exit interview can give you the opportunity to begin to clarify work expectation with the employee. Your goal is to regain not only a healthy employee but a productive one as well.

It is worth emphasizing that the outlined approach is a positive one. It does provide a "stick" for the compnay, which has a right to expect the employee to perform up to standards. Toleration gives up this legitimate company right. But this approach gives a big "carrot" to the employee, who has a real incentive to get help for his or her problem. And the "carrot" is there for the company as well. Everyone wins.

B-2

Management Session B

Current Trends in Labor Relations

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CURRENT TRENDS IN LABOR RELATIONS

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The Federal Mediation and Conciliation Service (FMCS) is an independent agency that was created by the 1947 Labor Management Relations Act, also known at the Taft-Hartly Act. We have 400 employees and of that, 248 are Mediators in 82 Field Offices throughout the United States.

FMCS is one of the smallest agencies in the Federal Government, with an annual budget of $22,000,000. Our Service is convinced that the return for that investment far exceeds the cost. Restoring Labor peace and preventing or stortening a strike have enhanced the National economy many times. Our technical assistance programs have also helped immeasurably in promoting improved Labor/Management relations that pave the way for successful contract negotiations.

By law, the moving party (the one who wishes to make changes in the labor agreement) must notify the FMCS 30 days prior to the expiration date of the agreement. For years the unions sent in 99% of the notices to Mediation.

Today, it is companies sending in notices to FMCS to seek changes in their labor agreement.

After the mediator receives the notice he will then contact the parties for the current status. The mediator will then get involved if the parties have reached an impasse or are at a point where they would like some assistance before proceeding with negotiations. There is no fee for the participation of the mediator.

One of the problems at the bargaining table is the inability of labor/management to suppress their suspicious feelings toward each other. Many times the mediator must overcome these obstacles before he can assist the parties in negotiating their labor agreement.

If personalities can be put aside then the mediator can get to the heart of the dispute. The mediator may accomplish this by bringing the two sides together and have a face to face discussion. Many times I will keep the parties apart and work with them separately. By doing this I can frankly discuss the open issues. In these separate discussions the parties will share in confidence their actual positions. The creditability of the mediator is absolutely vital to the process. The main job of the mediator is to get a settlement. It makes no difference to the mediator what kind of settlement, just a settlement that the parties can live with.

The Mediation Service also provides a Technical Assistance Program. When conflicts arise at the bargaining table and there are many grievances on file is usually a sign of a poor relationship. The mediator will offer his assistance to set up a training program in an effort to correct the problem. The program usually involves the union stewards and front line supervisors. These are the people who live with the problems every day. If we can show them how to develop respect for each other, then we are taking a step in the right direction. This is not only improving labor relations, but also human relations, just by using common sense. The programs consist of showing films, lectures, reversing roles, and forming discussion groups.

The other point I would like to make before I change into another topic is how mediators differ from arbitrators. We only assist the parties in arriving at a new agreement, arbitrators have the power to make a final and binding decision, usually in a grievance situation during the term of an agreement.

What's happening at the bargaining table today? There has been a whole new trend to the collective bargaining process. The Department of Labor said the medium increase for all industries in 1982 was 7%, down 2.7% from 1981. I am not seeing those kind of settlements coming out of my part of the country. I assume the reason the figures are high is because they are second and third year wage increases negotiated in 1980 and 1981. In 1982, because of the effects of the Chrysler settlement and the rest of the auto industry, give-backs and take-aways were having rippling effects across the country. This was not necessarily true in all industries, but in

major manufacturing and heavy industries. They too wanted relief in their labor agreements.

The trends at the bargaining table today are concessions, take-aways, relief, give-backs, freezes, deferred increases, and extensions. Take-away negotiations are characterized by a serious request or demand by management either to eliminate or to drastically reduce wage increases. To cut costs, management also focuses on reducing fringe benefits, such as health insurance, vacations and holidays. A factor that has made this very difficult at the bargaining table is that the union and the employees feel that they have already paid for these benefits or won them through previous negotiations.

While reducing wages or fringe benefits is a hallmark of take-away negotiations, one of the most important considerations is the perception by the employees as to whether or not such reductions are actually needed. You may be able to convince the union negotiating committee of the real need for such relief, but trying to convince the membership may well be an entirely different matter.

I have found where the need has been demonstrated well in advance of the bargaining process, the employees and the union will have a better understanding of the needs of the employer to make these concessions. Where management has kept their employees updated about the state of the business and kept the communication door open, they have had the least amount of trouble renewing their labor agreement.

In return for some of the relief given by the Teamsters, UAW and USWA, they have all negotiated some concessions from management, which benefit their members in the long run. There are guarantees or delays on plant shutdowns, or no layoffs after a certain seniority date, and programs for employees to share in the profits.

I mentioned earlier in my paper about the thirty day notice. The required form is called the F7 notice and it must be sent in if an agreement is not reached 30 days prior to the expiration date of a labor agreement. A good reason for the union not to send in a notice is when they know the company will want

concessions. Some labor agreements call for automatic renewal of the present agreement if the F7 notice is not sent into the Mediation Service.

I was recently involved in a case where the union did not send the notice. The union would have been pleased to renew the same agreement for one more year. The company was wise to this and sent me the notice. During negotiations the union gave the employer the impression they would strike on the termination date. This turned out to be a decoy. The company was concerned about their perishable products, and went ahead and laid off all of the employees. The union employees filed for unemployment benefits and the company protested the employees claim. The state has yet to make a determination. The union meanwhile had no plans on striking and intended to keep negotiating. The union believes these actions will keep the current agreement intact and therefore no employee would lose any benefits that the company wants to rengotiate.

The foregoing is simply to illustrate some of the new strategies being used by unions during this economic slump. There are many other things that were unusual about this case too numerous to mention at this time.

With the nation's unemployment rate running well over 10% and the current administration predicting more of the same through 1983 and maybe even 1984, this leaves little hope for the unemployed. The deficiet could be $200 billion plus in 1984. Government economists have said for every 1% the unemployment rate goes up, another $25 billion is added to the deficiet. Ex-Secretary Ray Marshall said last year that if unemployment can be lowered to 5% or 6%, the government would have a surplus. One other alarming fact is that plant utilization ran at 67% in 1982, only 2/3 of their capacity.

There was a recent article by Chet Swanson in "Enterprise", the journal of the University of Cincinnati College of Business Administration. He stated how he makes the following key point to an audience, usually a labor or management group. He has them play the roles and asks them three questions.

Role - Employee:
Question: Would you like wages to go up or down?
Answer: Up.

Role - Shareholder:
Question: Would you like dividends to go up or down?
Answer: Up.

Role - Consumer:
Question: Would you like prices to go up or down?
Answer: Down.

The only way wages and dividends can go up, while simultaneously the prices go down, is to have increased productivity. If productivity is to improve, labor and management must learn to work together - as simple as that!!!

Professor Mills from Harvard University laid some ground work by making the following points. He said labor must back off on the rules and restrictions it puts on management. Let management have control of the plants. Management should open their eyes to the problems of the workers. Have some sensitivity to their needs. It should be done by working together, not by writing more rules and restrictions for each other.

Instead of agravating the economic warfare between labor and management during this recession/recovery period, let's make supreme efforts to work together realizing we all have a common goal.

B-3

Management Session B

Pricing: A Practical Approach

John Thomas
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PRICING: A PRACTICAL APPROACH

John M. Thomas
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In a University of Michigan study on the plating industry, platers listed pricing as their major problem in 61% of the cases. (1)

What will be presented here is a simple and accurate approach to pricing. In fact, the system owes its accuracy to its simplicity. It is a system that allows the manager to visually tie his price estimates to his P&L statement, and in addition, to gauge his daily production against his pricing as a measure of his ongoing profitability.

This is not a new system. It has been used for decades by some of the most financially sophisticated manufacturing companies.

If profitability is the goal of the manufacturing organization, pricing is an indispensable key to that goal. All of us have had the experience of underestimating a price and know the difficulty of recovering from such a situation. If we have proper control of our production level and costs, and base our prices on our standard experience, there is no way to recover from bad pricing.

Before we get into the mechanics of this pricing system, let's review where we are to see what deficiencies currently exist and how another approach might deal with them.

Review of Industry Profit and Loss

The essence of this new approach is that it visually ties the price estimating to the P&L so that the manager can predict the effect his pricing will have on his P&L and so that he can track its effect as he goes through his daily production activities. Consequently, it is important to look first at where we are with regard to the Profit and Loss Statement.

For purposes of pricing and general management control, I find that a system that uses rounded numbers and relatively few accounts is easier. Consequently, that is the way the numbers will be presented here.

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(1) The Metal Finishing Industry: A Framework for Successes: Harold E. Arnett and Donald N. Smith, Division of Research, Graduate School of Business Administration, University of Michigan, Ann Arbor, Michigan.

A word of caution is necessary. This concept is to be used only with regard to pricing and general management control. In cost control, for example, it is important to break your costs down into pertinent accounts so that you can decide whether it is possible to lower your chemical costs from 22% to 20% of sales.

Within a few percent, the following chart should look familiar to most of you because it represents the average P&L statement of all plating shops surveyed by NAMF in 1981.

Chart 1. Median P&L Statement - All Companies (1)

Sales		100
	Chemicals	18
	Direct Labor	19
	Overhead	58
	Total Cost	95
Pre-Tax Profit		4.6

With a pre-tax profit of 4.6%, the plating industry is earning at a profit rate just about half that earned by all other manufacturing industries. Worse yet, this profit level is unchanged over the past ten years.

Chart 2. Median P&L Statement - All Companies (2)

		NAMF '81	NAMF '70
Sales		100	100
	Chemicals	18	17
	Direct Labor	19	28
	Overhead	58	50
	Total Cost	95	95
Pre-Tax Profit		4.6	4.5

One has to be struck by the similarity of these P&L statements over an eleven-year span, particularly so since the

(1) 1981 Financial Management and Executives Compensation Report: Prepared for Members of the National Association of Metal Finishers by Barry E. Miller Company, Reading, Pennsylvania.

(2) 1981 Financial Management and Executives Compensation Report: Prepared for Members of the National Association of Metal Finishers by Barry E. Miller Company, Reading, Pennsylvania.
1970 Financial Management Report, prepared for Members of the National Association of Metal Finishers.

numbers were collected by two different auditing firms. Incidentally, these numbers are available from at least four or five other sources and those sources report numbers almost identical with these.

Some might assume that his problems are unique and that other facets of plating have an easier time of it. That is not the case as the following chart will show.

Chart 3.

All Companies by Type of Plating - NAMF Study 1981 (1)

	All Co's	Rack	Barrel	Engr.
Sales	100	100	100	100
Chemicals	18	21	22	16
Direct Labor	19	17	12	21
Overhead	58	58	61	55
Total Cost	95	95	95	92
Pre-Tax Profit	4.6	4.4	5.0	7.9

Again, one has to be struck by the similarity of the P&L statements for operations as diverse as engineering plating and barrel plating. Also, note the remarkable similarity of the individual accounts.

Incidentally, a more detailed study of such diverse activities as precious metal plating, hand rack plating, and hand barrel plating shows a similar correlation, and thereby dispels many of our stereotyped ideas.

Several conclusions can be drawn. First, our problems are not as diverse as we might imagine. Perhaps the same pricing system will work for all of us.

Second, our profit margins are abysmally low and have been for a decade. All the hard work we have expended on production rates and cost control have not changed our historical profit level.

Third, unless we are all doing a bad job controlling our production levels and costs, pricing must be the missing element. Evidence will be presented to suggest that is the case.

Review of Current Pricing Practices

How good a job do we do on pricing? A survey reported in Industrial Finishing magazine suggests that we don't do very well

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(1) same as page 2

and that we might be our own worst competition in holding down our profit margins.

This study covered 24 states and 18 different types of jobs. The following chart will show an excerpt of only two jobs in six states. The range of error shown in this chart, however, prevailed across all 24 states and throughout the 18 jobs.

Chart 4. Survey of Prices - 1979 (1)

	4" x 7" x .060 (.0003 .00035)	Hex Head Bolt 1/4 - 20 x 2 (.0003 - .00035)
Ohio	.056 - .325	5.00 - 12.94
Indiana	.06 - .34	1.35 - 16.67
Michigan	.064	3.91 - 8.61
Pennsylvania	.05 - .12	9.00 - 20.00
New York	.09 - .27	14.00 - 25.00
Illinois	.057 - .35	9.50 - 15.00
Average	.17	13.38

One can quickly see that the general price variation ranged from 200% - 600% with specific instances much higher. It should be clear that this price variation is not the result of a few firms. This variation prevailed across all 24 states and throughout all 18 jobs.

Worse yet, when one considers the relative simplicity of these jobs being quoted as compared with the complex jobs we quote on daily, one must assume the price variation for our everyday, real-life situations may be at least as bad if not worse than the study indicates.

A pricing variation of 200% - 600% in an industry with a 4.5% profit margin is inconceivable. Perhaps we are after all our own worse competition.

Problems With the Current System

In many industries, a firm manufactures a product with a known selling price--a candy bar for instance. In this situation, management is concerned with production rates, holding down costs, and increased market share.

Our industry is not like that. Our Production is composed of jobs that are individually quoted with a great diversity of size, quantity, type of plating, and individual customer requirements. Most of the time there is no known market price.

(1) Survey of U. S. Plating Prices in Summer of 1979: Industrial Finishing Magazine, January, 1980.

Often it is necessary to do the pricing with incomplete information.

In my opinion most of the pricing problems stem from the pricing system commonly used. In this system, the manager measures the square footage of the piece to be plated, determines the cost of chemicals necessary to cover this square footage (usually from a chart), and then multiplies this answer by a factor (representing the fraction that chemical costs bear to his total costs). As we have seen, chemical costs average 20%; this appropriate factor would be "5" for the average company.

There is a lot of room for error in this formula. Measuring the part may be difficult. Determining the amount of plating on the back side versus the front side may be difficult. The chart of chemical costs per square foot may be wrong. These charts, after all, do assume some average level of chemical costs for cleaning, pickling, post treatment, et cetera. Your costs may be quite different from these. In addition, one has to factor in the cost increases for chemicals, which can be quite difficult if cleaners and acid are going up while nickel metal is going down.

More important to this error is the assumption that the average plating thickness off the production floor will be what you have estimated for the job, say .0004. This is quite an assumption given the varying current densities for most plated parts. Equally important is the practical problem of precisely hitting the plating thickness on the production floor with the myriad of jobs in process. If too much attention is paid to hitting the thickness exactly, the production level can fall dramatically.

In any event, the problem with this system is that any error introduced into the formula thus far will now be multiplied by five (the factor for chemical costs versus total costs). To determine the effect of this error on the P&L, we must now multiply this error by the number of parts to be processed, say a million.

I know that many platers at this point will fudge a factor into the calculation to bring the price closer to what he thought it should be based on his past experience with pricing and operations. Frankly, this probably gives a better answer than the formula gave, but the result is that the manager has compensated for the fact that the formula has broken down. Furthermore, the formula has little predictive value in the effect that job will have on the operation's profit and loss and gives no way to track progress throughout the year.

This formula is further complicated by the fact that actual production rates vary from the theoretical, calculated rates by

a wide margin. In my experience, most managers have an intuitive feel for pricing that is far more accurate than this formula.

The problem is that the manager is now forced to come up with a price which he has no reliable numbers to support. With no market price, the manager must guesstimate a price that will not allow his competition to take all his business. This is the real, practical world we all face in our pricing.

Because we know our own failings, we invariably look at our competition as a perfect competitor. I'll call him a phantom competitor because he is not real. Our phantom competitor does everything right. He doesn't have any downtime, his line rates are all perfect, his employees don't make mistakes and they give one hundred percent effort, one hundred percent of the time. He always has the right machine with the right chemicals to run every job; he always has the right rack or barrel for that particular job; all of his experiments work out as planned; he has lower wage rates, no benefits, no unexpected expenses.

Given the breakdown of a predictive formula, the manager must now guess a low price to protect his business. Remember he has only 4.5% allowable error before he starts losing money.

As we have seen, our P&L experiences are remarkably similar. If you aren't convinced of that at this point, a review of the NAMF survey of 1981 will show the spread for all companies at various sales levels and in different types of plating, and you will see that the correlation exists.

These statistics show that most platers do a good job in controlling production rates and costs. What they lack is a predictive method for quoting prices that is consistant with their actual experience.

Incidentally, the idea of overcoming the problems of under-pricing a job by increasing production rates and lowering costs below what was estimated is pure nonsense. This presumes that the manager is content with running an inefficient shop at all times except when necessary. All you get out of this exercise is a sore foot from kicking the employees.

The "New" Approach

Now let's look at the system based on the income statement, or as some call it, the machine-hour approach.

There is nothing new about this system. When a machine shop says he needs twenty dollars an hour for his grinder, he is using this system. Many large plants use this system to

value the output they must receive off each machine hour for each of their different operations.

Chart 5.

$$\frac{\text{Total Yearly Cost}}{\text{Total Actual Machine Hours}} = \text{Cost Per Hour}$$

The "Total Yearly Cost" figure is taken directly from your P&L statement and is very simply the total of all expenses for last year. This figure represents your successes and your failures. It has included in it all extraordinary charges, the cost of cutting grass, all chemical costs, the cost of all reruns, unproductive labor, customer returns, and your AES dues. In short, it is the total of all of your expenses. Unless you have done something grossly wrong, this is, after all, the total of all expenses that must be covered by your selling price.

"Total Actual Machine Hours" is the total actual machine hours that you were scheduled to run for this past year. This number comes from your production reports and includes every hour you were scheduled to run whether or not you were able to do so because of downtime. It does not include unscheduled machine hours due to lack of sales volume.

The distinction is this: If the machine was scheduled to run, you had employees scheduled in and other variable and overhead costs (heat, for example) committed, and those costs continue whether or not the machine breaks down and they become part of your total costs. Conversely, if a machine is scheduled down for lack of business, the only applicable costs are overhead costs, but with no business to absorb these costs, they must be covered by the actual jobs you do have. Consequently, by using as a denominator only the actual hours worked, these costs will be covered.

Chart 6. Example:

$$\frac{\$950{,}000 \text{ Cost}}{6{,}000 \text{ Actual Hours}} = \$158.00 \text{ / Hour}$$

$$\frac{\$158.00 \text{ / Hour}}{\text{Actual Pieces Produced}} = \text{Cost / Piece}$$

"Actual Pieces Produced" is a number derived from your actual production records. This is not a theoretical, calculated number that would be produced if you had perfect knowledge, prefect racks, no downtime, and a perfect operation. In actual experience, no manufacturing company produces anywhere near the theoretical, calculated line rate and you should not quote your prices as if you did.

At this point, you can see that you have tied your pricing to your real world experience. You have used your actual total

yearly cost; you have used your actual machine hours, and you have used your actual pieces produced per hour, and therefore you have produced a cost per piece that ties together your actual production rate.

Also you should visually be able to see the effect of your pricing on your income statement and have reduced your pricing problem to one of simple arithmetic.

What you need to make the system work is:

1) an accurate total dollar level of expenses: you should be able to get this easily from your P&L.

2) an accurate number of machine hours run: this is important because the number of machine hours will directly affect the level of total expenses. If you do not have this number now, it is important to develop it for accurate use. In the interim, you may make an educated guess as to the number of hours you actually ran and use this as a measure of profitability against the jobs you are currently running until you are able to develop the more accurate number.

3) an accurate number of pieces actually produced: again, you get this number from your daily production sheet, and if you do not have this information, it will be necessary that you develop it. However, your educated guess about this figure will probably be more accurate than your guess about Item #2. Still, I would caution you to continue checking your guess against the actual number of pieces produced in the upcoming months.

Some Refinements

Like any other system, this approach must be tempered with judgment. The advantage of this approach lies in its ability to quickly pull together your actual total experience with regard to costs and production rates. Because of its simplicity, you can easily see the effect of any assumptions or changes you make in this approach.

In this presentation, "Total Yearly Costs" was taken to be the actual cost experience for last year. To the extent that you expect this total cost level to change, for price increases in chemicals for example, you should use your budgeted level of costs for the upcoming year. In doing this, I would review my total costs by each account and make an assumption on the basis of experience as to the anticipated rise of that account. Naturally, some accounts will rise considerably and some hardly at all. Totaling these will give you the anticipated yearly cost for the upcoming year.

"Actual Hours" is taken to be the actual number of machine hours you ran last year. If your machine capacity was significantly underutilized last year and you anticipate a change, you should use the anticipated actual hours. Again, the premium is on being realistic.

If you are quoting a piece of work that uses significantly different levels of chemicals or labor than your average, you can further revise your hourly cost to reflect that change.

For example, let's suppose your shop regularly uses three people per line. Let's assume you are quoting a job that will use four people per line and that your labor costs including fringes is ten dollars per hour. In our example, you would add ten tollars per hour to an actual rate of $158 per hour for a new total of $168 per hour. This will raise your hourly line rate by 6%. This accurately reflects the additional expenditures your firm will incur as a result of taking on this job.

By contrast, a plater using the built-up pricing system with labor as a base instead of chemicals (as in our previous example) would find that he has increased his labor costs 33% and then multiplied that by four (the relationship of labor to total cost). He would then show an increased line rate cost of 33% which would be inaccurately high because his other costs would have been unaffected by the addition of one person.

If you have two machines of equal size, you simply split the total yearly costs in half before dividing by the "actual number of production hours".

If you have several machines of varying sizes, the procedure is simple. Allocate the total yearly costs to each machine according to a formula and then divide that part of the yearly cost by the actual machine hours for that machine. The formula can be square footage of plant space for each machine, man-hours, or any other division you feel is realistic.

In my case, I have four automatics--two large and two medium size. I split the costs according to the relative output of one machine versus the other on a standard size piece that we frequently run. The large machine will produce 50% more than the medium size. Thus, my costs are split: 30% - 30% - 20% - 20%.

Measuring the Effect of Pricing on the P&L

Let me show by way of example the contrast these two pricing systems would have on the Profit and Loss Statement.

We regularly plate a piece of tubing and also a piece of

shelving. Using the chemical-cost-per-square-foot system and assuming no error in calculation, the selling price of the tubing calculates to be ten cents and the selling price of the shelf calculates to be thirty cents. The problem is that I can get ten pieces of tubing in the same area occupied by one piece of shelving. Let's say I get twelve shelves an arm for a total selling price of $3.60 per arm. Alternatively, I get 120 pieces of tubing per arm at ten cents--or $12.00 per arm. Consequently, every time the machine indexes there is a difference of $8.40. The following chart will show the relationship.

Chart 7.

10¢	x	120 pieces / arm	=	$12.00 / arm					
30¢	x	12 pieces / arm	=	$ 3.60 / arm					
									Yearly Revenue
$12.00	x	50	x	21	x	5	x	50	$3,150,000
$ 3.60	x	50	x	21	x	5	x	50	945,000

The second half of this chart shows the effect on yearly revenue of choosing one job over the other. The calculation is $12 per arm times 50 arms per hour times 21 hours per day times 5 days per week times 50 weeks per year. The same is done at $3.60 per hour.

What we see is that one job will produce $2,000,000 additional revenue per year despite both jobs appearing equally desirable on a chemical-cost-per-square-foot basis. This is a dramatic difference but one that we confront every day in our operations.

This example better than any other illustrates the importance of keeping the P&L in front of your mind in pricing jobs and the importance of a pricing system that ties into the P&L. It is important to note that this example assumes that the calculation of square footage and chemical use was correct. This example does not include the possible errors mentioned in our previous discussion of the problems of calculating the correct square footage and chemical costs.

Thus, a plater with perfect calculation of the square foot for each part would nevertheless produce a difference in yearly revenue of $2,000,000 for these two different configurations. Without some system that will allow him to see the effect those calculations played on total revenue, the plater would be tied into a maze that would make it very difficult to see the advantage of going with the one job over the other.

Let's look at the illustration another way and keep in mind the importance of having the P&L in front of you. We know that our overhead cost equals 50% of our total cost. We also

know that these costs are relatively fixed expenses. Which yearly revenue number do you think my overhead cost is 50% of? Or to put it another way, do you really think my overhead will change very much if I take the thirty-cent job over the ten-cent job? If my overhead is correctly 50% of three million dollars, my revenue will be $600,000 short of covering my overhead and with no revenue left to cover chemicals or labor.

Using the System Daily

In managing a plant on a daily basis, I find I need a system that accurately systhesizes all the experiences going on in the plant at a time. There is no way I can pull all of this together in my mind on a three-shift operation and have an idea of the direction of our monthly P&L. I need a system that pulls together my costs, my production level, and my pricing in a simple fashion.

To do this, I keep in mind the chart we previously discussed.

Chart 8. P&L To Use In Pricing

Sales		100
Chemicals	20	
Direct Labor	25	
Overhead	50	
Total		95
Pre-Tax Profit		5

With this in mind I watch the production numbers and calculate mentally three prople at six dollars per hour equals eighteen dollars per hour, and this should be 25% of my selling price for that hour's production. I do the same when taking chemical inventory.

With these numbers in mind, I can quickly see whether we need to either adjust our production level if that is possible or to revise our quoting for similar jobs in the future.

Some Comments

This approach can be used in most manufacturing operations. In a stamping operation, for example, I would calculate an hourly machine time exclusive of material cost and then add the cost of material according to what is required for that specific job because the variation in material cost from job to job could be so great.

In a barrel plating line, the number of barrels produced per hour should be substituted for the number of racks produced

per hour. A barrel plater should realize that his actual costs per hour do not change much whether the barrel is full or half full. Also realize that the cost of production is unaffected by the selling price. If you calculate your cost per barrel to be twenty dollars and charge a customer ten dollars because he filled only half the barrel, you should realize that this is an acceptable decision, but it has cost you ten dollars.

Assuming you are doing your job right, there is no way to recover from a bad price. My experience is that it is easier to sell the right price on the initial bid than to go back to the customer with an exorbitant (percentage-wise) price increase. Requoting diminishes your credibility, and the increase is often impossible to get.

The best time to get a price increase is when you bid the job in the first place. In an industry earning 4.5%, you can double your profit by bidding $.1045 for a job that you would normally bid $.10.

Some platers who use a factor of five times the chemical cost to arrive at a selling price may wish that the factor could be eight. I think it is unrealistic to believe that you can get thirteen cents for a part that you have been selling for ten cents. Our customers won't buy it and our record for the past eleven years shows that we didn't get it. We have seen that you can double your profits by charging $.1045 for a part that you have been charging $.10. I think it is realistic to believe that you can get .0045 more for a ten-cent piece, and if you are successful in doing so, you will have accomplished what the industry has not accomplished in the past ten years.

Thinking back over the past several years, I cannot remember hearing a single plater say that he lost any business because his price was 10-1/2¢ per pound and his competitor's was 10¢. I hear a plater say that he lost business to a competitor at 6¢ per pound versus his price of 10¢. (Remember the Price Survey Chart.)

Nothing impacts the profit and loss statement as fast as a price increase or, conversely, as fast as bad pricing.

Neither this approach nor any other will save your business if it is inherently unsound. By inherently unsound, I mean that your production level is too low or that your costs are too high relative to your competition. Again, the P&L is important for you to study. Comparing your P&L with the industry P&L's will clue you in to the trouble spots. If your costs exceed the norm for all of the important categories, your selling price is probably too low, based on the assumption that the selling price is more likely the problem than is the fact that all of your expenses are out of control.

As a practice, we try to have all jobs returning the same level of profits. Our rationale is that we do not want winners and losers to balance off to some acceptable profit margin. My concern is that my competition will undercut me on the winners and leave me with the losers and consequently an unprofitable operation from which recovery would be almost impossible.

Another concern is that a competitor with a faulty pricing system will steal away even my good business. If the business was sufficiently large and I have calculated my costs correctly, this additional business may bankrupt him in time. My problem is that I would go bankrupt in the meantime. That is the essence of the importance of knowing your costs and pricing accordingly.

We have found by actual count that it is very difficult to rack a part for less than a penny or to unrack it for another penny. Happily, this coincides with our P&L, production level, and pricing system. Using the P&L formula, we see that eight cents becomes a typical selling price. There are exceptions, of course. Some jobs can be racked more quickly and some take longer. It is, however, a relationship that I keep in my mind. I recently quoted against a rack plater who quoted one-half cent per inch for tubing. Consequently, he charged two cents for each four-inch piece, of which the customer had many. There is no way that price could be correct. My practice is to ignore such situations rather than change my price schedule. Following the logic of this presentation, you can see that my price fell below his on the longer pieces.

Because barrel platers generally charge by the pound, we have found that our rack prices generally drop below the per-piece price of barrel plating when the weight of the piece reaches eight to twelve ounces. This puts to bed the fallacy that barrel plating is always cheaper than rack plating and is an example of how the pricing approach can open up a previously unexplored market.

I took a survey in our plant and found that two-thirds of our employees thought we made a profit of 50% or more and one-tenth of the employees thought we had a profit of 96%. They read in the newspaper that profits increased 50%, that is from 6% to 9%, and they remember the 50%.

Profit has been defined as, "the small number that remains when a very large number (expenses) is subtracted from another large number (sales)." I have found this useful in focusing on the very small error permissible in either the selling price or the expense level before losses start to occur.

If in studying your pricing you find that some jobs are drastically underpriced, you may find that you cannot recover

this increase all at once and you may not want to give up these jobs because of a high-volume relationship with your customer. One alternative is to discuss your situation with your customer and work out a series of stairstep increases at specific intervals, say four to six months, so that the price eventually comes in line.

My personal observation, and I think the statistics support it, is that most platers do a good job in maintaining an efficient production level and in controlling costs and that more emphasis on pricing is necessary if we are to achieve the profitability levels of other sectors of manufacturing. Some of you are saying to yourselves, "But he doesn't understand. Our production rates often run only 65% of the theoretical calculated rate; I never have the right racks; and my plant is located in an area of high absenteeism." The fact is I do understand and we all have those problems. We all see our own warts more clearly than we see those of others.

My advice is to check your P&L against the NAMF study, correct your problems if any, and price accordingly. Don't price for some theoretical perfect rack that you don't intend to buy. Also, don't wait until all your costs are in line with all the average costs in the NAMF study. Have confidence that your efforts in production and cost control have been producing results all along. Don't worry about that perfect phantom competitor; he doesn't exist. Focus on the pricing.

To quote Pogo, the famous comic strip character, "We have met the enemy and he is us."

B-4

Management Session B

Personnel Techniques of a Job Shop Plater

Milton F. Stevenson Sr.
Anoplate Corp.
Syracuse, NY

PERSONNEL MANAGEMENT IN THE JOB SHOP

Milton F. Stevenson, Sr.
Anoplate Corporation
459 Pulaski Street
Syracuse, NY 13204

Today I would like to talk with you about some ideas that several metal finishing job shops use regarding their plant personnel policies. Whether we are owners or managers it is most likely that our background is one of the following:

1) coming up the ranks through a shop
2) a technical background
3) son or daughter of the shop owner or
4) any combination of the above.

In most instances plating shop owners and managers do not have any business management training.

One key aspect in running our business is having and keeping adequate personnel. Whether you have five or fifty people working with you (notice I said with you not for you) some key buzz words we hear are "productivity","attitude", and "turnover". Since our shops are service oriented, the best way to provide that service is with adequately trained, reasonably happy, and relatively long term employees.

Let's discuss the following items that make an employee glad to be a part of your work force:

1. wage structure
2. fringe benefits
3. time off
   a) vacation time
   b) sick or personal leave time
   c) holidays
4. advances on wages
5. training
6. personnel handbook
7. hiring and firing practices
8. miscellaneous practices
9. communication
10. yearly individual compensation summary

1. WAGE STRUCTURE

To attract and maintain competent personnel we must provide wages consistent with not only our metal finishing competition but other industries in our area. By utilizing your local manufacturers association and trade association's such as the National Association of Metal Finishers, wage structures can be obtained. It is imperative that you do your share by contributing data when these surveys are conducted.

Wages should be reviewed at regular intervals so employees can look forward to being up graded if they have done a good job. Some shops adjust wages once a year, but we have chosen to review them twice a year. We feel our employees are more content with this arrangement.

2. FRINGE BENEFITS

Our shop provides not only medical and life insurance but a dental program as well. In addition we have both a pension plan and a profit sharing plan. Some or all of these benefits may be provided in varying amounts by your shop for your employees. We find it best to stay away from any plan which reduces the net pay of an individual such as a savings plan, or extra insurance plans, since most of our people look only at net pay not gross. I'm sure all of you have this same situation.

3. TIME OFF

In our shop Vacation time is earned as follows:
-- one week after one year of service
-- two weeks after two years
-- three weeks after fifteen years

We prefer to call extra days off personal leave days rather than sick days, so an employee does not have to say he is sick when he is not. These are earned days also:
-- one day after one year
-- two days after two years
-- three days after three years
-- four days after four years up to
-- five days after five years
This benefit remains at five days beyond five years.

Our holiday schedule for 1983:

Friday, Dec. 31	New Year's Day (falls on Sat.)
Friday, April 1	Floating Holiday #1
Monday, May 30	Memorial Day
Friday, July 1	Floating Holiday #2
Monday, July 4	Independence Day
Monday, Sept. 5	Labor Day
Thursday, Nov. 24	Thanksgiving Day
Friday, Nov. 25	Extra Anoplate Holiday
Friday, Dec. 23	Close at Noon
Monday, Dec. 26	Christmas (falls on Sun.)
Friday, Dec. 30	Close at Noon (Shop Buffet)

4. ADVANCE ON WAGES

Temporary loans are called "advance on wages". This term is used so that upon discharge or an employee terminating employment management may deduct the balance owed in full.

Our plant allows up to one week's gross pay after one year and two week's gross pay after two years or more.

A set amount, usually $25.00, is deducted each week from the employee's pay until the loan is paid back. A form must be signed by the employee agreeing to these arrangements.

One shop in Georgia has a loan fund limit such as $10,000.00 which is the total amount available. This owner feels improved morale and a decrease in garnishees are the major benefit of this practice.

5. TRAINING

Training of our plant personnel should hold a top priority in our business planning. The future growth of not only our business but our industry as well depends upon this. Key aspects are technical training, shop level training, and business management training. Sources are as follows:

TECHNICAL TRAINING

a) A.E.S. local, regional and national meetings, conferences, and symposia
b) A.E.S. Home Study Course
c) A.E.S. Intensive Training Course
d) Individual home study using books, Plating and Surface Finishing and Metal Finishing magazines
e) Supplier's schools

SHOP LEVEL TRAINING

a) Provide subscriptions to trade journals
b) Provide A.E.S. membership (only to those with ability to comprehend)
c) Internal schools run by your own plant personnel
d) 10 minute "stand up" talks in each department once a month or as necessary
e) Slides of Training in Job Shops

BUSINESS MANAGEMENT TRAINING

a) Local College or University
b) N.A.M.F. meetings
c) Home study - American Management Association type
d) Home study books
e) Local Chamber of Commerce and Manufacturing Association's
f) Seminars by individual management leaders

6. PERSONNEL HANDBOOK

This can be as basic as a list of rules posted on the bulletin board right up to a printed booklet. There are good sources of sample handbooks which can be used as a guide in making your own. The key is do not make a rule which you can not or will not enforce. We find in certain instances on method

of retaining a modest degree of flexibility is to use the phrase "unless previous arrangements are made". A book entitled "How to Prepare a Personnel Policy Manual" will be available after this session. The advantage of using a personnel handbook in your shop is that everyone knows what the rules are, what is acceptable and not acceptable, and in general how everyone stands. It is certainly a good management tool.

7. HIRING AND FIRING PRACTICES

Whatever practices you choose in this area, the most important factor is consistency. Treat everyone alike without exception. Stick to and enforce your own rules, to make the morale of your employees what it should be.

It has been suggested in one personnel policy manual that character, interest and ability are important in that order when hiring. Most discharges are for lack of interest or misconduct, and few for lack of ability. Some shops do not hire relatives of present employees, but we have found that to work well for us. A married couple are less apt to stay home in the morning than one employee by himself.

Conditions causing termination of employment must be clearly defined. Such things as poor attendance, lack of interest, behavior (drugs or alcohol use), and inability to perform assigned tasks, all these things may result in firing. Be sure to keep good records showing cause for discharge and again - be consistent.

8. MISCELLANEOUS PRACTICES

Some advantages which our shop provides in addition are:

a) tuition aid for employees
b) free coffe all day
c) athletic activities - sponsorship of bowling and softball teams
d) donuts for 8:30 a.m. break on all employee birthdays
e) shop anniversary party
f) New Years buffet
g) protective clothing - 3 acid resistant uniforms are provided per year
h) boots (shop pays 50% of cost)
i) a park with picnic tables and horseshoe pits

9. COMMUNICATION

It is imperative to the smooth running of your shop to communicate effectively with all your employees. They want to know if you plan to expand, or if work is down they want to know why and what you plan to do about it, and they want to know how they are doing and what their future with you will hold. It is important to communicate these concerns either verbally or in a note in pay or in a shop newsletter. Yes,

several metal finishing shops do have company newsletters printed regularly. That is a good way to get news home to wives also, because they too are interested in their spouses job situation.

Proper communication can make a definite contribution to the well being of your shop.

10. YEARLY INDIVIDUAL COMPENSATION SUMMARY

A moment ago I covered employee communication. We seldom give our employees the value of their total compensation package. This package when completed at the end of the year should be presented individually to each employee. Our form is as follows:

- -

Individual Compensation Summary

Employee:
Year:
Hire Date:
Present Wage:
Wages:
    Incentive Bonus
    Winter Bonus
    Total
Pension Plan:
Profit Sharing Plan:
Medical, Dental & Life Insurance:
    Your Contribution:
    Anoplate's Contribution:
Employer's Contribution to Social Security:

Workman's Compensation:
State Unemployment Insurance:
Federal Unemployment Insurance:
Disability Insurance:

Uniforms:
Boots:
Coffee:

Vacation Time:
Personal Leave Days:
Holidays:

Value of Total Compensation 1982:

- -

I would hope that the items we have discussed this afternoon have meaning for you in running your business. Several things I have mentioned came directly from other platers - in fact I try to take home at least one new idea each time I attend a meeting. Discuss with each other what works for you in the areas of personnel management, so that we all may learn to be more effective owners and managers in the metal finishing field.

B-5

Management Session B

Tax Saving Tips for the Individual AES Member

Daniel Leonhardt
Leonhardt Plating Co.
Cincinnati, OH

TAX SAVING TIPS FOR THE INDIVIDUAL AES MEMBER

Daniel Leonhardt
Leonhardt Plating Co.
5753 Este Avenue
Cincinnati, OH 45232

There have been many changes in the tax laws over the last couple of years. Companies have cut back on expenses in various categories including Association expenses.

I will explain how different AES expenses and other business deductions can be claimed on your IRS Form 1040 tax return. There are two methods of doing this; one is an adjustment to income that comes right off the top and the other is an itemized deduction that is included with ordinary deductions.

Initially, I will go through the various items that can be included in the adjustments or the deductions and then I will show where to list them on the return.

There have been numerous books written about tax saving ideas. However, the IRS itself provides many free publications and probably the best is Publication 17, Your Income Tax. They also have other free publications on specific tax items such as: Travel & Entertainment, Medical Expenses, Child Care, etc. Contact your local IRS office or send in the order form that is on the back of your tax form instruction package.

Travel can be a large adjustment to your income. If you are using your own vehicle, you may deduct 20¢ per mile to attend any AES Branch meeting, Regional meeting and of course, the Annual National Technical Conference. If you are a Branch officer, you might have a couple of officer meetings and expenses. Members of Regional Committees and all National Boards and Committees may have travel expense. If you do not drive to a meeting, any means of transportation is deductible, taxi, bus, airplane, etc.

If you stay overnight, all of your necessary expenses including hotels and meals are deductible.

Anytime you attend an AES sponsored educational seminar such as the AES-EPA Pollution Control Seminar, the Electronics Symposium, the Intensive Training Course, etc.; there is a deduction for the fee and of course any travel expenses as were previously mentioned.

Form 2106 - Employee Business Expense

Since it is more advantageous to take an adjustment than a deduction, we will first look at Form 2106, Employee Business Expense. In Part I, line 1, put the total cost of fares for airplanes, buses and taxies. Line 2 is for meals and lodging. Line 3 is for automobile expenses. In this example, our plater attended the AES/Federal/State/ Municipal/ Industrial Waste Management and Control Conference, the AES Intensive Training Course, and several local AES meetings.

Automobile expense is figured in Part II and can be taken one of two ways. You can keep track of all of your gas, oil, and repairs and deduct them along with the depreciation on the car, or you can use the standard mileage method. In this case since there is not much mileage involved, it would be simplier and more advantageous to use the standard mileage method of 20¢ per mile for the first 15,000 miles and 11¢ for anything over 15,000 miles.

All of the costs are totaled and if the employer pays any reimbursment, it is deducted on line 7. The balance is carried to line 24 on the front of Form 1040.

The adjustments are totaled including the business expenses, any IRA contributions and don't overlook the Marriage Deduction for a working couple. (Schedule W) For 1982 it was 5% of the lower income of a working couple and for 1983 it will be 10% of the lower income up to a maximum of a $3000 adjustment. The remaining figure on line 32 will be your adjusted gross income or AGI.

Schedule A - Itemized Deductions

Because of the change for 1983, I did not list medical deductions in the example. The change is that previously any medical expense over 3% of the AGI was deductible. In 1983, it will be any amount over 5% of the AGI. If you do have enough medical deductions, don't forget transportation for your trips back and forth to the Doctor or hospital. Another tip is don't forget eyeglasses and contact lens.

Deductions for taxes include state, local, real estate, and state sales tax. A couple of things to remember are: Did you pay any additional state or local tax after what was deducted from your check? Did your locality have any additional piggyback sales tax? This can be added to the amount listed in the chart in the instructions. Don't forget your sales tax on any new or used motor vehicle.

Interest expense includes interest paid on your mortgage, second mortgage, home improvement loan, finance company, Visa, Master Card, and any other payments that include interest.

For contributions, let's look at the worksheet. Since the IRS only requires totals on Schedule A, it is a good idea to make a list of everything for your own records so that you know where you got the totals.

Special uniforms for volunteer organizations and mileage to and from their activities are two things that should not be overlooked. If a business associate passes away and you send flowers, technically that is not a business deduction because you will not gain anymore business from that man. However, if you make a donation to a charity or a fund such as the AES Research Fund or the AES Scholarship Fund, you will have a deductible charitable donation.

Miscellaneous deductions include AES dues, AES meeting expenses, tax return preparation fees, educational expenses and others. This is where the fee for the Intensive Training Course goes. Also any safety equipment that you pay for out of your pocket such as safety shoes, safety glasses, rubber boots etc. If you buy any tools for work including such items as a pocket calculator, it is listed here.

The Schedule A figures are all totaled and after the standard deduction is subtracted, the net total is carried forward to page 2 of the 1040.

In our example the total tax is $2866.00 and the refund will be $634.00. The total amount of AES expenses were $1870.00 Without the AES expenses, the total amount of tax would have been $3331.00 and the refund would have been only $169.00, a difference of $465.00. If there had been $10,000.00 more income in this example, the savings would

have been $626.00 because of the higher tax bracket.

Filling out the IRS form was the easy part. Let's back up and see what records you must have to substantiate these deductions if the IRS would question any of them.

Receipts are the most important item to save. The hotel, plane fare, and auto rental receipts are the easy ones to keep and most are self-explanatory. It is a good idea to charge your meals in order to get a receipt or keep the stub from your order check. For lack of anything else, a note with the date, amount, and description will normally suffice.

A diary or appointment calendar is a must. The new AES calendar already has a lot of useful information printed in it. Mark down all of your meetings and also note your mileage. Also mark down your charitable meetings and note the mileage for them.

For each trip you should fill out some sort of expense sheet. Total up your expenses and attach all of your receipts to it.

In closing, I would like to give a couple of other tax saving tips.

Even though medical deductions will be cut back in 1983 as was previously mentioned, don't forget to include all of your medical insurance if you qualify for any medical deductions. Besides any part of your hospital insurance premium that you pay, there is also dental insurance, contact lens insurance, the portion of your auto insurance if it is listed separately for medical insurance, and some of those extra policies that the Scouts or the school includes in their fees.

Divorce can be a difficult time for those involved. Taxes are usually the furtherest thing from your mind. But, do get some advice either from your tax advisor or your attorney before accepting any agreements. You will have things like custody, alimoney, gain on sale of assets etc. If your attorney gives you tax advice along with the divorce, make sure he gives you a breakdown on his bill, because his tax advice is a deduction, while divorce fees are not.

If there was some helpful advice that you received today and you think that you missed some deductions from last year, remember, you can ammend your return for any of the last three tax years.

One last bit of advice is to get some professional advice. Question your friends, relatives, or associates to find somebody that you can trust and know is qualified. And remember, your tax advisor's fee is deductible.

Form **2106**

Department of the Treasury
Internal Revenue Service (0)

Employee Business Expenses

(Please use Form 3903 to figure moving expense deduction.)

▶ **Attach to Form 1040.**

OMB No. 1545-0139

1982

54

Your name	Social security number	Occupation in which expenses were incurred
JOE PLATER	123 45 6789	PLATING FOREMAN
Employer's name	**Employer's address**	
ABC PLATING CO	CINCINNATI OH 45211	

Part I Employee Business Expenses Deductible in Figuring Adjusted Gross Income on Form 1040, Line 32

1	Reimbursed and unreimbursed fares for airplane, boat, bus, taxicab, train, etc	1	300
2	Reimbursed and unreimbursed expenses for meals and lodging while away from your main place of work	2	490
3	Reimbursed and unreimbursed car expenses from Part II	3	104
4	Reimbursed and unreimbursed outside salesperson's expenses other than those shown on lines 1, 2, and 3 ▶	4	
5	Reimbursed expenses other than those shown on lines 1 through 4	5	—
6	Add lines 1 through 5	6	894
7	Employer's payments for these expenses only if not included on Form W-2	7	—
8	If line 6 is more than line 7, subtract line 7 from line 6. Enter here and on Form 1040, line 24	8	894
9	If line 7 is more than line 6, subtract line 6 from line 7. Enter here and on Form 1040, line 7	9	

Part II Car Expenses (Use either your actual expenses or the mileage rate.)

	Car 1	Car 2	Car 3
A. Number of months you used car for business during 1982	____ months	____ months	____ months
B. Total mileage for months in line A	470 miles	____ miles	____ miles
C. Business part of line B mileage	470 miles	miles	miles

Actual Expenses (Include expenses on lines 1 and 2 only for the months shown in line A, above.)

		Car 1	Car 2	Car 3
1	Gasoline, oil, lubrication, etc	1		
2	Other	2		
3	Total (add lines 1 and 2)	3		
4	Divide line C by line B, above	4	%	%	%
5	Multiply line 3 by line 4	5		
6	Depreciation (based on percentage shown on line 4). Note: *Do not complete line 7 if you use ACRS or 12 months is entered on line A above. Go to line 8.*	6		
7	Divide line 6 by 12 months	7		
8	Multiply line 7 by line A, or enter the amount from line 6 if line 7 was not completed	8		
9	Section 179 expense deduction (see instructions)	9		
10	Business parking fees and tolls	10		
11	Total (add lines 5, 8, 9, and 10). Enter here and in Part I, line 3	11		

Mileage Rate

12	Enter the smaller of (a) 15,000 miles or (b) the total mileage (Car 1 + Car 2 + Car 3) from line C, above	12	470 miles
13	Multiply line 12 by 20¢ (11¢ if applicable, see instructions)	13	94
14	Enter the total mileage, if any (Car 1 + Car 2 + Car 3) from line C that is over 15,000 miles	14	miles
15	Multiply line 14 by 11¢ and enter here	15	
16	Business part of car interest, parking fees, tolls, and State and local taxes (except gasoline tax)	16	10
17	Total (add lines 13, 15, and 16). Enter here and in Part I, line 3	17	104

Part III Information About Educational Expenses Shown in Part I or on Schedule A (Form 1040)

1 Did you need this education to meet the basic requirements for your business or profession? ☐ Yes ☒ No

2 Will this study program qualify you for a new business or profession? ☐ Yes ☒ No

Note: *If your answer to question 1 or 2 is "Yes," stop here. You cannot deduct these expenses, even if you do not intend to change your business or profession.*

3 If "No," list the courses you took and their relationship to your business or profession. ▶ A.E.S. INTENSIVE TRAINING COURSE - TO MAINTAIN AND IMPROVE JOB SKILLS AS A PLATING FOREMAN

Business Mileage

A.E.S.	Monthly Meetings	100 miles
AES.	Committee Meetings	30 miles
A.E.S.	Regional Meeting	40 miles
A.E.S.	Intensive Training Course	300 miles
		470 miles

470 miles x .20/mile = $94.00

Form **1040** Department of the Treasury—Internal Revenue Service **U.S. Individual Income Tax Return** **1982** (0)

For the year January 1–December 31, 1982, or other tax year beginning , 1982, ending , 19 . OMB No. 1545-0074

Use IRS label. Otherwise, please print or type.

Your first name and initial (if joint return, also give spouse's name and initial) Last name: JOSEPH E. + MARY A. PLATER

Your social security number: 123 45 6789

Present home address (Number and street, including apartment number, or rural route): 123 DIPPER STREET

Spouse's social security no.: 987 65 4321

City, town or post office, State and ZIP code: CINCINNATI OH 45211

Your occupation ▶ PLATING FOREMAN

Spouse's occupation ▶ HOUSEWIFE

Presidential Election Campaign ▶ Do you want $1 to go to this fund? — Yes — No

If joint return, does your spouse want $1 to go to this fund? — Yes X No

Note: *Checking "Yes" will not increase your tax or reduce your refund.*

For Privacy Act and Paperwork Reduction Act Notice, see Instructions.

Filing Status Check only one box.

1 — Single

2 X Married filing joint return (even if only one had income)

3 — Married filing separate return. Enter spouse's social security no. above and full name here ▶

4 — Head of household (with qualifying person). (See page 6 of Instructions.) If the qualifying person is your unmarried child but not your dependent, enter child's name ▶

5 — Qualifying widow(er) with dependent child (Year spouse died ▶ 19). (See page 6 of Instructions.)

Exemptions Always check the box labeled Yourself. Check other boxes if they apply.

6a X Yourself — 65 or over — Blind

b X Spouse — 65 or over — Blind

Enter number of boxes checked on 6a and b ▶ 2

c First names of your dependent children who lived with you ▶ ROBERT, SUSAN

Enter number of children listed on 6c ▶ 2

d Other dependents: (1) Name	(2) Relationship	(3) Number of months lived in your home	(4) Did dependent have income of $1,000 or more?	(5) Did you provide more than one-half of dependent's support?

Enter number of other dependents ▶

Add numbers entered in boxes above ▶ 4

e Total number of exemptions claimed

Income Please attach Copy B of your Forms W–2 here.

If you do not have a W–2, see page 5 of Instructions.

7	Wages, salaries, tips, etc.	7	30 000
8	Interest income *(attach Schedule B if over $400 or you have any All-Savers interest)*	8	200
9a	Dividends *(attach Schedule B if over $400)* 300, 9b Exclusion 200		
c	Subtract line 9b from line 9a	9c	100
10	Refunds of State and local income taxes *(do not enter an amount unless you deducted those taxes in an earlier year—see page 9 of Instructions)*	10	
11	Alimony received	11	
12	Business income or (loss) *(attach Schedule C)* ▶	12	
13	Capital gain or (loss) *(attach Schedule D)*	13	
14	40% capital gain distributions not reported on line 13 (See page 9 of Instructions)	14	
15	Supplemental gains or (losses) *(attach Form 4797)*	15	
16	Fully taxable pensions, IRA distributions, and annuities not reported on line 17	16	
17a	Other pensions and annuities. Total received 17a		
b	Taxable amount, if any, from worksheet on page 10 of Instructions	17b	
18	Rents, royalties, partnerships, estates, trusts, etc. *(attach Schedule E)*	18	
19	Farm income or (loss) *(attach Schedule F)* ▶	19	
20a	Unemployment compensation (insurance). Total received 20a		
b	Taxable amount, if any, from worksheet on page 10 of Instructions	20b	
21	Other income (state nature and source—see page 10 of Instructions) ▶	21	
22	**Total income.** Add amounts in column for lines 7 through 21 ▶	22	30300

Please attach check or money order here.

Adjustments to Income (See Instructions on page 11)

23	Moving expense *(attach Form 3903 or 3903F)*	23		
24	Employee business expenses *(attach Form 2106)*	24	894	
25	Payments to an IRA. You **must** enter code from page 11 (3)	25	2250	
26	Payments to a Keogh *(H.R. 10)* retirement plan	26		
27	Penalty on early withdrawal of savings	27		
28	Alimony paid	28		
29	Deduction for a married couple when both work *(attach Schedule W)*	29		
30	Disability income exclusion *(attach Form 2440)*	30		
31	**Total adjustments.** Add lines 23 through 30 ▶	31		3144

Adjusted Gross Income

32	**Adjusted gross income.** Subtract line 31 from line 22. *If this line is less than $10,000, see "Earned Income Credit" (line 62) on page 15 of Instructions. If you want IRS to figure your tax, see page 3 of Instructions* ▶	32	27156

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Schedules A&B (Form 1040)
Department of the Treasury Internal Revenue Service (0)

Schedule A—Itemized Deductions

(Schedule B is on back)

▶ Attach to Form 1040. ▶ See Instructions for Schedules A and B (Form 1040).

OMB No. 1545-0074

1982

07

Name(s) as shown on Form 1040: JOE PLATER

Your social security number: 123 45 6789

Medical and Dental Expenses (Do not include expenses reimbursed or paid by others.) *(See page 17 of Instructions.)*

1	Medicines and drugs	1		
2	Write 1% of Form 1040, line 33	2		
3	Subtract line 2 from line 1. If line 2 is more than line 1, write zero	3		
4	Total insurance premiums you paid for medical and dental care	4		
5	Other medical and dental expenses:			
a	Doctors, dentists, nurses, hospitals, etc	5a		
b	Transportation	5b		
c	Other (list—include hearing aids, dentures, eyeglasses, etc.) ▶	5c		
6	Add lines 3 through 5c	6		
7	Multiply amount on Form 1040, line 33, by 3% (.03)	7		
8	Subtract line 7 from line 6. If line 7 is more than line 6, write zero	8		
9	Write one-half of amount on line 4, but not more than $150	9		
10	**COMPARE** amounts on line 8 and line 9, and write the **LARGER** amount here ▶		10	—

Taxes *(See page 18 of Instructions.)*

11	State and local income	11	1100	
12	Real estate	12	900	
13	a General sales (see sales tax tables)	13a	300	
b	General sales on motor vehicles	13b		
14	Other (list—include personal property) ▶	14		
15	Add lines 11 through 14. Write your answer here ▶		15	2300

Interest Expense *(See page 19 of Instructions.)*

16	a Home mortgage interest paid to financial institutions	16a	2000	
b	Home mortgage interest paid to individuals (show that person's name and address) ▶	16b		
17	Credit cards and charge accounts	17	200	
18	Other (list) ▶ AUTO LOAN 350; FINANCE CO 125	18	375	
19	Add lines 16a through 18. Write your answer here ▶		19	2575

Contributions *(See page 19 of Instructions.)*

20	a Cash contributions. (If you gave $3,000 or more to any one organization, report those contributions on line 20b.)	20a		
b	Cash contributions totaling $3,000 or more to any one organization. (Show to whom you gave and how much you gave.) ▶	20b		
21	Other than cash (see page 19 of Instructions for required statement)	21		
22	Carryover from prior years	22		
23	Add lines 20a through 22. Write your answer here ▶		23	

Casualty and Theft Losses and Miscellaneous Deductions *(See page 20 of Instructions.)*

24	Total casualty or theft loss(es) (attach Form 4684)	24		
25	a Union and professional dues	25a		
b	Tax return preparation fee	25b		
26	Other (list) ▶	26		
27	Add lines 24 through 26. Write your answer here ▶		27	

Summary of Itemized Deductions *(See page 20 of Instructions.)*

28	Add lines 10, 15, 19, 23, and 27	28	
29	If you checked Form 1040, Filing Status box: 2 or 5, write $3,400; 1 or 4, write $2,300; 3, write $1,700	29	
30	Subtract line 29 from line 28. Write your answer here and on Form 1040, line 34a. (If line 29 is more than line 28, see the Instructions for line 30 on page 20.) ▶	30	

A

For Paperwork Reduction Act Notice, see Form 1040 Instructions.

Contributions

Church	520 —
United Way	52 —
Boy Scouts	25 —
Scout Leaders Uniform	35 —
AES Scholarship Fund	25 —
AES Research Fund	25 —
Heart Fund – Cancer Society – Etc – Receipts	25 —
Miscellaneous Donations No Receipts	25 —

Mileage: Boy Scouts 300
Church 200
500 X .09 = 45 —

777 —

Used clothing to Goodwill 3/19/83

2 coats @ 5.00	=	10.00
3 dresses @ 3.00	=	9.00
2 pants @ 2.00	=	4.00
3 shirts @ 2.00	=	6.00
2 pr Shoes @ 2.50	=	5.00
		# 34.00

Schedules A&B (Form 1040)
Department of the Treasury Internal Revenue Service (0)

Schedule A—Itemized Deductions

(Schedule B is on back)

▶ Attach to Form 1040. ▶ See Instructions for Schedules A and B (Form 1040).

OMB No. 1545-0074

1982

07

Name(s) as shown on Form 1040: JOE PLATER

Your social security number: 123 45 6789

Medical and Dental Expenses (Do not include expenses reimbursed or paid by others.) (See page 17 of Instructions.)	1 Medicines and drugs	1			
	2 Write 1% of Form 1040, line 33	2			
	3 Subtract line 2 from line 1. If line 2 is more than line 1, write zero		3		
	4 Total insurance premiums you paid for medical and dental care		4		
	5 Other medical and dental expenses:				
	a Doctors, dentists, nurses, hospitals, etc		5a		
	b Transportation		5b		
	c Other (list—include hearing aids, dentures, eyeglasses, etc.) ▶		5c		
	6 Add lines 3 through 5c		6		
	7 Multiply amount on Form 1040, line 33, by 3% (.03)		7		
	8 Subtract line 7 from line 6. If line 7 is more than line 6, write zero		8		
	9 Write one-half of amount on line 4, but not more than $150		9		
	10 **COMPARE** amounts on line 8 and line 9, and write the **LARGER** amount here ▶			10	—
Taxes (See page 18 of Instructions.)	11 State and local income		11	1100	
	12 Real estate		12	900	
	13 a General sales (see sales tax tables)		13a	300	
	b General sales on motor vehicles		13b		
	14 Other (list—include personal property) ▶		14		
	15 Add lines 11 through 14. Write your answer here ▶			15	2300
Interest Expense (See page 19 of Instructions.)	16 a Home mortgage interest paid to financial institutions		16a	2000	
	b Home mortgage interest paid to individuals (show that person's name and address) ▶		16b		
	17 Credit cards and charge accounts		17	200	
	18 Other (list) ▶ AUTO LOAN 350 FINANCE CO 125		18	375	
	19 Add lines 16a through 18. Write your answer here ▶			19	2575
Contributions (See page 19 of Instructions.)	20 a Cash contributions. (If you gave $3,000 or more to any one organization, report those contributions on line 20b.)		20a	777	
	b Cash contributions totaling $3,000 or more to any one organization. (Show to whom you gave and how much you gave.) ▶		20b		
	21 Other than cash (see page 19 of Instructions for required statement)		21	34	
	22 Carryover from prior years		22		
	23 Add lines 20a through 22. Write your answer here ▶			23	811
Casualty and Theft Losses and Miscellaneous Deductions (See page 20 of Instructions.)	24 Total casualty or theft loss(es) (attach Form 4684)		24		
	25 a Union and professional dues		25a	41	
	b Tax return preparation fee		25b	50	
	26 Other (list) ▶ SAFETY SHOES -45 WORK TOOLS -20 INTENSIVE TRAINING COURSE -395 ENVIRONMENTAL MEETING 185 - AES MEETINGS -120 - ON CALL 24 HRS ½ TELEPHONE -120		26	885	
	27 Add lines 24 through 26. Write your answer here ▶			27	976
Summary of Itemized Deductions (See page 20 of Instructions.)	28 Add lines 10, 15, 19, 23, and 27			28	6662
	29 If you checked Form 1040, Filing Status box { 2 or 5, write $3,400 / 1 or 4, write $2,300 / 3, write $1,700 }			29	3400
	30 Subtract line 29 from line 28. Write your answer here and on Form 1040, line 34a. (If line 29 is more than line 28, see the Instructions for line 30 on page 20.) ▶			30	3262

A

For Paperwork Reduction Act Notice, see Form 1040 Instructions.

Tax Computation (See Instructions on page 12)	33	Amount from line 32 *(adjusted gross income)*		33	27156
	34a	If you itemize, complete Schedule A (Form 1040) and enter the amount from Schedule A, line 30		34a	3262
		Caution: If you have unearned income and can be claimed as a dependent on your parent's return, check here ▶ ☐ and see page 12 of the Instructions. Also see page 12 of the Instructions if: • *You are married filing a separate return and your spouse itemizes deductions, OR* • *You file Form 4563, OR* • *You are a dual-status alien.*			
	34b	If you do not itemize, complete the worksheet on page 13. Then enter the allowable part of your charitable contributions here		34b	
	35	Subtract line 34a or 34b, whichever applies, from line 33		35	23894
	36	Multiply $1,000 by the total number of exemptions claimed on Form 1040, line 6e		36	4000
	37	Taxable Income. Subtract line 36 from line 35		37	19894
	38	Tax. Enter tax here and check if from ☒ Tax Table, ☐ Tax Rate Schedule X, Y, or Z, or ☐ Schedule G		38	2866
	39	Additional Taxes. (See page 13 of Instructions.) Enter here and check if from ☐ Form 4970, ☐ Form 4972, ☐ Form 5544, or ☐ section 72 penalty taxes		39	
	40	**Total.** Add lines 38 and 39 ▶		40	2866
Credits (See Instructions on page 13)	41	Credit for the elderly *(attach Schedules R&RP)*	41		
	42	Foreign tax credit *(attach Form 1116)*	42		
	43	Investment credit *(attach Form 3468)*	43		
	44	Partial credit for political contributions	44		
	45	Credit for child and dependent care expenses *(attach Form 2441)*	45		
	46	Jobs credit *(attach Form 5884)*	46		
	47	Residential energy credit *(attach Form 5695)*	47		
	48	Other credits—see page 14 ▶	48		
	49	**Total credits.** Add lines 41 through 48		49	
	50	**Balance.** Subtract line 49 from line 40 and enter difference (but not less than zero) ▶		50	2866
Other Taxes (Including Advance EIC Payments)	51	Self-employment tax *(attach Schedule SE)*		51	
	52	Minimum tax *(attach Form 4625)*		52	
	53	Alternative minimum tax *(attach Form 6251)*		53	
	54	Tax from recapture of investment credit *(attach Form 4255)*		54	
	55	Social security (FICA) tax on tip income not reported to employer *(attach Form 4137)*		55	
	56	Uncollected employee FICA and RRTA tax on tips *(from Form W–2)*		56	
	57	Tax on an IRA *(attach Form 5329)*		57	
	58	Advance earned income credit (EIC) payments received *(from Form W–2)*		58	
06	59	**Total tax.** Add lines 50 through 58		59	2866
Payments Attach Forms W–2, W–2G, and W–2P to front.	60	Total Federal income tax withheld	60 3500		
	61	1982 estimated tax payments and amount applied from 1981 return	61		
	62	Earned income credit. If line 33 is under $10,000, see page 15 of Instructions	62		
	63	Amount paid with Form 4868	63		
	64	Excess FICA and RRTA tax withheld (two or more employers)	64		
	65	Credit for Federal tax on special fuels and oils *(attach Form 4136)*	65		
	66	Regulated Investment Company credit *(attach Form 2439)*	66		
	67	**Total.** Add lines 60 through 66 ▶		67	3500
Refund or Amount You Owe	68	If line 67 is larger than line 59, enter amount **OVERPAID** ▶		68	634
	69	Amount of line 68 to be **REFUNDED TO YOU** ▶		69	634
	70	Amount of line 68 to be applied to your 1983 estimated tax ▶	70		
	71	If line 59 is larger than line 67, enter **AMOUNT YOU OWE.** Attach check or money order for full amount payable to Internal Revenue Service. Write your social security number and "1982 Form 1040" on it. ▶ (Check ▶ ☐ if Form 2210 (2210F) is attached. See page 16 of Instructions.) ▶ $		71	

Please Sign Here

Under penalties of perjury, I declare that I have examined this return, including accompanying schedules and statements, and to the best of my knowledge and belief, it is true, correct, and complete. Declaration of preparer (other than taxpayer) is based on all information of which preparer has any knowledge.

▶ Your signature | Date | ▶ Spouse's signature (if filing jointly, BOTH must sign)

Paid Preparer's Use Only

Preparer's signature ▶ | Date | Check if self-employed ▶ ☐ | Preparer's social security no.

Firm's name (or yours, if self-employed) and address ▶ | E.I. No. ▶ | ZIP code ▶

January, 3☆
Rochester Branch
Joint Meeting with SME
Party House, Rochester, NY

January 10-11
AES/Federal/State/Municipal/
Industrial Waste Management & Control
Conference For Surface Finishing Industry
Sheraton World, Orlando, FL

January, 11☆
Baltimore-Washington Branch
Work Shop
Petrucci's, Laurel, MD
Contact: Fred Borleis 301-727-6770

JANUARY 1983

SUN	MON	TUE	WED	THU	FRI	SAT
DECEMBER S M T W T F S 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31	FEBRUARY S M T W T F S 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28					1
2	CHURCH MEETING 7:30PM ☆3	4	SCHOOL BOARD 7:30 PM 5	6	7	8
AIRPORT 3:30 PM 9	AES/Federal/State/Municipal/Industrial Waste Management & Control Conference for Surface Finishing Industry Sheraton World Orlando, FL 10	☆11	12	13	14	15
16	SCHOOL BINGO 7:00 17	18	AES OFFICERS MEETING 7:30 PM $10.00 19	20	21	22
23/30	AES MEETING 6:30 PM $12.00 24/31	25	26	BOY SCOUT COMMITTEE 7:30 PM 27	28	29

MILEAGE
BUSINESS - 25
CONTRIBUTIONS - 20

WEEKLY EXPENSE REPORT

TO _____ (Attach Receipts) FROM JOE PLATER

FOR WEEK ENDING _____

TIME RECORD
START HOUR _____ DATE _____
RETURN HOUR _____ DATE _____

		SUN 1/9/83		MON 1/10/83		TUES 1/11/83		WED		THUR		FRI		SAT		TOTALS FOR WEEK	
		CITY ORLANDO FL	DEPART / ARRIVE	CITY ORLANDO	DEPART / ARRIVE	CITY ORLANDO	DEPART / ARRIVE	CITY	DEPART / ARRIVE	CITY	DEPART / ARRIVE	CITY	DEPART / ARRIVE	CITY	DEPART / ARRIVE		
1	HOTEL - MOTEL			48	15	48	15									96	30
2	BREAKFAST			4	95	4	95									9	90
3	LUNCH																
4	DINNER	15	50	20	50											36	00
5	PLANE - RAIL - BUS FARE	300	00													300	00
6	LOCAL TAXIS - BUS FARES	5	00			5	00									10	00
7	AUTO EXPENSE REPAIR - TIRES - SUPPLIES																
8	GAS - OIL																
9	LUBRICATION - WASH																
10	GARAGE - PARKING					10	00									10	00
11	TOLLS																
12	PHONE - TELEGRAMS																
13	TIPS	2	00	4	00	2	00									8	00
14	ENTERTAINMENT																
	TOTALS	322	50	77	60	70	10									470	20
	NUMBER OF CALLS MADE LIST CUSTOMER ON REVERSE SIDE																
	NUMBER OF HOURS WORKED																

STATE BUSINESS PURPOSE — PEOPLE ENTERTAINED — PLACE OF ENTERTAINMENT AND TIME — (LIST GIFTS ON REVERSE SIDE)

EXPENSES TO ATTEND AMERICAN ELECTROPLATERS' SOCIETY FEDERAL / STATE / MUNICIPAL / INDUSTRIAL WASTE MANAGEMENT AND CONTROL CONFERENCE IN ORLANDO, FLORIDA ON JANUARY 10-11, 1983

I HEREBY CERTIFY THAT THE ABOVE EXPENDITURES REPRESENT CASH SPENT FOR LEGITIMATE COMPANY BUSINESS ONLY AND INCLUDES NO ITEMS OF A PERSONAL NATURE.

Signed _____

DATE	REPAYMENT RECAP	AMOUNT	
	ADVANCE RECEIVED		
	REIMBURSED		
	TOTAL		
	EXPENSE FOR WEEK		
	OVER OR SHORT		

MILEAGE RECORD	
END OF TRIP	
LESS START	
MILES PER TRIP	

APPROVAL

CASHIERS MEMO	
CHECK NO.	
DATE	AMOUNT

Tops Form 1244 Litho in U.S.A.

(OVER)

C-1

Environmental I
Session C

Process Modifications: The First Step in Wastewater Treatment

Robert S. Capaccio, P.E.
Mabbett, Capaccio & Associates, Inc.
Cambridge, MA

PROCESS MODIFICATIONS: THE FIRST STEP IN WASTEWATER TREATMENT

by
Robert S. Capaccio, P.E.
Mabbett, Capaccio & Associates, Inc.
Cambridge, Massachusetts

General:

The size, scope and complexity of a wastewater treatment system is dictated by both the quantity and quality of the process waste streams, as well as the effluent discharge limitations that a facility is required to meet. Prior to the establishment of wastewater treatment system design criteria, the process operations should be closely studied to determine areas where chemical conservation and rinsewater flow reduction techniques could be implemented. These techniques have a significant impact on reducing the capital and operating costs of a wastewater treament system, and if implemented properly, a negligible effect on product quality.

Chemical Conservation Techniques:

Many articles have been written on various chemical conservation techniques. Some of the more typical techniques that have been applied to electroplating shops are listed in Table 1. Additional information on the minimization of dragout can be found in the references (1, 2).

The reduction of chemical dragout should be the first order of business in implementing a pollution-control program, subsequent to the inventory/data gathering phase. By keeping the chemicals out of the rinse tanks and in the process baths where they belong, a lower water rinse flow becomes acceptable, process chemical purchases are reduced, wastewater treatment facility costs are lowered and treatment sludge generation is reduced.

Rinsewater Conservation Techniques:

Following dragout control, the next step in the pollution-control program should be rinsewater conservation. The quantity of rinsewater utilized in the typical electroplating and printed circuit board manufacturing shop is often excessive and can often be reduced through implementation of more efficient rinsing techniques. Table 2 lists typical rinsewater conservation methods that can have application (references 1, 2).

The familiar rinsing equations, shown in Figure 1 for parallel and series tanks, can be utilized to indicate the benefits from recycling rinsewater. Typically, reductions of between 90 to 95% for a double rinsetank and 95 to 97% for a triple rinsetank can be accomplished, depending on the rinsing ratio of Cp/Cn and rate of dragout (references 3, 4, 5).

Case Studies:

Three case histories will be presented which exemplify the savings in water usage that can be accomplished utilizing accepted rinsewater conservation technology. One company, A, is a printed circuit board manufacturer, while the remaining two, B and C, are electroplating shops.

1. Company A is a New Hampshire-based manufacturer of custom printed circuit boards. The major processes generating wastewater are listed in Table 3. With input on product quality control aspects from the facility chemist, the major thrust was rinsewater flow reduction in the copper/ solder pattern plate line and the solder strip operation with dragout tanks installed in the copper deposition line, copper/ solder pattern plate line, solder strip and hydroetch operation. Table 4 indicates the flow reduction and dragout tank modifications accomplished.

   Overall, a flow reduction of nearly 35% was achieved, with a significant reduction in the treatment system requirements, due to batch treatment possibilities from the implemented dragout tanks. On-going studies will determine the most cost-effective mode of batch treatment/reclaim.

2. Company B is a major electroplating job shop. The process lines are indicated in Table 5. Each line was investigated via dragout studies and laboratory analysis with input on product quality criteria furnished by company personnel (Tables 6 to 12). Total flow reductions are summarized in Table 13. Table 14 indicates the impact on purchase water costs and sewer user charges. The impact on wastewater treatment costs has not been quantifie, but will approach 25-30 percent. Management o f this particular company has implemented all the re- comm endations and is currently acquiring the necessary wastewa ter treatment components from the resale market, further r educing wastewater treatment costs.

3. Company C is a captive electroplating shop. Process rinsewater consumption and subsequent reductions are

summarized in Table 15. These reductions are detailed in Figures 2 and 3. Company personnel are presently implementing the recommendations. Capital cost estimates (equipment and installation) for the industrial wastewater treatment system have been reduced from $343,000. to $162,000., in part by implementing the modifications.

Summary:

The above case histories indicate that by implementing rinsewater/dragout reduction techniques, significant cost-reductions can be accomplished. These methods should be implemented prior to the formulation of design criteria for purchase of a cost-effective wastewater treatment system.

Table 1

Chemical Conservation Techniques

- Mimimize Bath Chemical Concentrations
- Maximize Bath Operating Temperature
- Utilize Wetting Agents
- Efficiently Rack Parts For Best Drainage
- Design Parts To Minimize Dragout
- Withdraw Parts At Slow Rate
- Install Rest Bars Over Process Tanks
- Utilize Drainage Boards
- Utilize Wet Air Knives or Fog Sprays
- Utilize Stagnant (Still) Rinse Tanks

Figure 1

Rinsing Equations

1. $Q = \frac{(Cp\Theta^n)^{1/n}}{Cn}$ PARALLEL TANKS

2. $Q = [(Cp/Cn)^{1/n} + 1/n]\Theta$ SERIES TANKS

where: Q = Rinse flow rate

Cp = Concentration of salts in process bath

Cn = Concentration of salts allowed in final rinse

Θ = Dragout rate

n = Number of rinse baths

Table 2

Rinsewater Conservation Techniques

- Countercurrent Rinsing
- Spray and Fog Rinsing
- Flood Rinsing
- Still Rinsing
- Reuse of Rinsewater
- Rinsewater Agitation
- Conductivity Controlled Rinsing
- Flow Restriction (Regulating) Devices
- Higher Temperature Rinsing

Table 3

Company A
Process Operations

- Electroless Copper Deposition
- Copper/Solder Pattern Plate
- Nickel/Gold Tab Plate
- Immersion Tin
- Hydroetch
- Solder Strip
- Resist Strip
- Developer
- Wave Solder Area
- Screen Wash
- Scrub and Deburr Operations
- Reflow
- Filter Backwash
- Water Treatment Regeneration

Table 4

Company A
Process Flow/Dragout Reductions

1. Copper/Solder Pattern Plate - 24 gpm to 6 gpm

   Instituted double countercurrent rinsing, flow restriction valving and air agitation. Installed dragout rinse following tin lead plating tank.

2. Copper Deposition - No flow reduction

   Installed dragout rinse following microetch and two dragout rinses following electroless copper deposition tank. Batch treat/reclaim as required.

3. Solder Strip - 7.5 gpm to 3.0 gpm

   Installed two dragout rinses followed by a double countercurrent rinse tank.

4. Hydroetch - No flow reduction

   Installed two dragout rinses following immersion etch tank. Batch treat/reclaim as required.

Total Flow Reduction - 71 gpm to 48 gpm
- 33% reduction

Table 5

Company B
Production & Cleaning Lines

LINE	OPERATION	TYPE
1	Zinc Plating	Manual barrel
2	Zinc Plating	Automatic barrel
3	Zinc Plating (Cyanide)	Automatic barrel
4	Nickel Plating	Manual barrel
5	Zinc Plating	Automatic barrel
6	Nickel Plating	Automatic rack
7	Copper Plating (Cyanide) Brass Plating (Cyanide) Tin Plating	Manual barrel
8	Nickel Plating	Manual barrel
Misc.	Alkaline Cleaning	Manual tumblers

Note: Line 6 usage discontinued.

Table 6

Company B
Line 1 Analysis

Tank Identification

1. High Temperature Soap Clean (150°F)
2. Rinse
3. H_2SO_4 Clean
4. Rinse
5. Zinc Plating
6. Not used
7. Alkaline Clean
8. Alkaline Clean
9. Alkaline Clean
10. Rinse (Iridite)
11. Rinse-TCC (Iridite)

Wastewater Sources

Tank No.	Present Flow Rate, gpm	Suggested Flow Rate, gpm	Comments
2	3.9	3.0	a - counter-current system at 2.5 gpm
4	5.3	a	
6	0.0	a	
10	3.1	3.1	
11	3.5	2.0	
TOTALS	15.8 gpm	10.6 gpm	

Recommendations

1. Install/calibrate flow restriction valves to tank numbers 2 and 11 as indicated.
2. Fabricate tank numbers 4 and 6 into a double counter-current rinsing system with feedwater flowrate restricted to 2.5 gpm.
3. Supply low level air agitation to rinse tank numbers 2, 4, 6, 11.

Table 7

Company B
Line 2 Analysis

Tank Identification

1. Alkaline Clean
2. Alkaline Clean
3. Rinse
4. HCl Clean
5. Rinse
6. Zinc Plate (80°F)
7. Rinse
8. Rinse
9. Rinse
10. Rinse (Iridite)

Wastewater Sources

Tank No.	Present Flow Rate, gpm	Suggested Flow Rate, gpm	Comments
3	5.9	3.0	a - counter-current system at 3.0 gpm
5	5.3	a	
7	1.2	a	
9	2.4	a	
11	1.0	1.0	
TOTALS	14.4 gpm	8.7 gpm	

Recommendations

1. Install/calibrate flow restriction valve to tank number 5 as indicated.
2. Interconnect tank numbers 7, 8 and 9 to form triple counter-current rinsing system with feedwater flow-rate restricted to 3.0 gpm.
3. Supply low level air agitation to rinse tank numbers 3, 5, 7, 8, 9.

Table 8

Company B
Line 3 Analysis

Tank Identification

1. Alkaline Clean (2-stage)
2. Alkaline Clean (2-stage)
3. Rinse
4. H_2SO_4 Clean
5. H_2SO_4 Clean
6. Rinse
7. Rinse
8. Zinc Plate (Cyanide)
9. Rinse
10. Rinse
11. Rinse
12. Recovery Drip
13. Rinse
14. Recovery Drip
15. Rinse
16. Rinse
17. Rinse (Iridite)

Wastewater Sources

Tank No.	Present Flow Rate, gpm	Suggested Flow Rate, gpm	Comments
3	1.2	1.2	a - assumes 5 gpm
6	5.6	b	total for tank
7	0.0	b	numbers 10, 11,
9	0.0	0.0	15 and 16.
10	a	c	
11	a	c	b - counter-
12	0.0	0.0	current system
13	a	c	at 2.5 gpm.
14	0.0	0.0	
15	a	c	c - counter-
16	a	c	current system
17	3.0	2.0	at 4.0 gpm.
TOTALS	14.8 gpm	9.7 gpm	

Table 8
(Continued)

Recommendations

1. Interconnect tank numbers 6 and 7 to form a double counter-current rinsing system with influent feed rate set at 2.5 gpm.

2. Interconnect tank numbers 10, 11, 13, 15 and 16 to form a five-stage counter-current rinsing system with influent feed rate set at 4.0 gpm.

3. Interconnect tank numbers 9, 12, and 14 to form a dragout recovery system for periodic recycling to zing plating tank.

4. Install/calibrate flow restriction valve to tank number 17 as indicated.

5. Supply low level air agitation to rinse tank numbers 6, 7, 10, 11, 13, 15 and 16.

Table 9

Company B
Line 4 Analysis

Tank Identification

1. Alkaline Clean
2. Alkaline Clean
3. Rinse
4. Not Used
5. H_2SO_4 Clean
6. Nickel Plate
7. Nickel Plate
8. Nickel Plate
9. Nickel Plate
10. Nickel Plate
11. Nickel Plate
12. Nickel Plate
13. Rinse
14. Rinse (heated)
15. Rinse (misc.)

Wastewater Sources

Tank No.	Present Flow Rate, gpm	Suggested Flow Rate, gpm	Comments
3	22.1	a	a - counter-current system at 4.0 gpm.
4	0.0	a	
13	3.5	3.0	
14	0.2	0.2	
15	2.6	2.6	
TOTALS	28.4 gpm	9.8 gpm	

Recommendations

1. Interconnect tank numbers 3 and 4 to form a double counter-current rinsing system with influent feed rate restricted to 4.0 gpm.
2. Install/calibrate flow restriction valve to tank number 13 as indicated.
3. Supply low level air agitation to rinse tank numbers 3, 4 and 13.

Table 10

Company B
Line 5 Analysis

Tank Identification

1. Alkaline Clean (140°F)
2. Alkaline Clean (4-stage)
3. Rinse
4. Risne
5. HCl Clean (3-stage)
6. Rinse (2-stage)
7. Zinc Plate
8. Rinse
9. Rinse (2-stage)
10. Rinse
11. Rinse (3-stage)

Wastewater Sources

Tank No.	Present Flow Rate, gpm	Suggested Flow Rate, gpm	Comments
3	2.0	a	a - counter-
4	0.4	a	current system
6	2.0	2.0	at 1.5 gpm
8	0.0	0.0	
9	0.0	b	b - counter-
10	2.0	b	current system
11	2.0	b	at 1 gpm
TOTALS	6.4 gpm	4.5 gpm	

Recommendations

1. Interconnect tank numbers 3 and 4 to form a double counter-current rinsing system with influent feed rate restricted to 1.5 gpm.

2. Interconnect tank numbers 9, 10 and 11 to form a triple counter-current rinsing system with influent feed rate restricted to 1.0 gpm.

3. Utilize tank number 8 as recovery rinse with recycle to plating tank.

4. Supply low level air agitation to tank numbers 3, 4, 6, 9, 10 and 11.

Table 11

Company B
Line 7 Analysis

Tank Identification

1. Alkaline Clean (150°F)
2. Rinse
3. H_2SO_4 Clean
4. Tin Plate
5. Brass Plate
6. Copper Plate
7. Rinse

Future - Cyanide Rinse

Wastewater Sources

Tank No.	Present Flow Rate, gpm	Suggested Flow Rate, gpm
2	3.9	3.0
7	3.9	3.0
Future	0.0	3.0
TOTALS	7.8 gpm	9.0 gpm

Recommendations

1. Install/calibrate flow restriction valves to tank numbers 2 and 7 as indicated.
2. Install a new tank with influent flow rate set at 3.0 gpm to provide segregation of cyanide bearing wastewaters.
3. Provide low level air agitation to rinse tank numbers 2, 7 and future.

Table 12

Company B
Line 8 Analysis

Tank Identification

1. H_2SO_4 Clean
2. Rinse
3. Nickel Plate
4. Nickel Plate
5. Nickel Plate
6. Nickel Plate
7. Nickel Plate
8. Nickel Plate
9. Nickel Plate
10. Nickel Plate
11. Nickel Plate
12. Nickel Plate
13. Nickel Plate
14. Nickel Plate
15. Nickel Plate
16. Nickel Plate
17. Rinse
18. Rinse (130°F)

Wastewater Sources

Tank No.	Present Flow Rate, gpm	Suggested Flow Rate, gpm
2	3.2	3.2
17	10.1	5.0
18	0.5	0.5
TOTALS	13.8 gpm	8.7 gpm

Recommendations

1. Install a 5 gpm flow restriction valve on the influent feed line to tank number 17.
2. Supply low level air agitation to rinse tank numbers 2 and 17.

Table 13

Company B
Total Plant Water Consumption Summary

LINE	PRESENT DISCHARGE, gpm	SUGGESTED DISCHARGE, gpm	ESTIMATED REDUCTION, gpm
1	15.8	10.6	5.2
2	14.4	8.7	5.7
3	14.8	9.7	5.1
4	28.4	9.8	18.6
5	6.4	4.5	1.9
6	13.1	0	13.1
7	7.8	9.0	(1.2)
8	13.8	8.7	5.1
Tumblers	22.5	17.5	5.0
TOTALS	137 gpm	78.5 gpm	

Percent reduction in flow = $\frac{137-58.5}{137}$ = 57%

Table 14

Company B
Economic Impact of Water Conservation

OPTION	FLOW RATE gpm	PURCHASE WATER, $/yr[1]	SEWER USER CHARGE, $/yr[2]	TOTAL COST
1. No Change - Present Conditions	137	$37,200	-----	$37,200
2. No Change - Conditions in 1984	137	$37,200	$1,400 to $5,300	$38,600 $42,500
3. Implement Water Conservation Now	79	$24,000	-----	$24,000
4. Implement Water Conservation in 1984	79 79	$24,000	$ 800 to $3,000	$24,800 $27,000

SUMMARY[3]

A. Annual savings available now: $13, 200.

B. Annual savings available in 1984: $13,800 to $15,500.

Notes

1. Present billing structure assumed stable until 1984.

2. Currently under review but expected to be from $0.21 to $0.80 per 1000 cubic feet depending upon type of waste treatment implemented in New Bedford, MA. The higher end of the noted range is expected.

3. Does not include savings from smaller pretreatment system sizing and reduced WWT operation costs.

Table 15

Company C
Rinsewater Consumption Summary

Process[a] Number	Description	Rinsewater Flowrates, gpm Measured Conditions[b]	Following Modifications[b]
1	Cleaning	26.5	5.0
2	Zinc Plating	17.7	5.0
3	Cadmium Plating	11.4	1.5 (5 max.)
4	Silver Plating	(10 max.)	(5 max.)
5	Nickel Plating	5.7	2.0[c] (5 max.)
6	Tin Plating	5.0	2.0[c] (5 max.)
7	Cyanide Dip	6.6	2.0[c] (5 max.)
8	Cadmium Plating	(10 max.)	(2 max.)
9	Copper Plating	(10 max.)	(2 max.)
10	Zinc Plating	(10 max.)	(2 max.)
11	Strip Rinse	2.0	(1 max.)
12	Brite Dip	12.0	2.0
13	Miscellaneous	17.0	4.0 (6 max.)
	TOTALS	103.9	23.5 (50 max.)

PERCENT REDUCTION - 77%

Notes:

a. Numbers coincide with Process Schematics Figures 2 & 3.

b. Intermittent flows shown in parentheses.

c. Estimated average continuous flow due to production.

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2. U.S. Environmental Protection Agency. Contol and Treatment Technology for the Metal Finishing Industry: In-Plant Changes, EPA 625/8-82-002, Cincinnati, Ohio, 1982.

3. Mohler, J.B. "The Performance of a Rinsing Tank." Metal Finishing, August, 1982, pp. 21-28; and September, 1982, pp. 35-39.

4. Mohler, J.B. "Dual Purpose Rinsing." Plating & Surface Finishing, September, 1979, pp. 48-49.

5. European Institute of Printed Circuits. "Symposium On Utilization of Water in PCB Production," EIPC, March, 1981.

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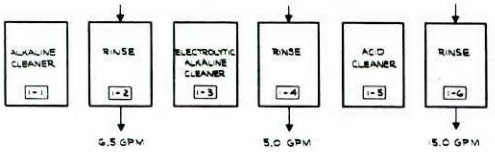

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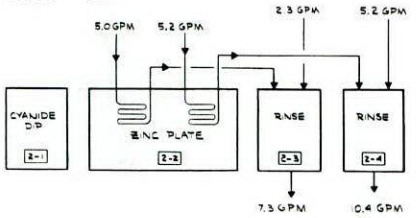

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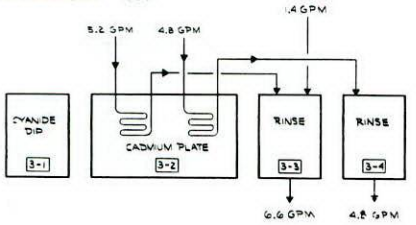

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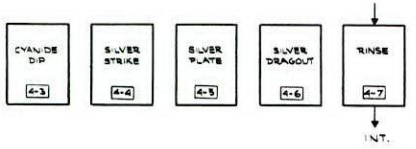

NOTE: INT. INTERMITTENT

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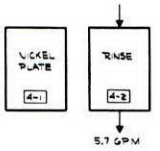

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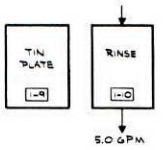

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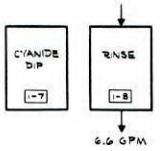

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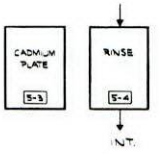

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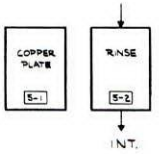

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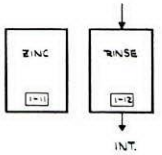

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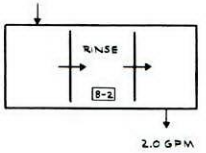
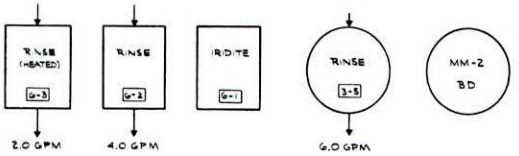


BRITE DIP (ZN) (12)



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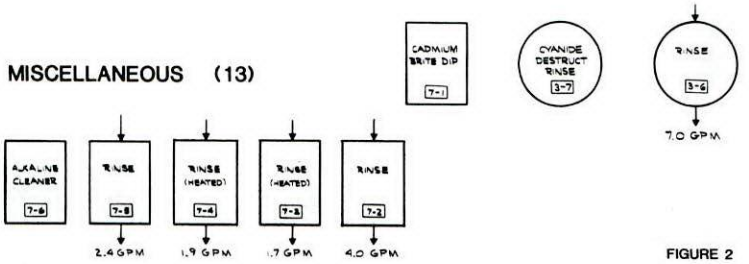

FIGURE 2

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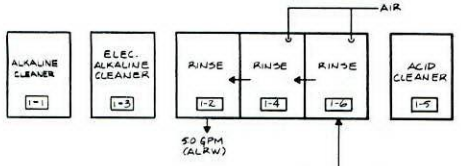

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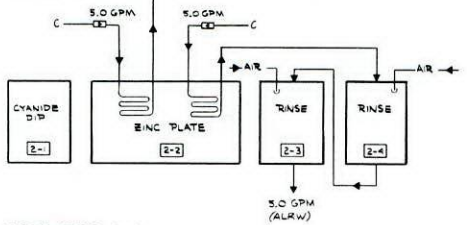

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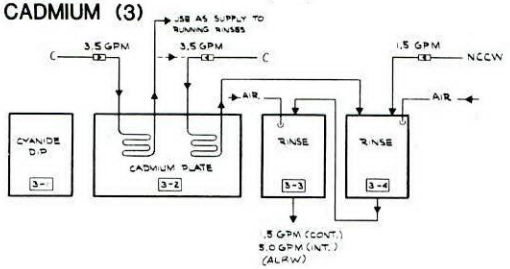

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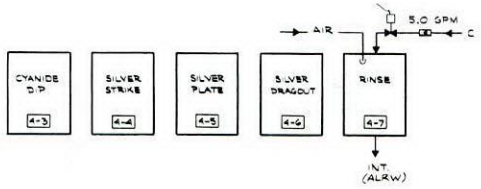

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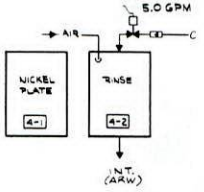

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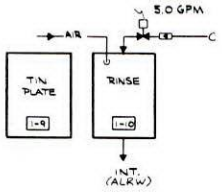

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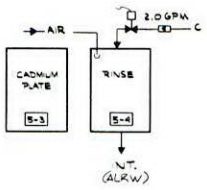

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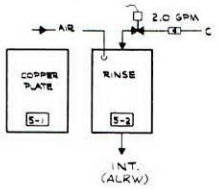

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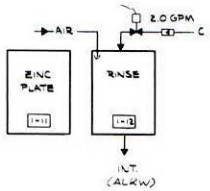

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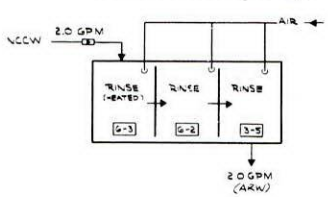





LEGEND

	FLOW RESTRICTION VALVE
	SOLENOID VALVE
C	CITY WATER
W	WELL WATER
NCCW	NON CONTACT COOLING WATER
INT	INTERMITTENT
ARW	ACIDIC RINSEWATER DRAIN
ALRW	ALKALINE RINSEWATER DRAIN

MISCELLANEOUS (13)

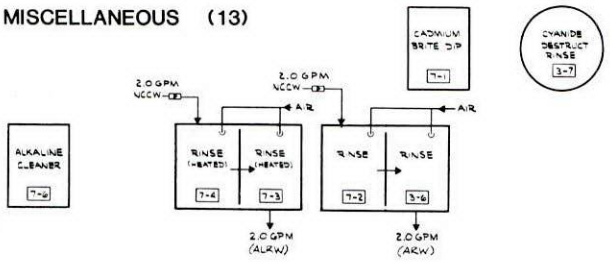

FIGURE 3

C-2

Environmental I
Session C

What's New with Reverse Osmosis in Metal Finishing Waste Treatment

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C_3 International
Minneapolis, MN

WHAT'S NEW WITH REVERSE OSMOSIS IN METAL FINISHING WASTE TREATMENT

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C3 International
3423 N.E. Maplewood Drive
Minneapolis, Minnesota 55423

I. Introduction

The unit operation of reverse osmosis is readily adaptable to the treatment of metal finishing wastes for the following reasons:

- It is a low energy process utilizing pump energy only
- The equipment is simple and easy to maintain
- It is a continuous process as opposed to batch treatment
- It is possible to use this process to continuously return the solute to the plating bath as well as to recover all of the rinse water.

Because reverse osmosis has the ability to separate dissolved solids (both inorganic and organic) from pure water, this process is used to concentrate the dissolved solids portion of the plating rinse stream. In virtually all cases, the pure water can be recycled back to the process, and, depending upon a number of factors, the concentrate stream can be returned to the plating bath, directed to the waste treatment system, or hauled away. Ideally, to achieve "zero discharge:, the concentrate stream should be returned to the plating bath; however, factors such as bath temperature, (which determines the rate of evaporation from the plating bath) degree of contamination of the rinse water, source of rinse water and engineering design considerations of the reverse osmosis system determine its disposition.

The production rate of a particular reverse osmosis membrane is a function of such important variables as:

Feed water temperature

Dissolved solids type and concentration in the feed water

Applied pressure

System Design

Particular membrane polymer characteristics

Obviously, to be effective, the membrane polymer must be resistant to chemical attack by the dissolved solids in the solution in which it is operating. Whereas all of the commercially available polymers exhibit excellent tolerance to certain chemical extremes, none has yet been developed that will satisfactorily function in all extremes, i.e., there is no "optimum" membrane at this time. The chemical factors that present the greatest problems to membrane polymers include pH extremes, strong oxidizing agents and aromatic hydrocarbons. Another polymer characteristic that is important to manufacturers of reverse osmosis membrane is rejection, usually expressed as a percentage. The condition that can most significantly affect membrane performance is "fouling" resulting from suspended or precipitated solids coating the membrane surface. A "fouled" membrane will usually show a reduction in both pure water (permeate) flow and permeate quality. Proper prefiltration is absolutely essential to insure optimum membrane life; however, for baths that are continuously filtered and otherwise properly maintained, the reverse osmosis system usually requires no more than 5 micron prefilter cartridges.

The resistance of a membrane element to fouling is also a function of its configuration. To date, the only practical configurations for most reverse osmosis applications are the hollow fiber permeator (Figure 1) and the spiral wound module (Figure 2). Because of the close packing density and small diameter of the fibers in the permeator, it is much less widely used than the spiral wound configuration.

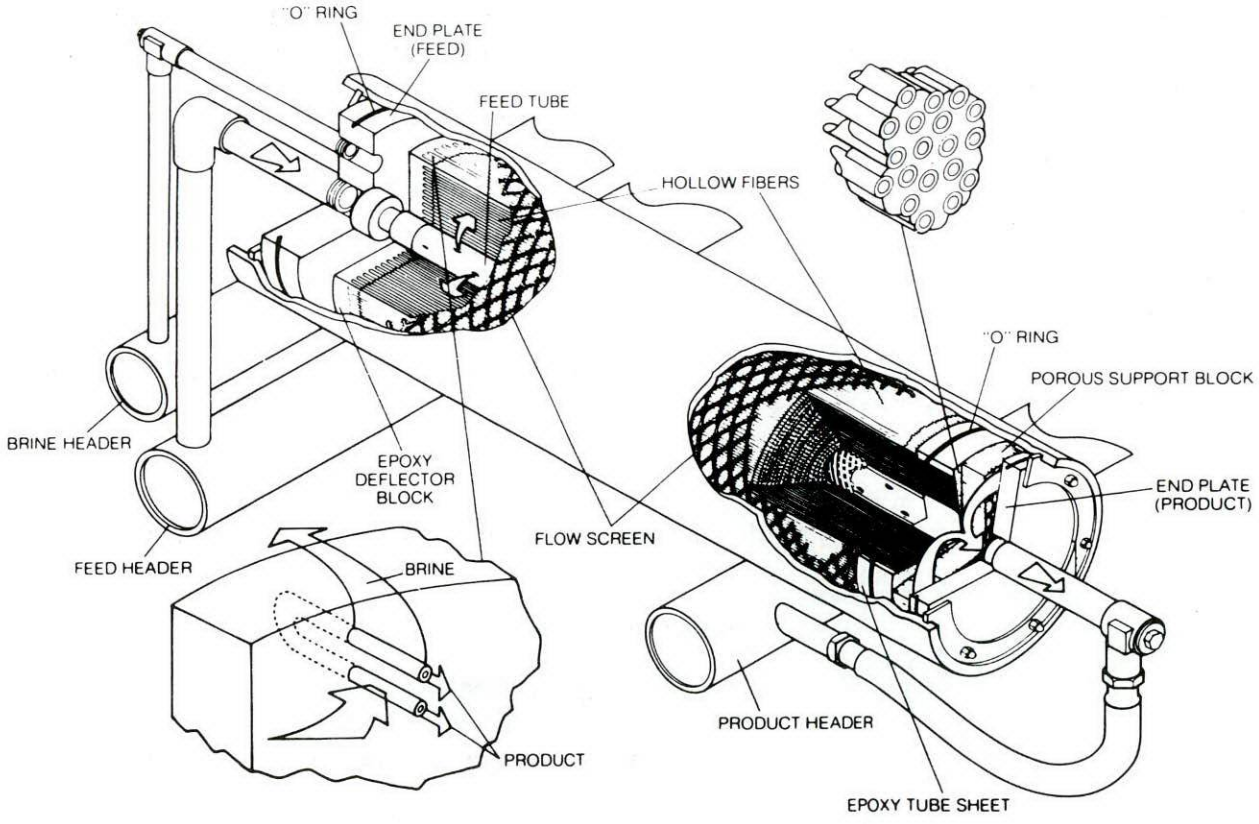


Figure 1. Hollow Fiber Membrane Element

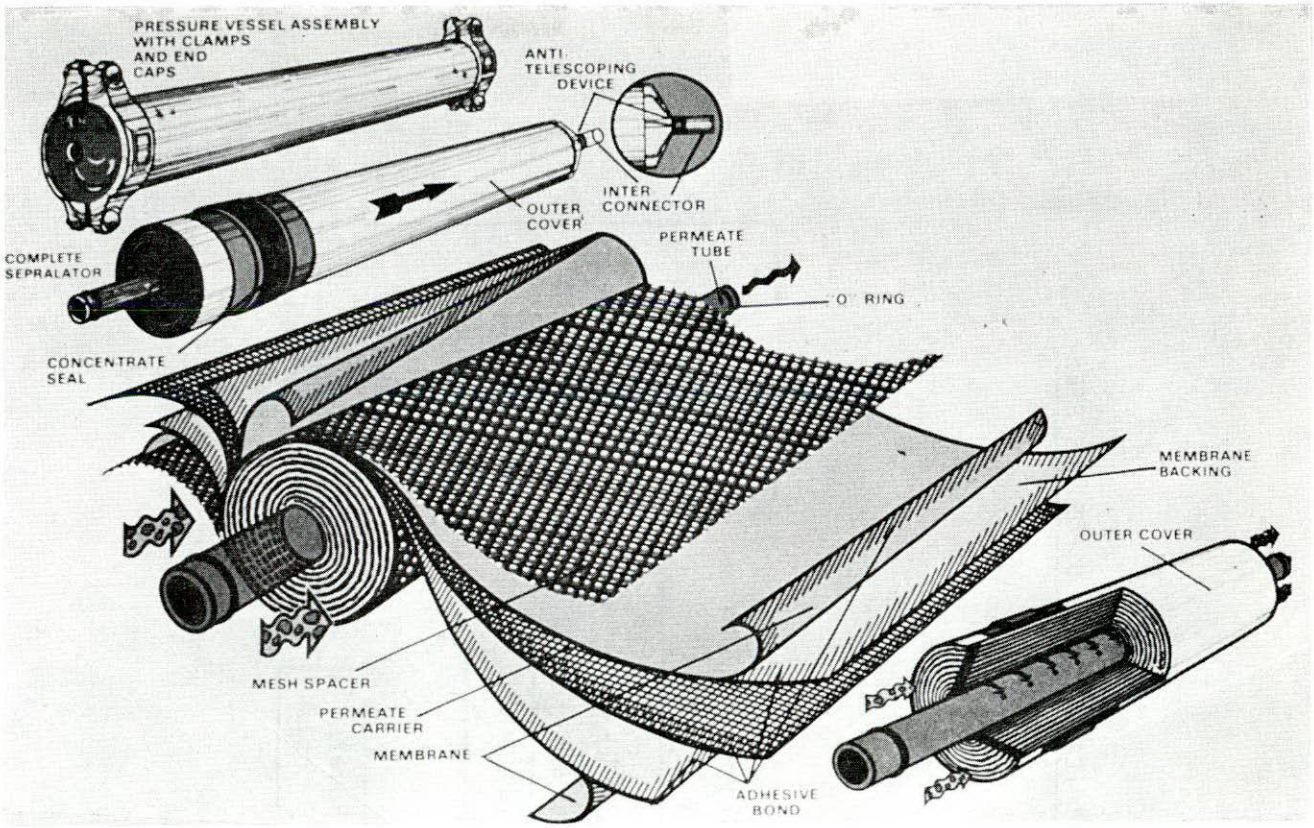


Figure 2. Spiral Wound Membrane Element

Figure 3 represents a typical reverse osmosis system operating on the first rinse and returning the concentrate to the plating tank.

Figure 4 illustrates a reverse osmosis system returning the concentrated bath constituents to a "drag-out" tank for eventual return to the plating tank.

This paper summarizes the existing reverse osmosis installations and addresses the potential applications resulting from the introduction of the new thin film composite membrane polymers.

FIGURE 3 - TYPICAL REVERSE OSMOSIS SYSTEM

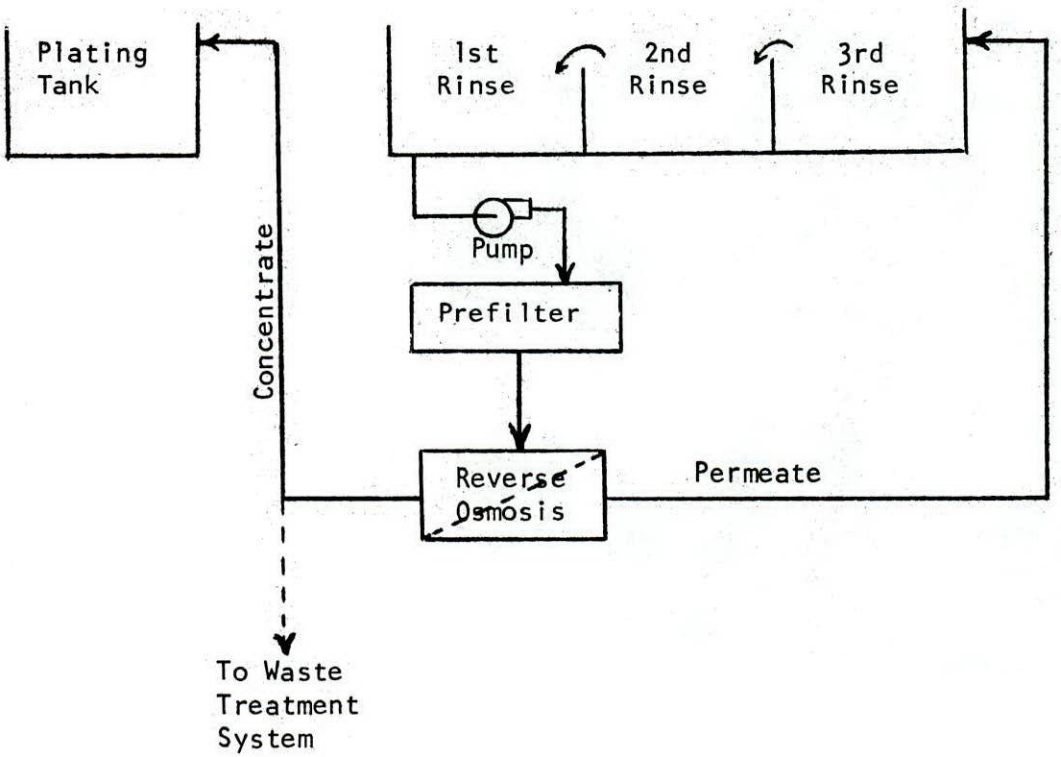
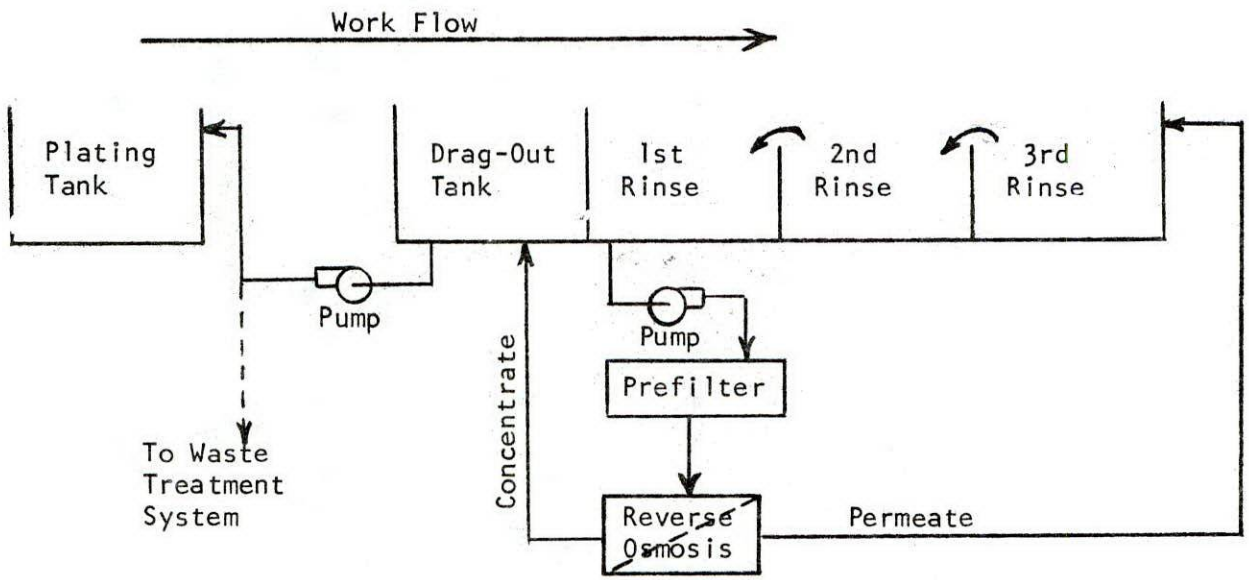


FIGURE 4 - REVERSE OSMOSIS SYSTEM UTILIZING "DRAG-OUT" RINSE



II. Review of Existing Applications

A. Nickel Installations

There are at least 150 systems operating on various nickel baths, mostly utilizing cellulose acetate membrane elements and with recoveries in the range of 90-97%. The relatively high evaporation rate resulting from the elevated bath temperature generally allows complete recycle of the concentrate stream as well as the permeate stream.

Type of Bath	Membrane Element	Membrane Life	System Payback	Years of System Operation	Items Plated
Watts	Spiral Cellulose Acetate	2 years	12 months	4	Luggage Hardware
Watts	Spiral Cellulose Acetate	1 year	12 months	5	Wire Shelving
Watts	Spiral Cellulose Acetate	1 year	16 months	5	Wire Shelving
Watts	Spiral Cellulose Acetate	1 year	24 months	5	Steel Stamping
Watts	Spiral Cellulose Acetate	1-1/2 years	36 months	7	Job Shop
Watts	Spiral Cellulose Acetate	1-1/2 years	24 months	8	Job Shop
Watts	Spiral Cellulose Acetate	1 year	30 months	5	N/A
Watts	Spiral Cellulose Acetate	2 years	8 months	6	Electrical Devices
Watts	Spiral Cellulose Acetate	4 years	11 months	8	Plumbing Hardware
Watts	Spiral Cellulose Acetate	3 years	8 months	9	Steel Furniture
Watts	Spiral Cellulose Acetate	1-1/2 years	18 months	6	Electrical Devices
Bright Nickel	Spiral Cellulose Acetate	1-1/2 years	14 months	11	Plumbing Hardware

(Continued)

Type of Bath	Membrane Element	Membrane Life	System Payback	Years of System Operation	Items Plated
Bright Nickel	Spiral Cellulose Acetate	2 years	36 months	4	N/A
Bright Nickel	Spiral Cellulose Acetate	1-1/2 years	12 months	5	Automotive Bumpers
Bright Nickel	Spiral Cellulose Acetate	2 years	8 months	9	Hand Tools
Bright Nickel	Spiral Cellulose Acetate	2-1/2 years	20 months	8	Brass Stampings
Sulfamate	Spiral Cellulose Acetate	2 years	13 months	5	Electrical Terminals
Sulfamate	Hollow Fiber Polyamide	2-1/2 to 3 years	N/A	3	P.C. Board Contacts

B. Copper Sulfate Installations

Approximately 12 reverse osmosis systems are operating on rinses from proprietary copper foil manufacturing processes.

Number of Systems	Feed Flow (gpm)	Membrane Element	Concentrate Composition	System Recovery	Membrane Life	Years of System Operation
10	60	Hollow Fiber, Polyamide and Cellulose Triacetate	Waste Treatment	75%	1-3 years	5
2	40	Spiral Wound, Thin Film Composite	Reuse	87.5%	1 year	7

Pretreatment requirements:

Hollow fiber polyamide element - 1 micron filter cartridge

Hollow fiber cellulose triacetate element - 3 micron filter cartridge

Spiral wound thin film composite element - 5 micron filter cartridge

C. Zinc Sulfate Installations

One reverse osmosis system is operating on the zinc sulfate rinse from a proprietary copper foil manufacturing process. The system utilizes spiral wound thin film composite membrane elements with a feed rate of 45 gpm and recovery of 87.5%. Although the system has been in for more than seven years, the thin film composite element has been in for just over a year and is working well.

The concentrate stream is further reduced in volume in an evaporator (operating at 90% recovery) and returned to the bath.

D. Brass Cyanide Installations

Approximately five reverse osmosis systems are operating on the brass cyanide rinses from a proprietary copper foil manufacturing process. Both polyamide and cellulose triacetate hollow fiber membrane elements are utilized. Feed rate is approximately 60 gpm per system at a recovery of 90%. The systems have been operating for five years and the membrane element life is 3-4 years. Pretreatment is one micron filter cartridges for the polyamide elements and 3 micron filter cartridges for the cellulose triacetate elements.

E. Copper Cyanide Installations

1. Printed circuit contact plating application - first flowing rinse fed to a polyamide hollow fiber membrane element at a rate of approximately 210 gph.

   The system is operating at approximately 90% recovery, with a portion of the concentrate recycled to the plating bath and remainder to the waste treatment system. All of the permeate is reused in the rinse stream.

   The system has been operating for more than three years. Pretreatment is one micron filter cartridge followed by activated carbon. Membrane elements have lasted for 2-1/2 to 3 years.

2. Medical device plating application - lead brass substrate, first rinse fed to a polyamide hollow fiber membrane element.

   The system is operating at 93% recovery, with approximately one-half of the concentrate recycled to the plating bath and the rest to the waste treatment system. All of the permeate is reused in the rinse stream.

   The system has been in operation for more than seven years. Pretreatment is by 1.2 micron filter cartridges followed by 0.45 membrane filters, and the membrane life is about 4-1/2 years.

F. Chrome Installations

A copper foil manufacturer has been investigating the use of spiral wound thin film composite membrane elements for use in recovering hexavalent chrome from the rinses in a proprietary manufacturing process. Hollow fiber membrane elements lasted only 1-2 months before irreversibly fouling, while the spiral wound configuration has performed satisfactorily for over 6 months with only 5 micron cartridge filtration as pretreatment.

III. The Promise of New Membranes

The preceding section lists a number of existing applications for zero discharge reverse osmosis systems. It should be noted that with few exceptions, the bulk of the existing installations utilize spiral wound cellulose acetate reverse osmosis membrane elements operating on nickel plating rinses. The viability of reverse osmosis technology in zero discharge applications is a function of the chemical characteristics of the membrane element, and the characteristics of the plating bath.

Until recently, the spiral wound membrane configuration has only been available with cellulose acetate polymer, the chemical characteristics of which have limited its application to low pH baths such as nickel; the temperature of the plating bath determines the evaporation rate of water from the bath, thereby fixing the maximum concentrate rate from the reverse osmosis system.

A new family of polymers known as thin film composites is now available from six or seven membrane manufacturers. These thin film composites exhibit improved application characteristics as indicated on the following chart.

	Spiral Wound Cellulose Acetate	Hollow Fiber Polyamide	Spiral Wound TFC
pH Stability	2-8	4-11	2-12
Fouling Resistance	Good	Poor	Good
Oxidation Resistance	Good	Poor	Fair-Poor
Temperature Stability	95°F.	95°F.	120°F.

An important definition is in order here:

The recovery of a reverse osmosis system is defined as that portion of the feed stream quantity that goes through the membrane and comes out as permeate. Recovery is always expressed as a percentage, so 100 minus recovery is that percentage of the feed stream that becomes the concentrate. Most zero discharge systems operate at recoveries in excess of 95% (the concentrate stream is less than 5% of the feed stream volume). Obviously, for systems

operating on plating baths with lower temperatures, because the evaporation rate is lower, the recovery must be higher in order for all of the concentrate stream to be fed directly to the plating bath. It also stands to reason that as the recovery goes up (the concentrate volume goes down), the concentration of salts in the concentrate stream will increase. This increase can be rather marked; for example, the concentration of salts in a system operating at 98% recovery is 2-1/2 times greater than the concentration in a system operating at 95% recovery.

Thus, the osmotic pressure at these high recoveries becomes the limiting factor in system design.

This means that regardless of the membranes used, lower temperature baths are more difficult to treat with reverse osmosis than those operating above 120°F. In order to overcome this problem, such techniques as air agitation of the plating bath, supplemental evaporation of the concentrate stream, using the concentrate in an air scrubber and bleeding part of the bath into the reverse osmosis unit have all been used with success.

Specific testing of two different thin film composite membranes has been performed on zinc cyanide, copper cyanide and brass cyanide rinses.

Both membranes exhibited excellent rejection of the zinc, copper and cyanide ions; however, the low temperature of these baths require that one or more of the techniques outlined in the preceding paragraph be utilized.

Although some testing remains to be done an all electroplating baths other than nickel, reverse osmosis has proved be be a viable process for "zero discharge" applications, and will continue to become an important waste treatment process in the future.

- END -

C-3

Environmental I
Session C

BPT to BAT

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BPT TO BAT

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Oliver Stanley, General Electric Company, Florence, SC

Several years ago the General Electric Company decided to upgrade the wastewater treatment system at its manufacturing plant in Florence, South Carolina. The improvements included increasing the hydraulic and chemical treatment capacity, as well as the degree of treatment. Based on discussions with an independent consulting firm, it was decided that a phased program of system improvements should be implemented.

It was also decided that reducing the load being generated, rather than enlarging the existing plant, was the best way to increase the effective hydraulic and chemical treatment capacity. The first phase of the program was a water and waste reduction study of the existing plating facilities. The goal of this study was to reduce water consumption by 30 percent to provide for increased future production, without having to increase the size of the existing treatment plant.

Table 1 lists the various waste producing operations.

Table 1

MANUFACTURING OPERATIONS

1. Printed Circuit Board Fabrication
2. Aluminum and Zinc Die Casting
3. Zinc Plating
4. Chromium (VI) Plating Surface Preparation
5. Copper-Tin Plating
6. Plastic Injection Molding
7. Chemical Polishing and Cleaning
8. Precious Metal Plating

The consultant made a detailed study of each tank in each of the plating lines and proposed a series of general recommendations. Specific recommendations (along with detailed specifications and drawings) were made where major changes were required. The following is a summary of the general recommendations:

a. The water inlet should be changed to add water through a perforated sparger pipe laid along the bottom of the tank, parallel to but on the opposite side from, the overflow weir.

b. Tanks that are used infrequently should have a conductivity controller to actuate a solenoid valve, to start and stop water as required.

c. Tanks that are used on a regular basis should utilize a fixed water flow controller.

d. Rinse tanks should be air agitated with a perforated air sparger pipe laid diagonally across the tank. The sparger pipe should be weighted to keep it in position.

e. Top sprays should be used with a solenoid in the water supply line and actuated by the automatic conveyor, so that water is sprayed only as the rack is lifted up through the zone of influence.

f. Where possible, a master water supply valve should be placed in the water supply to each individual processing line. Thus, whenever a particular line is not in operation, the water supply to that one line can be shut off without disturbing the flow settings.

g. Tank bridges should be provided between tanks so that dragout will drain to the tank of origin.

General Electric implemented the recommendations and realized a reduction of water usage of approximately 40 percent.

Phase II encompassed a detailed study of the existing wastewater treatment system for optimizing its operation and reducing chemical consumption and sludge generation.

The existing system, as shown in Figure 1, consisted of three segregated pretreatment systems followed by combined final treatment. The final stages of treatment consisted of: pH adjustment and precipitation in the final mix tank; addition of lime for coagulation in a secondary final mix tank; addition of polymer; and flocculation followed by settling and sludge dewatering in a solid bowl centrifuge, with centrate return for treatment.

The three pretreatment systems were:

a) Cyanide and copper chelates - Wastewater flowed by gravity to a membrane-lined holding basin and transfer sump. Wastes were then pumped to a two-stage system for alkaline chlorination.

b) Chrome - Wastewater from chrome plating and chromate conversion coating operations flowed to a membrane-lined holding basin and transfer sump. Wastes were then pumped to an acid/sulfonation system for reduction of hexavalent chrome.

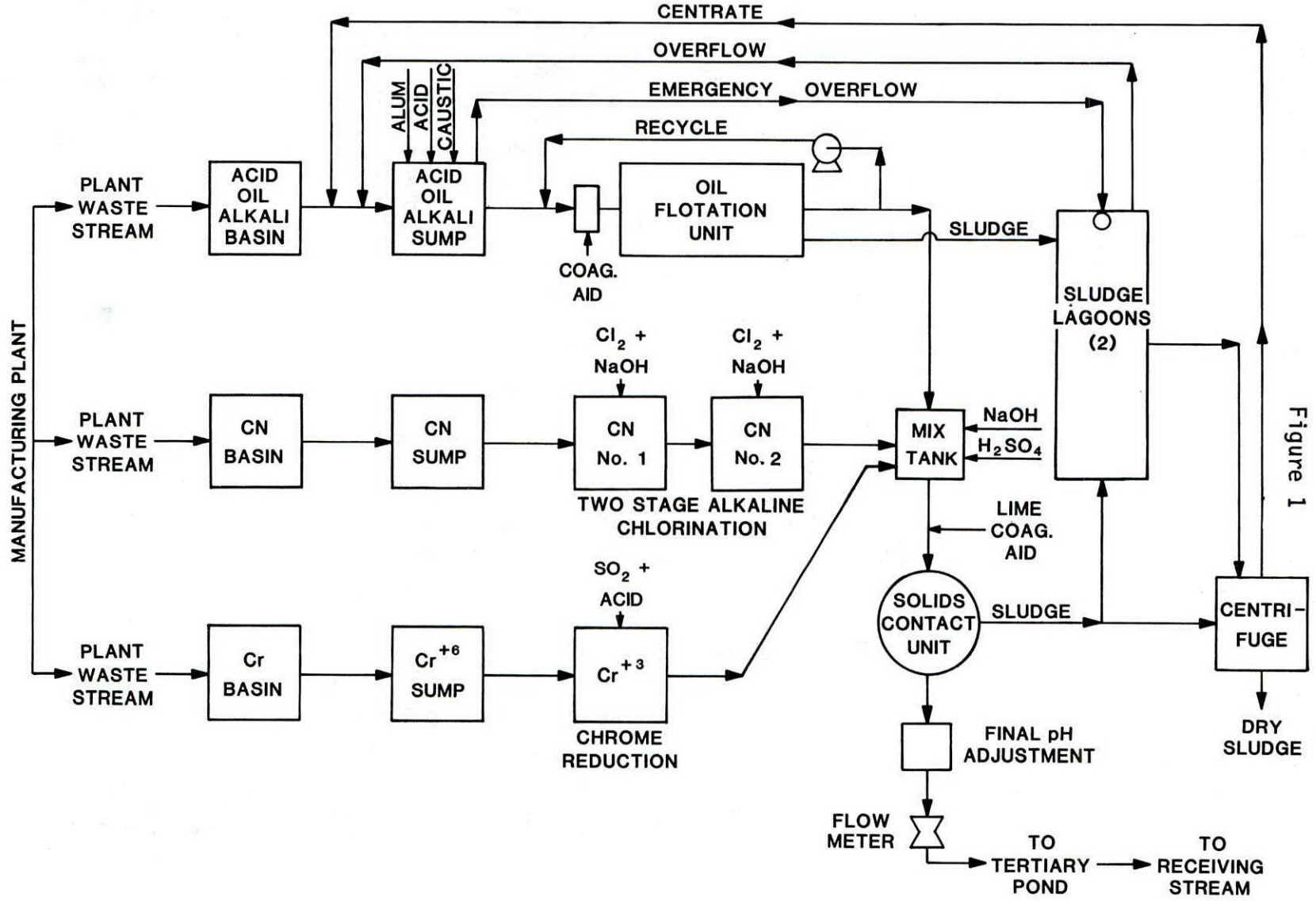

CENTRATE
OVERFLOW
EMERGENCY OVERFLOW
RECYCLE
ALUM
ACID
CAUSTIC
PLANT WASTE STREAM
ACID OIL ALKALI BASIN
ACID OIL ALKALI SUMP
COAG. AID
OIL FLOTATION UNIT
SLUDGE
SLUDGE LAGOONS (2)
MANUFACTURING PLANT
Cl_2 + NaOH
Cl_2 + NaOH
PLANT WASTE STREAM
CN BASIN
CN SUMP
CN No. 1
CN No. 2
TWO STAGE ALKALINE CHLORINATION
MIX TANK
NaOH
H_2SO_4
LIME COAG. AID
SO_2 + ACID
SOLIDS CONTACT UNIT
SLUDGE
CENTRI-FUGE
PLANT WASTE STREAM
Cr BASIN
Cr^{+6} SUMP
Cr^{+3}
CHROME REDUCTION
FINAL pH ADJUSTMENT
DRY SLUDGE
FLOW METER
TO TERTIARY POND
TO RECEIVING STREAM

Figure 1

c) Acid-Alkaline - Oil (A-A-O) - Wastewaters flowed by gravity to a membrane-lined holding basin and treatment/transfer sump where pH was controlled and alum was added as an oil/water emulsion breaker. Wastes were then pumped to a dissolved air flotation (DAF) unit where polymer was added to enhance solids separation.

The following recommendations were made and implemented to optimize treatment and reduce sludge:

a) The holding basins were designed to be operated at one of three levels in the case of cyanide and chrome, and one of two levels in the case of AA-O. All three systems were being operated at the minimum level.

It was recommended that the cyanide and chrome basins be operated at mid-level and the A-A-O at the upper level, and that air agitation be added to each of the three basins. The goal in each case was concentration equalization, since the plant does not have a separate dump handling system for concentrates.

b) All pretreatment reaction tanks were air agitated, as was the final mix (or neutralization) and precipitation tank. While air agitation in the cyanide and chrome pretreatment tanks increases chemical consumption, it does not affect effluent quality. Air agitation in the final mix tank was affecting effluent quality.

Enough air was entrained in the flow to produce an excessive amount of floaters in the clarifier. A recommendation was made and implemented by General Electric to replace the air system with a mechanical agitator. This was difficult and expensive, due to tank dimensions and low head room. It was accomplished by using an angle drive and a two-piece shaft. This modification improved the performance of the clarifier but did not eliminate all solids carryover.

c) The 10-year-old existing plant was experiencing difficulties with the pH and ORP electrode assemblies and the reference electrodes, which were of the old remote KCL reservior variety. All pH and ORP electrode assemblies and electrodes were replaced to improve the reliability of these sensors and the control loops they served.

d) Jar tests were conducted on the A-A-O system. Based on these tests, the control pH was lowered and alum dosage reduced. This improved the operation of this subsystem and reduced the quantity of sludge produced.

Phase III consisted of an evaluation of the modified existing system effluent quality. Periodically, the effluent would be out of specification in heavy metals. Studies on filtered and unfiltered wastewater samples indicated that the problem vacillated between metals in solution and metals in fine suspension.

From the above, it was concluded that a polishing filter would resolve the problem of particulate carryover from the clarifier, but that a modification of chemistry would be required to remove the soluble or complexed metal. The resulting recommended system was a combination of insoluble starch xanthate (ISX) and a filter.

Phase IV was a pilot test of this proposed system. Since ISX had become commercially available, a supply was ordered and a refrigerated milk chest was borrowed to prevent deterioration of the ISX.

Parallel tests were run on two different types of filters -- a diatomaceous (D.E.) filter and a moving bed sand filter. In the initial test (see Figure 2), ISX was fed to an agitated reaction vessel, and separate pumps fed the sand filter and a precoated D.E. filter. The D.E. filter produced high clarity water that was low in metals. The filter runs, however, were very short. A body feed system was added that extended the runs somewhat, but significantly added to sludge volume because of the D.E.

The sand filter experienced no pressure drop problems, but did not remove the ISX. Settling tests on an ISX slurry indicated a very fine, almost colloidal, suspension that would not readily settle -- even with polymer addition. Discussions with the manufacturer of the ISX indicated that they were now using a much finer milled starch to make the ISX.

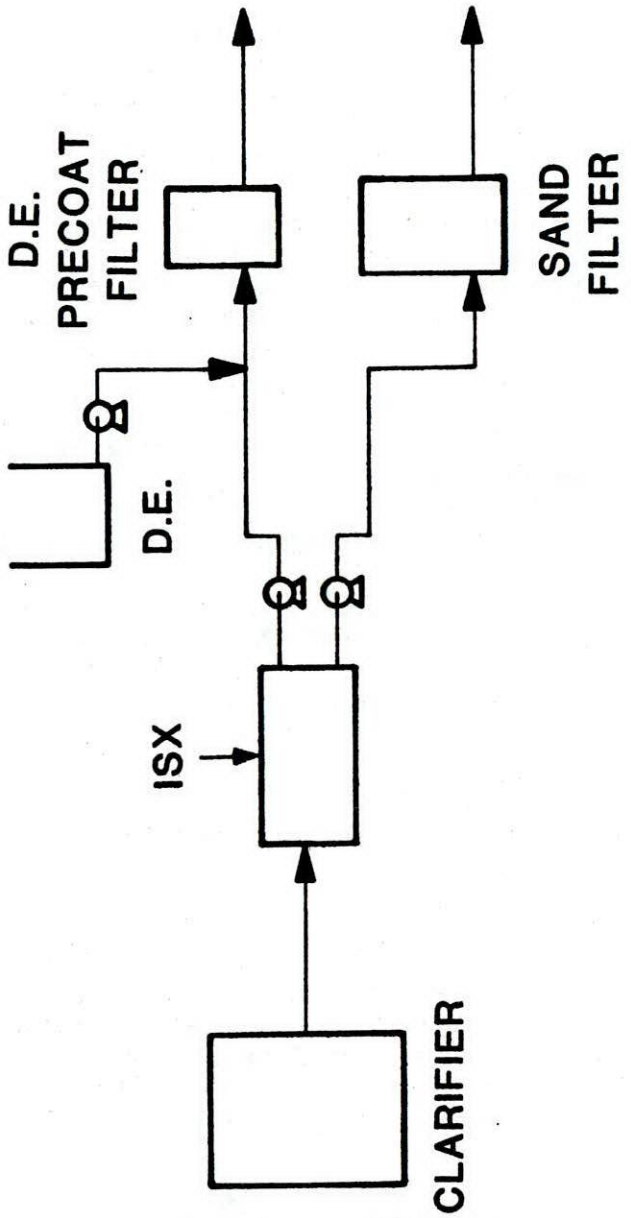
Laboratory jar tests indicated that small additions of alum and polymer after the ISX reactor would produce a separable floc. Despite the fact that our experience with the D.E. filter was not typical of previous experience, we decided to reject it for this particular application because of high consumption of filter aid.

The pilot studies were continued (See Figure 3), with the sand filter preceded by pretreatment with ISX, followed by coagulation with alum, addition of polymer, and flocculation. This treatment train provided repeatable and excellent effluent quality.

Phases V and VI were the detailed design and construction of an add-on polishing waste treatment system (see Figure 4). The new system consists of ISX reaction, alum coagulation, polymer addition, flocculation, and sand filtration. The system has the flexibility to operate in any one of several modes, from the simplest mode of sand filtration for removal of suspended solids, to the full mode for removal of collodial solids and complexed metals.

The final pH adjustment tank was utilized as a wet well for dual transfer pumps. A proportional level control system was utilized to throttle a pneumatically positioned butterfly valve and to provide a proportional modulating control offlow to the polishing system, thus eliminating shock hydraulic loadings. The control signal is also used, with a pneumatic to pulse duration transducer, to provide automatic proportional control of chemical feed metering pumps for ISX, alum, and polymer.

Figure 2



- Nearly 2-1/2 million workers were disabled.
- Ten times as many person-days were lost from job-related disabilities as from strikes.
- Estimated new cases of occupational diseases totaled 300,000.

In terms of lost production and wages, medical expenses and disability compensation, the burden on the nation's commerce was staggering. Human cost was beyond calculation. Therefore, the Occupational Safety and Health Act (OSH Act) of 1970 (P.L. 91-596) was passed by a bipartisan Congress "...to assure so far as possible every working man and woman in the Nation safe and healthful working conditions and to preserve our human resources".

In general, coverage of the Act extends to all employers and their employees in such varied fields as construction, longshoring, industrial manufacturing, and organized labor.

The following are not covered under the Act:

- Self-employed persons;
- Workplaces already protected by other federal agencies under other federal statutes.

OSHA'S PURPOSE

Under the Act, the Occupational Safety and Health Administration (OSHA) was created within the Department of Labor to:

- Encourage employers and employees to reduce workplace hazards and to implement new or improve existing safety and health programs;
- Establish "separate but dependent responsibilities and rights" for employers and employees for the achievement of better health and safety conditions;
- Maintain a reporting and recordkeeping system to monitor job-related injuries and illnesses;
- Develop mandatory job safety and health standards and enforce them effectively; and
- Provide for the development, analysis, evaluation and approval of individual state occupational health and safety programs.

Occupational Health and Safety Considerations for Electroplaters

by
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INTRODUCTION

The health and safety of individuals employed in the electroplating-metal finishing industry is an important area of concern due to the myriad of potential chemical and physical hazards inherent to the various process operations. Both employers and employees have specific responsibilities under existing federal, state, or local laws and regulations to help ensure that adverse health and safety impacts are minimized. This paper provides a general overview of legal responsibilities, current developments and trends, and outlines the primary program elements of an in-plant Occupational Health and Safety (OHS) program. Reference publications including some which were utilized in preparing this manuscript are also provided for additional information.

A review of specific hazards associated with electroplating-metal finishing process operations is not presented because it is the authors opinion that most platers must first understand their basic responsibilities are under existing regulations and what are the key elements of health and safety programs. Many of the publications presented in Table 1 provide specific information regarding such hazards and administrative procedures or engineering approaches-technologies available for abatement and control.

BACKGROUND

Millions of American workers are potentially exposed every day to chemical, physical, and biological occupational health and safety hazards while on the job. These hazards may directly affect the individual worker, his family, and the general public. Until recently however, no uniform and comprehensive provisions existed for employee protection against workplace health and safety hazards.

In 1970, the U.S. Congress considered annual figures such as these:

- Job-related accidents accounted for more than 14,000 worker deaths.

The typical concentration ratio of recovered solution to dragout is 115 to 1. The range is from a low of 35 to 1 up to the high of 202 to 1. With this concentrating ability of E.D., there has been no volume problem due to the direct addition of the recovered concentrate.

	D O Rinse Troy oz/gal.	Concentrate Troy oz/gal.	Conc. Volume Gallons	Ratio Feed to Concentrate
Week #1	.024	2.7	20.5	112:1
Week #2	.026	2.4	25.0	93:1
Week #3	.030	3.2	17.0	108:1
Week #4	.020	2.2	16.1	108:1
Week #5	.020	1.7	15.0	85:1
Week #6	.020	1.6	15.0	80:1

TABLE #2

GOLD DRAGOUT VS. RECOVERY

Case History III

Stratford Metal Finishing of Winston-Salem, North Carolina had a serious problem. Their shop is situated over a stream and the discharge limits were below 1 mg/l for all metals. The shop has been in existence for many years and the space available for effluent treatment was minimal. In fact, the available space was so small that they did not have room to segregate the nickel rinses from the cyanide-bearing rinses.

This resulted in nickel complexing with the cyanide giving excessive treatment times, chemical usage, and nickel in the discharge.

The solution devised by Stratford Metal Finishing was the treatment of plating rinses to allow recycle of the treated water for use in rinsing. Although Stratford terms their water use "closed loop", there is the inevitable discharge of water to reduce the build-up of dissolved solids. Occasionally certain solutions such as spent strippers and floor spills are barreled and shipped to a licensed hauler.

Electrodialysis plays an important role in the total effluent treatment package. The only way Stratford could make this system functional was to eliminate nickel, mixing with the cyanide in the treatment tanks. They were not concerned with the recovery value of the nickel solution, but in eliminating nickel from their rinses so their recycle system would work.

This would allow Stratford to operate the E.D. in the constant voltage mode to effect the greatest extraction of nickel ions from the dragout while allowing the concentration of nickel in the recovered solution to float. The concentration of the recovered solution was unimportant as there was considerable evaporation from the plating tanks, therefore sufficient room for recycle.

The chrome plating solutions are also operated in a "closed loop". A proprietary membrane separation process is used for the concentration and recovery of chrome plating solutions. The recovered concentrate is used to replenish the plating tanks.

Rinses from the cyanide plating tanks are handled by conventional chemical treatment to oxidize the cyanide and precipitate the metals. Rinses from the cleaners and pickles are neutralized by conventional means also. The entire effluent flow is then passed through a large filter press to remove solids. The clean effluent is then partially deionized through the use of an anion-cation exchange unit before reuse.

This system does not save any money compared to a conventional system; in face it costs more to operate. But the peace of mind obtainable by being able to cement over all the drains in the building has been more than worth the expense to the owners.

The description of operation is sure to raise a few eyebrows among the readers of this paper. This method of recycle is not being recommended as general practice. Stratford Metal Finishing was faced with the option of reducing the metal content in the effluent to virtually unattainable levels or closing down. They chose a third option; elimination of all discharge and sealing all the drains in the building. Hard work, constant attention to details, and an owner determined to make the system work, have contributed to its success. This example is presented not as an operating recommendation, but only to demonstrate how Electrodialysis is contributing to successful recovery and recycle.

In operation, the system consists of a single dragout rinse following nickel plate continuously purified by E.D., followed by a 1% Chromic Acid solution as an activator before chrome plate. Sulfuric acid is added to the dragout tank to maintain conductivity and allow the greatest recovery of nickel. The operation is shown in Figure #4.

The 1% Chromic Acid solution is sent to a licensed hauler about once a month.

This system has been in operation for over 18 months. During this period, the average concentration of nickel in the dragout rinse has

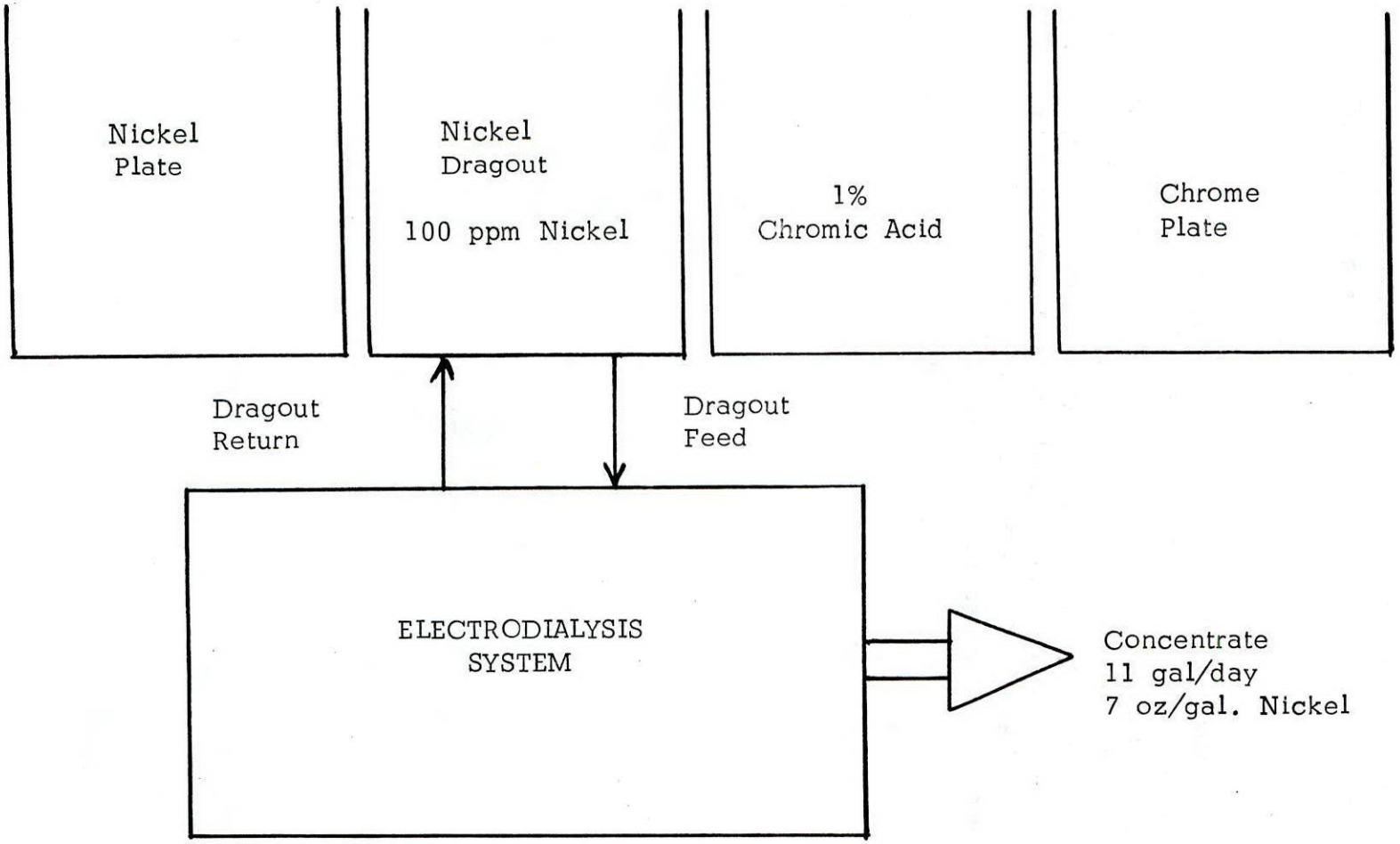


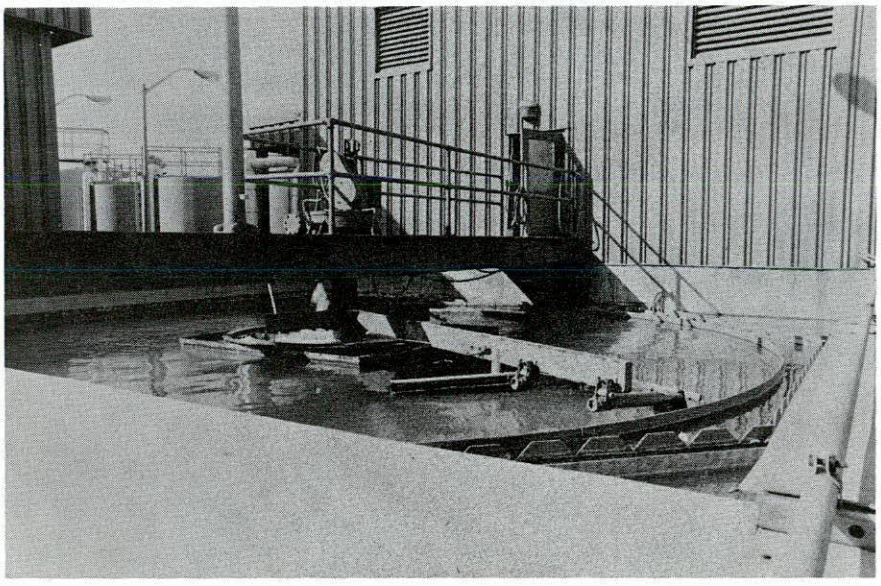
FIGURE #4

RECOVERY SYSTEM AT STRATFORD METAL FINISHING

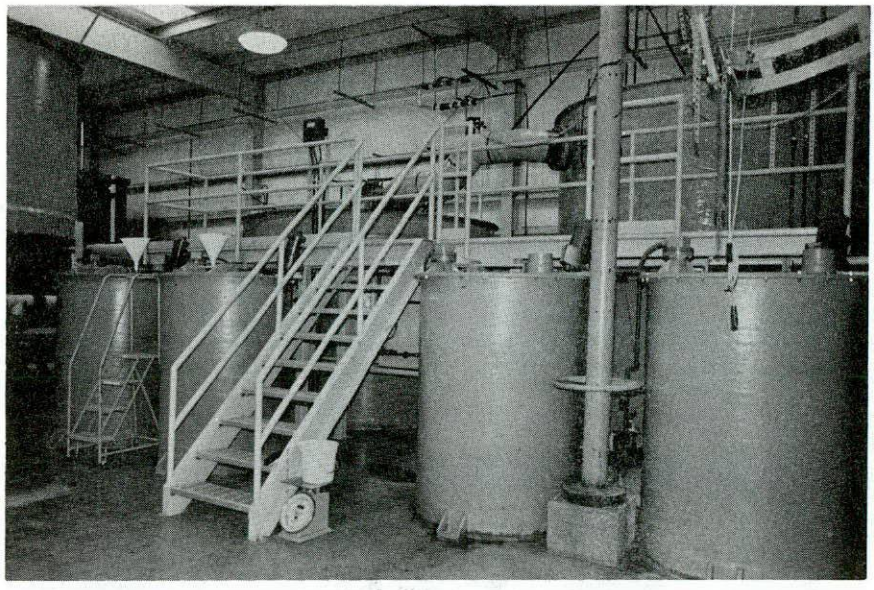
been below 100 mg/l. and the average recovered solution is 11 gallons per 16 hour day of nickel solution at 75% of bath strength. There has been no significant drag-in of nickel or chloride into the chrome plating tank. And there has been no nickel detected in the effluent treatment system.

Summary

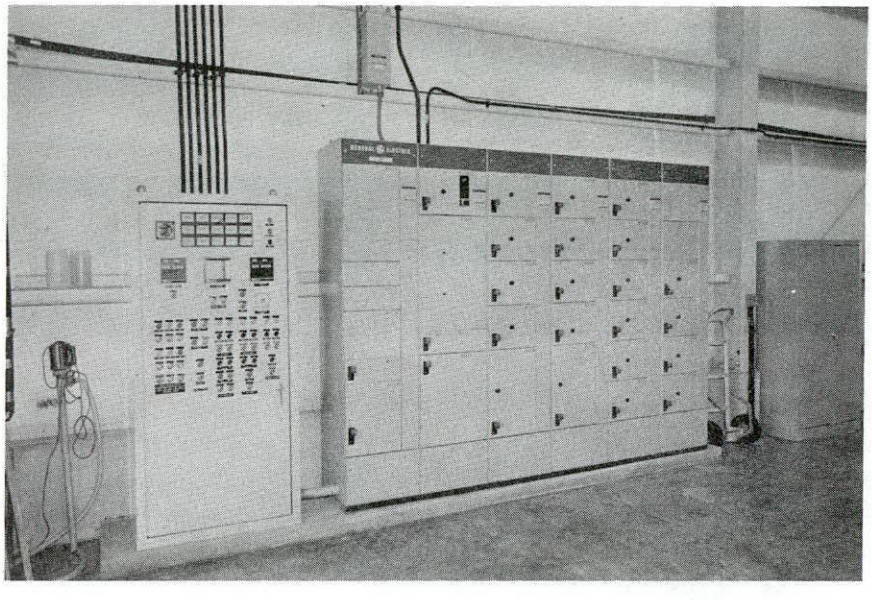
Electrodialysis has also been successfully used in a number of other applications. Concentration of Ferric Chloride wastes for volume reduction before disposal. Recovery of Cadmium Cyanide, tin, and tin-lead plating baths. E.D. has application in the processing of licorice where it is used to remove unwanted material. Being a relatively new process, additional areas of application are being found. With the increased emphasis on recovery rather than disposal, E.D is taking its place among the proven recovery technologies.



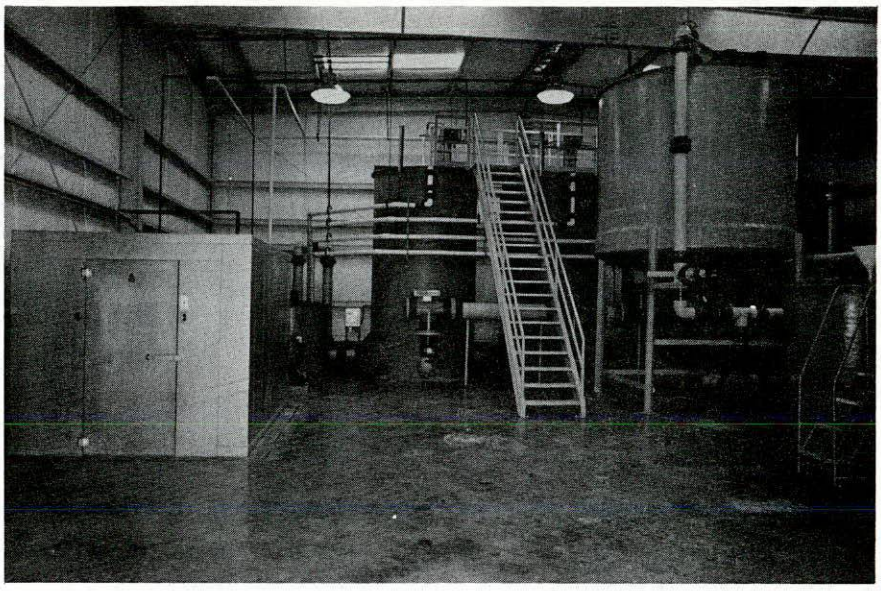
CLARIFIER



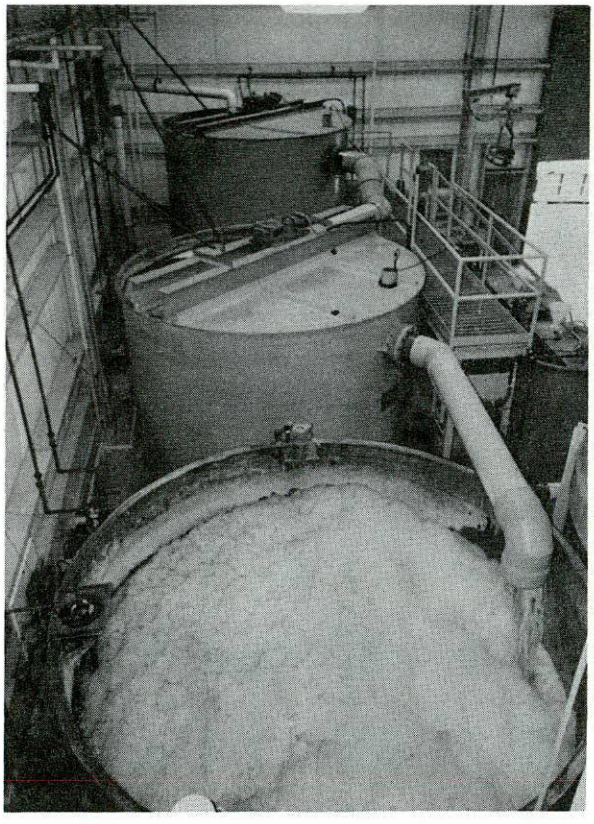
CHEMICAL MAKE-UP TANKS



CONTROL PANELS



FILTERS



REACTION TANKS

facture of the ISX has eliminated the need for alum. In the full scale system, the use of polymer has been sufficient to produce high clarity effluent in most cases.

Occasionally, the clarifier effluent will contain fine colloidal-type solids which pass through the filter. When this occurs, the alum feed is reinstated to form the floc necessary for producing the clarity and metal removals required.

The system, then, is highly flexible. If the problem is soluble copper due to increase in the proportion of chelates in the wastewater, ISX feed can be increased to compensate. If, on the other hand, the problem is solids removal in the clarifier, alum feed can be used to solve the problem. Thus, an analysis of clarifier effluent and filter effluent enables the effluent quality to be optimized, and sludge production and operating costs minimized.

Using a phased approach, General Electric was able to increase the effective capacity of their existing wastewater treatment system. They were also able to add a polishing system capable of meeting variable production needs and environmental standards.

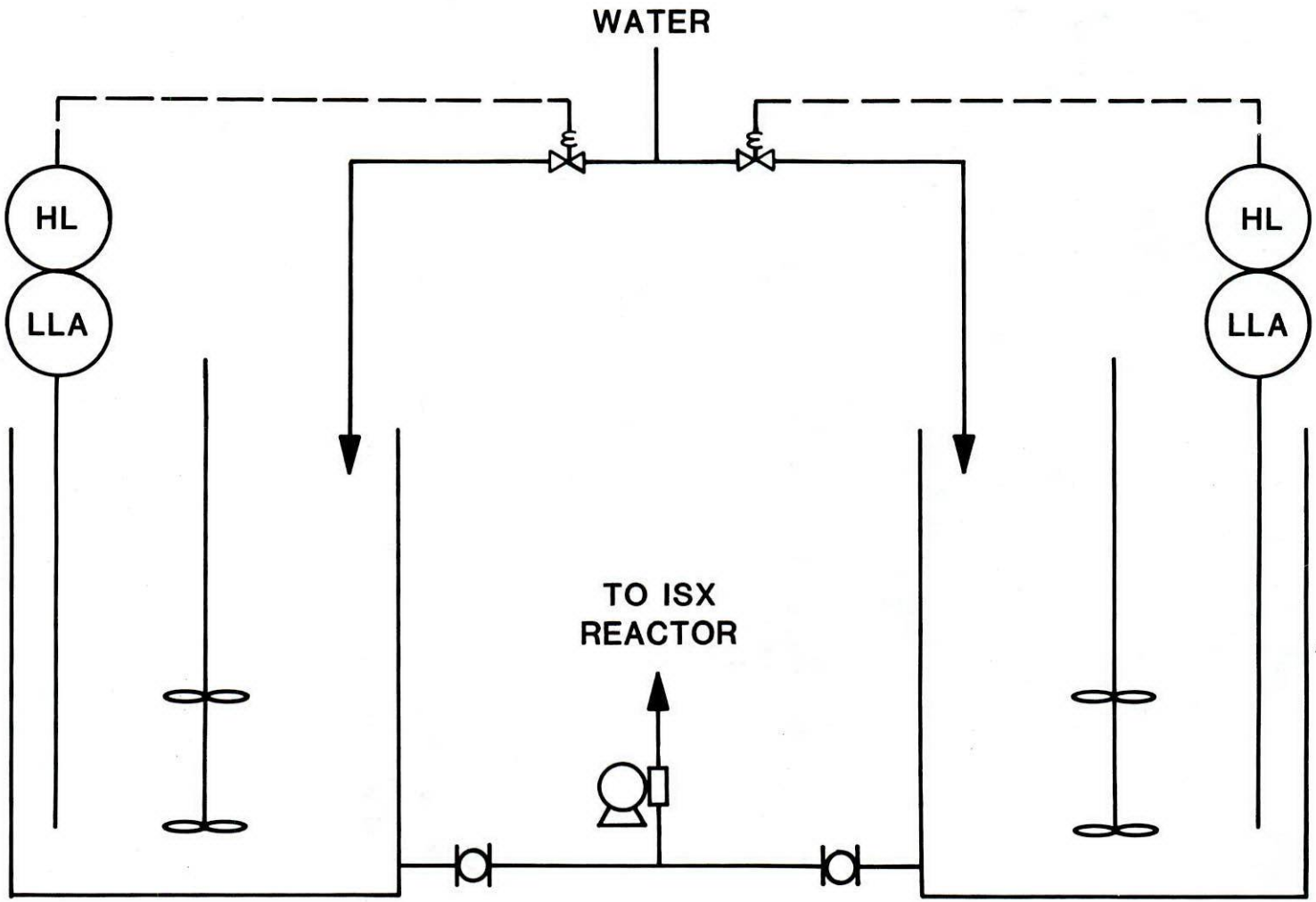


Figure 5

The pumps will transfer the clarifier effluent to the ISX reaction tank. ISX readily reacts with heavy metals by an ionic exchange mechanism to form a very insoluble complex. Its solubility product is considerably less than that of the heavy metal hydroxide; hence, it is better able to precipitate and remove metals in the presence of chelating agents. A metering pump feeds the ISX (see Figure 5) in proportion to flow, and a pH control system is used to automatically and proportionally control the sulfuric acid feed to maintain the desired pH.

The acid feed must maintain the pH in this reactor at approximately 7.0. The acid demand is created by the ISX slurry, which is highly alkaline, plus the fact that the clarifier effluent has a pH of 9.5.

Flow is by gravity from the ISX reaction tank to the alum coagulation tank. To facilitate the removal of collodial suspended solids in the sand filters, alum is added by a metering pump in proportion to flow. A pH control system is used to automatically and proportionally control the feed of caustic soda, thus maintaining the desired pH by overcoming the acidity of the liquid alum.

Following alum coagulation, wastewater flows by gravity to a holding tank where automatically throttled pumps transfer the waste to the flocculation tank. These pumps have the same type of level control system as the clarifier effluent transfer pumps. An in-line static mixer was included in the transfer line, and polymer is fed by a metering pump in proportion to flow just upstream of the static mixer to enhance flocculation. The flocculated waste then flows by gravity to four parallel upflow sand filters that are automatically and continually cleaned. The piping system is designed to provide minimal head loss and to split flow, with only minor adjustment of the filter inlet valves without destroying the floc. Filters were designed at the low end of the design range. Four filters were used, so that with one filter out of service we were still within the upper end of the design range.

Wastewater is introduced into the bottom of the filter, and flows up through the sand bed and over the filtrate weir. An air lift in the filter lifts the dirty sand from the bottom of the filter to a washer, and clean sand is deposited on top of the sand bed. This provides continuous operation without shutdown for backwash. The reject stream containing the solids removed by the sand bed flows by gravity to the reject waste tank, from where it is transferred back to the original system. The reject stream is approximately 10 percent of flow in this particular application. The filtrate flows by gravity and ties back into the original treatment system effluent outfall.

In the original system, lime was added as a coagulant aid. The new system, with its recycle of solids from the sand filter, has enabled General Electric to reduce lime consumption from approximately 400 to 100 pounds per day. This lime reduction reduces chemical consumption and sludge production.

The ISX used in the pilot studies required the use of alum, with a dosage of approximately 50 mg/l as aluminum oxide (AlO_3). A modification in the manu-

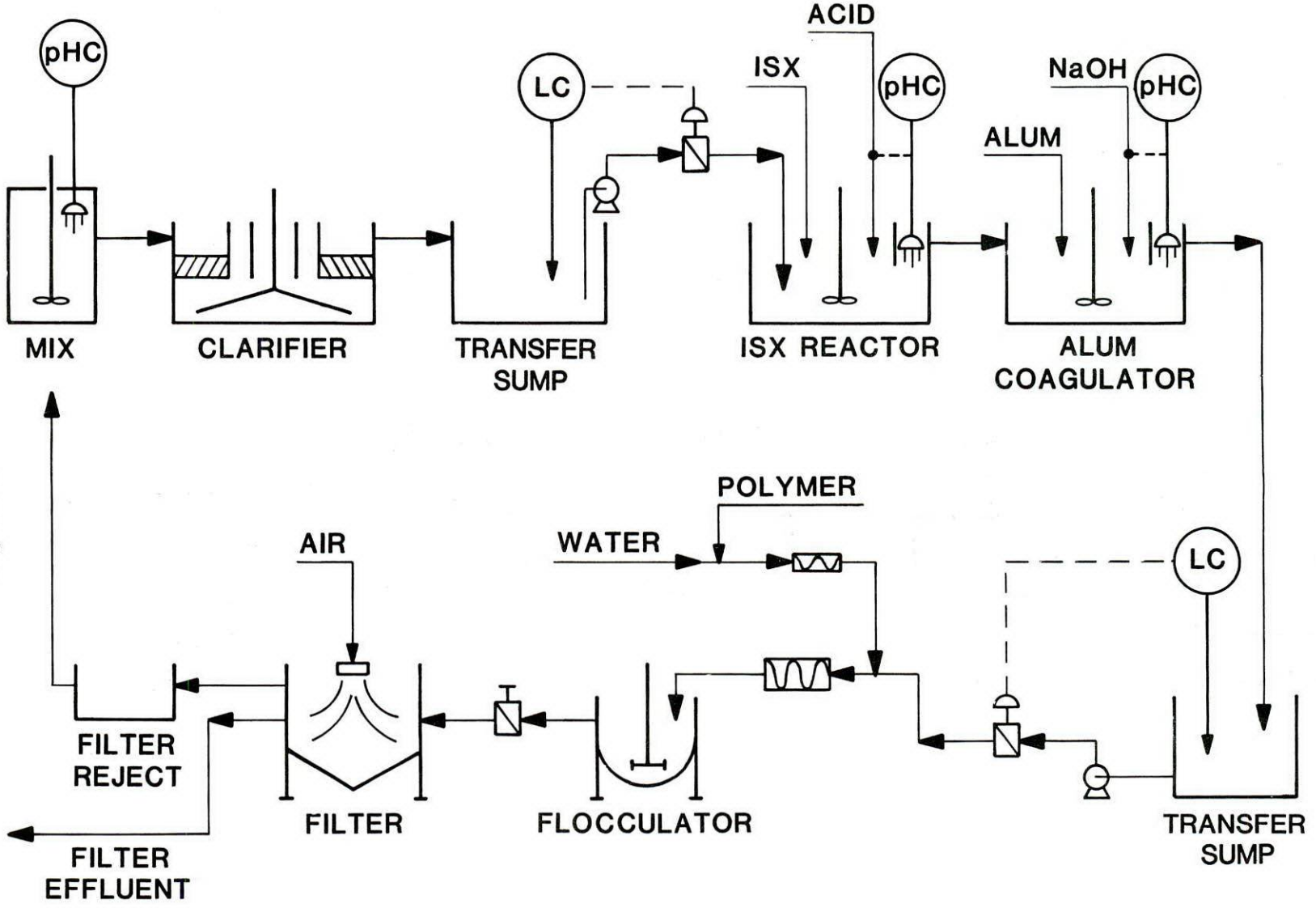
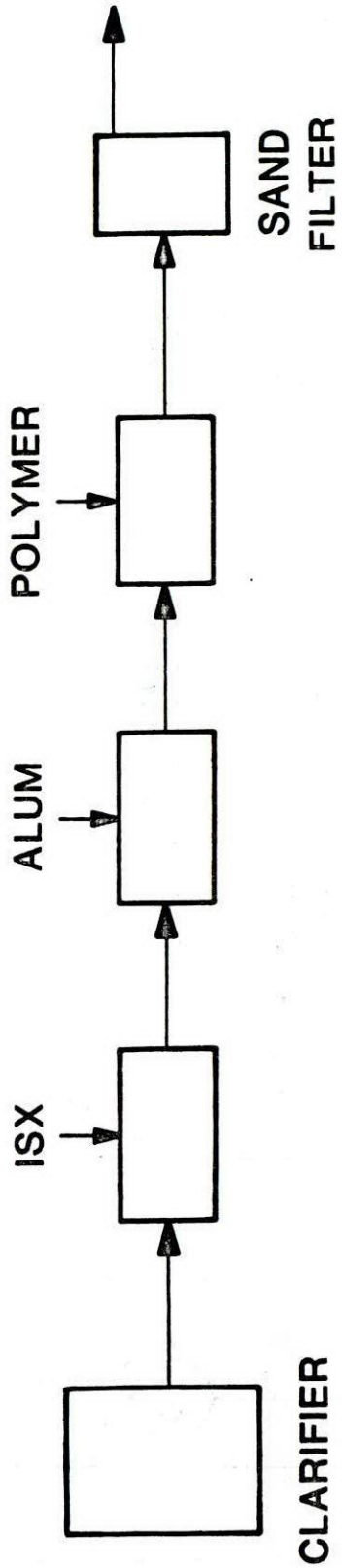

pHC
LC
ACID
ISX
pHC
NaOH
pHC
ALUM
MIX
CLARIFIER
TRANSFER SUMP
ISX REACTOR
ALUM COAGULATOR
POLYMER
AIR
WATER
LC
FILTER REJECT
FILTER
FLOCCULATOR
TRANSFER SUMP
FILTER EFFLUENT

Figure 4

Figure 3



When the concentration of gold in the third tank exceeds a pre-set level, the resin on the second tank is retired, the ion-exchange on the third tank is moved to the second, and fresh resin is installed on the third tank. This system effectively recovers over 99% of the gold dragout.

Within the recovery area, the drums containing the dragout solution from each plating line are stored and segregated as to type of bath. When a sufficient quantity has been collected, the solution is concentrated through the E.D. machine. Analysis of the stripped solution by A.A. confirms the complete removal of gold before being sent to waste treatment. The concentrate is also analyzed for gold content and then bottled and placed in stock as replenishment solution for the individual lines. The foreman signs out for the recovered solution just as he does for new products. Very close control is kept over the recovered solutions. In the first 10 weeks of operation, over 180 troy ounces of gold were recycled directly into the plating tanks. The analysis of these solutions is tabulated in Table #1.

LOT #	VOLUME	CONCENTRATION	TROY OUNCES
1	63 l	1.44	24.0
1A	38 l	0.556	5.6
2	68 l	1.39	25.0
2A	54 l	0.28	4.0
3	69 l	0.92	16.8
4	31 l	1.74	14.3
4A	32 l	0.31	2.6
5	36 l	2.23	21.2
5A	36 l	0.37	3.5
6	30 l	3.12	24.8
6A	36 l	0.55	5.2
7	61 l	1.25	20.2
7A	54 l	0.12	1.7
8	43 l	0.98	11.2
			180.1

TABLE #1

ANALYSIS OF RECOVERED SOLUTIONS

Case History II

Hadco Printed Circuits, Inc. is also a leader in the P.C. industry. Their plant in Derry, New Hampshire contains two tab plating machines. Their concern for closer in-house control over gold usage and recovery led them to consider electrodialysis. After a short in-house trial, an E.D. recovery system was purchased.

Although initially the E.D. was moved to the most active tab plating machine as production warranted, too much gold was being lost and a better system was found.

The belt rinse and first rinse after the plating tank were combined into a common rinse on each line. An overflow was constructed on each tank which directed the rinse on each line to a common tank. The solution from this tank was then pumped back to the rinse tanks through two flow control valves. The E.D. machine was then operated off the common tank to recover gold from both machines at once. Once this was done, the ion exchange columns which had been on the first rinse were transferred to the second rinse to complete the recovery loop.

As Hadco operated, they found a few problems which they had to address. A build-up of organics in the first rinse tanks was resulting in poor rinsing and a residual film on the boards. The replacement of 50% of the filter cartridges on the E.D. machine with carbon purification cartridges reduced the problem to an acceptable level.

The engineers were also concerned with the build-up of metallic contaminants in the plating tank, due to their recovery with E.D. Early analysis showed metallic contaminants being concentrated in the same ratio that they were present in the dragout. At this time, the E.D. was being operated at maximum recovery rate, maintaining the dragout well below .01 troy oz/gal.

By reducing the recovery rate to allow the dragout concentration to rise to .02-.03 troy oz/gallon, it was found that the proportion of gold to contaminants was at a much greater ratio than earlier. Also the recovered concentrate was at a much higher gold concentration than with prior operation. Typical gold concentrations in the recovered solution were between 1.5 and 3 troy oz/gal. (Table #2).

Periodic replacement of the dragout solution with fresh water was found to be necessary. The combination of metallic impurity and soluble salt build-up required this for smooth operation. The solution which was removed was drummed and shipped to the gold stripping area for use in make-up of new stripping solutions. At the same time, the second rinse was stripped by ion exchange and discarded.

The concentrate is collected in a three gallon plastic carboy placed at the side of the machine. With concentration as high as 4.6 troy oz/gal. of gold, the carboy was locked in a steel box for security reasons. Once analyzed, it is added directly to each of the tab plating machines. The volume and concentration is recorded as a part of the total gold inventory system within the plant.

E-3

Environmental II
Session E

Occupational Health and Safety Considerations for Electroplaters

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No where has electrodialysis been better accepted than in the electronics and printed circuit industry. Although there is much similarity in the processing of circuit boards between different companies, the applications of electrodialysis are quite individual.

Case History #1

Circuit-Wise of North Haven, Conn., one of the major circuit manufacturers, was one of the first companies to apply electrodialysis for gold recovery. The major consumer of gold was their tab plating machine. After a period of evaluating competitive methods, E.D. was chosen as the most favorable recovery technique.

Initially, the E.D system was operated on the dragout rinse following the plating station. Within a week of installation, the belt rinse, which formerly was only operated intermittently due to excessive gold loss, was combined with this dragout rinse. The addition of an ion exchange column on the second rinse effectively closed the loop on gold effluent.

The concentrate from the E.D. was analyzed for gold content and metallic contamination and was determined to be suitable for direct recycle to the plating tank. The system was operated in this manner for eight months with no significant build-up of contaminants in the plating tank. Over 35 troy ounces of gold were recovered in the first month of operation. Since the price of gold was over $800/oz. at that time, the E.D. equipment was amortized in only one month. Direct recycle of the recovered concentrate had also eliminated inventory costs for gold at the refiner and refining costs.

The total amount of gold recovered over this eight months was 150 troy ounces. The recovered concentrate ranged from a low of 0.14 troy oz/gal. to a high of 5.26 troy oz/gal. of gold. The engineers encouraged by this performance looked for additional ways to recover gold from their wide range of processes.

The culmination of this research is now operating at Circuit-Wise. Gold recovery is enclosed in a separate high security area. Within this room, E.D. is the heart of the recovery system.

On the production floor, each gold plating area is organized with a dragout tank following the plating station. The second rinse tank is also a dead rinse as is the third rinse. The first dragout rinse is withdrawn into drums periodically to maintain the concentration of gold below 0.1 oz/gal. The second and third rinses are continuously circulated through separate ion exchange cartridges.

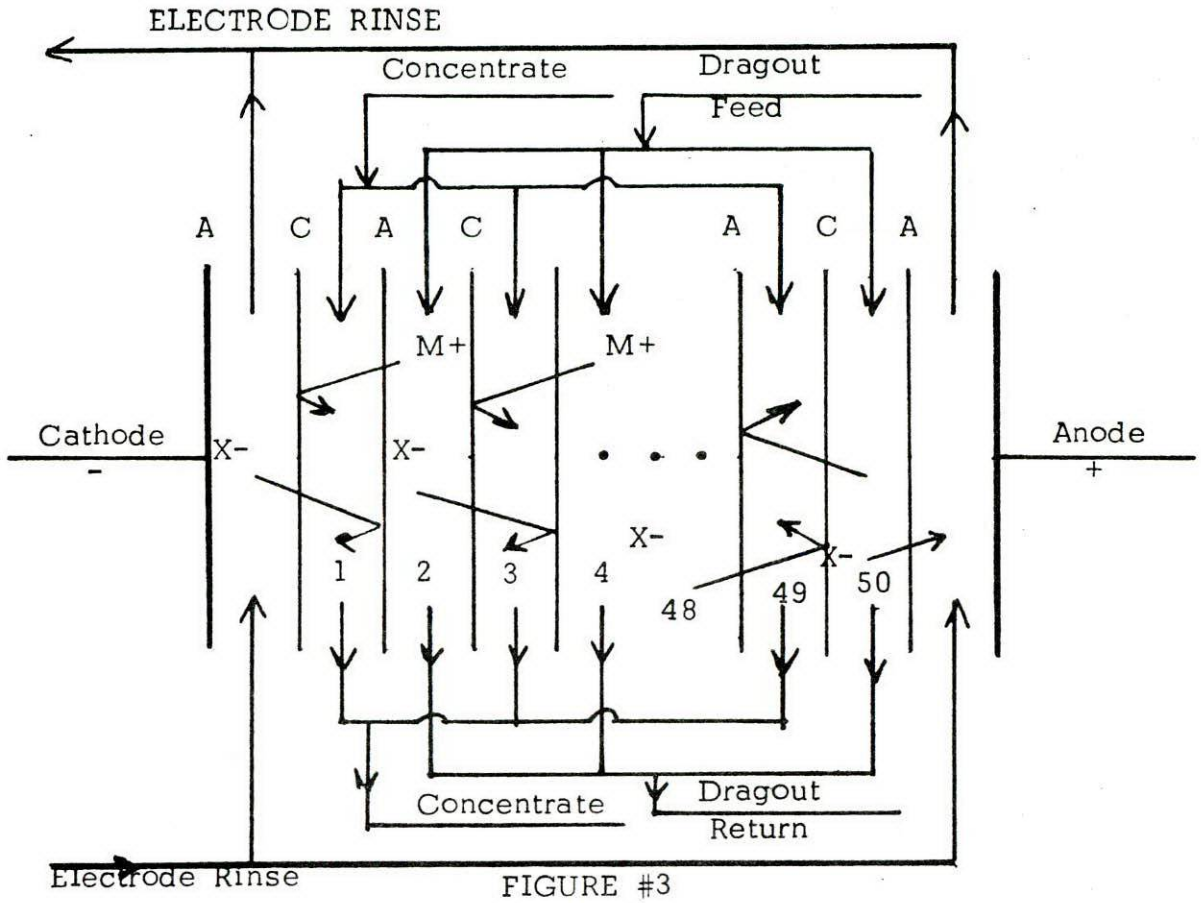

FIGURE #3

Typical electrodialysis recovery systems contain between 10 and 100 cell pairs. The passage of a direct current through the stack causes the ions in the solution to move in the direction of the oppositively charged electrode. The cations such as nickel, copper, zinc, etc. are attracted to the left towards the cathode, but can only move to the next adjacent cell where they are prohibited from further migration by an anionic membrane. Likewise the anions such as sulfate, chloride, cyanides, etc. are attracted to the right side, but again are prohibited from further migration by the presence of a cationic membrane. The use of a stacked multicell concept makes it possible to obtain a metal concentration many times that of the electrochemical equivalents passed.

In practice, electrodialysis is operated on a dragout rinse. The solution from the dragout rinse is continuously recirculated through the E.D. stack which removes and concentrates the ionic species from the dragout and returns ion depleted water to the tank. The flow rate is high through the machine due to the turbulent flow requirements and only 20% of ions in solution are removed in a single pass. Therefore, E.D. must be operated on a still rinse; it is not suitable for a flow situation.

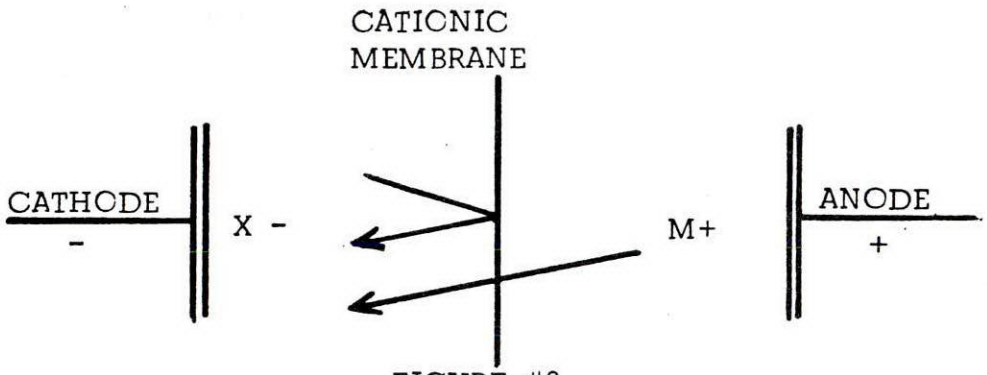

FIGURE #2

These membranes are thin sheets of reinforced plastic which have been subsequently impregnated to impart the appropriate ionic characteristic. Membranes are then arranged in parallel cells, alternating anion and cation between an anode and cathode. Specially designed spacer/gaskets separate the membranes forming leak-tight, flow directing compartments between adjacent membranes. This assembly is held in compression by a pair of end plates and tie rods or other clamping device. The compartments or cells direct the solution feed to the cell over supporting baffles which separate the membranes and induce turbulent flow. Turbulent flow is required to prevent boundary layer depletion of ions along the membrane surface. The anode is normally constructed of platinized titanium while the cathode is stainless steel.

Figure 3 is a schematic operational drawing of a typical E.D. stack. At the opposite ends are the stainless steel cathode and the platinized titanium anode. Each electrode is in a cell around which flows a compatible salt solution of electrolyte whose purpose is to collect and dispel resulting gases such as hydrogen and oxygen, and impart overall electrical conductivity to the stack. Adjacent to each electrode is an appropriate membrane chosen to prevent the migration of metal ions into the electrode compartments and subsequent plating out. Subsequently there are a number of individual cell compartments of alternating layers of anionic and cationic membranes. The even numbered cells are the paths for the feed solution; the feed solution being constantly recirculated from a dragout or reclaim tank. The odd number cells are the collecting or concentrating cells in which the concentrated plating solution is collected and recirculated. The repeating stack unit of a cation exchange membrane, a diluting spacer, an anion exchange membrane and a concentrating spacer is termed a cell pair.

SUCCESSFUL ELECTRODIALYSIS APPLICATIONS

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Introduction

Metal recovery from electroplating solution dragout has become a prime concern for many metal finishers lately. To satisfy this demand for solution recovery, many new recovery systems have been introduced into the market. Electrodialysis (ED) has been one of the more successful systems introduced over the past five years. The principles of electrodialysis, its application, and case histories will be reviewed in this paper.

Principles & Applications

Electrodialysis is a membrane process which can be used for the separation, concentration, or removal of ionic species from water. Ions are transported through these ion exchange membranes by the driving force of an electrical potential across the membranes. To accomplish this ion separation, the membranes employed are in two distinct forms -- anionic and cationic.

Anion exchange membranes allow only negatively charged ions such as sulfate or chloride, and negatively charged complexers such as metallic cyanides to pass through, while blocking the passage of positive ions. (Figure 1).

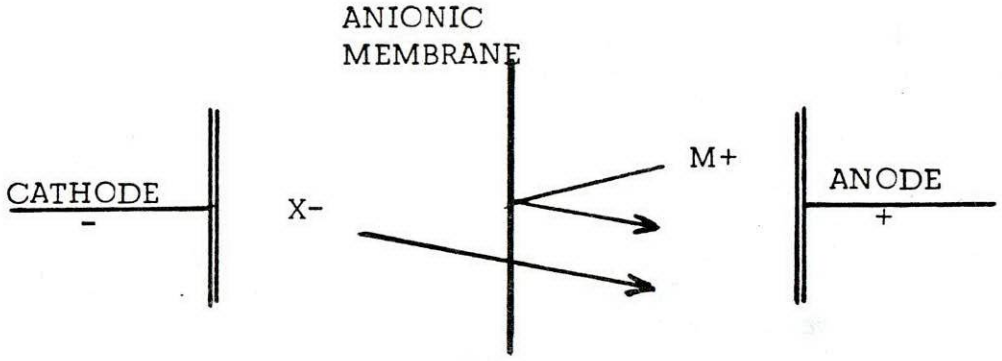

FIGURE #1

Cation exchange membranes allow only positively charged ions such as nickel, copper, zinc and potassium in solution to pass through while blocking the passage of negative ions. (Figure 2)

E-2

Environmental II
Session E

Successful Electrodialysis Applications

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7. Wozniak, Daniel J., and Jerry Y. C. Huang, "Variable Affecting Metal Removal from Sludg", Journal WPCF, 54, 12, 1574-80, Dec. 1982

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In the recent issue of this journal (9) the current items include:

New coagulants
Coagulant recovery
Improved rapid mixing and floculation
Direct filtration
Declining rate filtration

We feel that we are working on one or two of these promising results.

These results have been verified in independent third party laboratories which gives a good indication that the field tests were verified.

Anyone interested in more information can contact either author now or by mail.

Thank you.

The removal of metals from solution is also a function of pH and chelate metal bond strength but for high pH rather than low. In this reaction the function is to exceed the solubility product constant and form a precipitate of the metal. Our investigations into these parameters play for metal removals resulted in the optimization of our formuli and chemical processes as shown.

Annually WATER/Engineering and Management publishes a list of unconventional solutions and approaches to the problems of water and waste treatment (8). Among the ideas proposed by their distinguished group of experts between 1954 and 1970 are shown in TABLE IX.

As you will note many of these are now conventional solutions and most all have moved out of the exotic class.

TABLE IX

Proposed or Predicted Ideas Between 1954 and 1970 (8)

- Better pretreatment of water before filtration;
- higher filtration rates;
- wider application of diatomaceous earth filtration;
- higher water quality standards;
- rapid test for coliform bacteria;
- better process control for coagulation and disinfection;
- reclaiming wastewater as a drinking water source;
- more use of desalting systems;
- greater use of polyelectrolyte coagulant aids and liquid alum;
- greater use of microstraining;
- importation of Canadian water;
- elimination of lake eutrophication;
- storage of treated wastewater and storm waters in underground caverns as a supply source for drinking water;
- higher coagulation, sedimentation and filtration rates;
- lower chlorine dosage because of better pretreatmnt processes;
- automated chemical and bacterial analysis, and
- new synthetic chemicals to control tastes and odors and to disinfect.

TABLE VIII

INDEPENDENT SLUDGE ANALYSIS*
Taken April 8, 1982

Parameter	EP TOXICITY*	mg. metal Kg. dry sludge MASS ANALYSIS**
Arsenic	< 0.01 mg/l	< 1 ppm
Barium	0.1 mg/l	39 ppm
Cadmium	0.05 mg/l	3.9 ppm
Chromium-Total	-	44 ppm
Chromium-Hex	0.01 mg/l	-
Lead	0.3 mg/l	48.7 ppm
Mercury	< 0.01 mg/l	< 1 ppm
Selenium	< 0.01 mg/l	< 1 ppm
Silver	0.05 mg/l	14.6 ppm
Nickel	1.5 mg/l	490 ppm
Copper	0.07 mg/l	89.7 ppm
Zinc	0.09 mg/l	107.3 ppm
Iron	1.3 mg/l	6,340 ppm
Total Cyanide	< 0.01 mg/l	< 1 ppm

* Test done by State Certified Independent Laboratory.
*Sample extracted for 24 Hrs @pH 5.0 w/0.5N Acetic Acid.
**Based on Dry Weight.

DISCUSSION

Metal removals from sludges for all metals using 1-3% solids concentration acidification processes are dependent upon pH condition, the sludge solid concentration, the specific metal and the length of exposure time. Irving and Williams (6) described the general pattern of orders of the relative metal organic chelate bond strengths. These bond strengths are thought to be a function of the metal involved in the complex. For a pH value of 2.0 the following order of metal removal efficiency has been reported by Wozniak and Huang (7).

pH 2.0 Zn>Ni>Cu>Pb>Cr

The treatment of two industrial chelated wastewaters using two different ABCEL chemicals is shown in Table VI. Tests were conducted on one liter samples using four minutes mixing time. In the first sample heavy metal removal ranged from 98.1 to 99.8% WHILE in sample two the removals were 97.1% for zinc to 100% for chromium. These results generally agree with those obtained on unchelated wastewaters.

TABLE VII

REMOVAL OF OILS, GREASE AND PHOSPHATE FROM AN INDUSTRIAL WASTEWATER

SAMPLE	HEXANE SOLUBLE (OIL & GREASE)	% REMOVAL	pH	PHOSPHATE (PO_4)	% REMOVAL
PLANT A					
UNTREATED	752 mg/l		6.8	56.4 mg/l	
TREATED w/AB210					
@ 4.5 g/l	24 mg/l		6.9	0.52 mg/l	98.9
@ 6.0 g/l	77 mg/l		6.8	0.46 mg/l	99.0
AB220 TREATED					
@ 4.5 g/l	70 mg/l		6.8	0.37 mg/l	
@ 6.0 g/l	68 mg/l		6.8	0.43 mg/l	
PLANT B					
UNTREATED	204 mg/l		6.9	43.0 mg/l	
TREATED w/AB130		% REMOVAL			% REMOVAL
@ 3 g/l	50 mg/l	81.0	7.2	2.08 mg/l	95.0
@4.5 g/l	66 mg/l	68.0	7.5	0.92 mg/l	98.0

This is a sample of the results obtained using ABCEL compounds. Other tests with other types of industrial wastewater were equally successful.

TABLE VI

TREATMENT OF CHELATED WASTEWATER

SAMPLE #1 *

UNTREATED		TREATED		PERCENT REMOVAL
Copper	11.3 mg/l	Copper	0.08 mg/l	99.3
Nickel	25.7 mg/l	Nickel	0.4 mg/l	98.4
Zinc	4.6 mg/l	Zinc	0.01 mg/l	99.8
Chromium	1.6 mg/l	Chromium	0.03 mg/l	98.1
Iron	78.1 mg/l	Iron	1.30 mg/l	98.3

SAMPLE #2 **

UNTREATED		TREATED		PERCENT REMOVAL
Copper	8.5 mg/l	Copper	0.13 mg/l	98.5
Nickel	19.3 mg/l	Nickel	0.2 mg/l	98.9
Zinc	3.5 mg/l	Zinc	0.1 mg/l	97.1
Chromium	1.2 mg/l	Chromium	0.0 mg/l	100.0
Iron	58.6 mg/l	Iron	0.90 mg/l	99.8

The above results were achieved without previously evaluating the wastewater samples. Test were performed on 1 liter samples of wastewater mixed for 4 minutes.

* reagent 20020
** reagent 25020

TABLE V

EFFECT OF MIXING (REACTION) TIME ON COPPER REMOVAL IN 500 ml OF COPPER SOLUTION WITH INITIAL CONCENTRATION OF 10.0 ppm Cu USING 0.75g AB 200

MIXING TIME MIN.	FINAL CONC. mg/l	pH OF FILTRATE	SETTLING TIME MIN.
1:00	0.6	6.2	3:00
2:00	0.3	6.2	3:00
3:00	0.1	6.6	1:30
4:00	0.0	6.6	1:30

As mixing time is increased, the removal of copper is more effective, settling time decreases and a more favorable pH level is achieved. It is also indicated that an increased mixing time may allow for a lower amount of blend required.

RESULTS

Actual industrial wastewater samples were treated using AB2020 and AB250 in concentrations of 2 gram per liter. The results of treatment of wastewater samples from three (3) stations for removal of copper from etching solutions is shown in Table III. These results between the untreated copper wastewater and the treated wastewater shows 93.79 per cent removal.

Table IV shows a series of test using AB200 for removal of copper ions from aqueous solution. In all cases the mixing time was three (3) minutes, the initial concentration of copper 10mg/l. The pH of the treated solution increased with increasing weights of the blend from pH 6.1 to 6.6. As the weight of reagent was increased from 0.25 gr. to 1.0 g per 500 mls of solution the percent removal of copper increased from 89 to 100% and the settling time decreased from 2:60 to 1:00 minutes.

The effect of mixing, i.e., reaction time on the removal of copper ions from 500 mls solution containing 10.0mg/l Cu is shown in Table V. To all samples 0.75 grams of AB 200 were added the pH of the filtrate did increase from 6.2 to 6.6 with increases in mixing time from 1 to 4 minutes more important the removal of copper ions increased from 94 to 100% and the settling time decreased.

TABLE III

PARTIAL RESULTS OF WASTEWATER SAMPLES
TAKEN FROM (3) STATIONS ON TWO PC BOARD COPPER ETCHES

Water Sample Number	Type	gal/min Flow	Untreated Copper	Treated	%	* Chemical & Quantity
1A	Abrading	7.5	2.5 mg/l	0.17ppm	93	AB2020 2.0g/l
1C	Rinse	40.0	9.85mg/l	0.50ppm	95	AB250 2.0g/l
1E	Final bur	3.4	8.72 "	0.16ppm	98	AB2020 2.0g/l
2E		30.0	2.90 "	0.10ppm	97	AB2020 2.0g/l

*Proprietary material

TABLE IV

DETERMINATION OF WEIGHT OF AB 200
FOR BEST COPPER (Cu) REMOVAL
IN 500 ml

WEIGHT OF BLEND	MIXING TIME MIN.	INITIAL CONC. MG/l	FINAL CONC. MG/l.	pH OF FILTRATE	SETTLING TIME MIN.
0.25g	3	10.0	1.10	6.1	2:60
0.50g	3	10.0	0.20	6.3	2:00
0.75g	3	10.0	0.10	6.4	1:66
1.00g	3	10.0	0.00	6.6	1:00

For the removal of copper (Cu) (above initial concentration), the most effective weight of blend is between 0.75g and 1.00g per 500 ml of solution.

Studies in our laboratories have shown that under controlled conditions at pH levels varying from 3 to 11 and using specific pollutants, the sludge will not appreciably leach. The ability of the sludge to be nonleaching is one of the most unique properties, and tests are continuously being performed to verify this property under a variety of conditions. (See Table VIII). The sludge produced from any wastewater stream must, of course, be evaluated before deciding if it is truly non-leaching under conditions of its eventual storage.

The action of the ABCEL compounds has been found to be suitable for removal of a large number of pollutants as listed. In addition, the compounds also have been effective in lowering the BOD and COD levels as well as controlling pH without further treatment. The constant testing of industrial wastewater supplied to our laboratories by industry to determine the most suitable formulation for their needs leads to the discovery of new removal properties of the compounds. Unlike other adsorption methods, ABCEL does not create carbon or resinous conditions in the treated water.

The mechanics employed are relatively basic and not extremely expensive. The system requires only one vessel which functions as a reaction and settling tank with a high speed agitator to assure fine distribution of the chemical, and a filtering and dewatering device which are usually one and the same. In the case of greater flows, more than one reaction container is used, but each functions as reaction and settling tank. Therefore, extensive systems with separate units for each phase of the treatment are not necessary. The capital costs for these systems are low. Space used is kept at a minimum. Usually one can modify existing systems to use this new chemical approach.

The major proposed changes in the water quality standards program include: (1) focusing on priority water bodies; (2) determining the attainability of uses by analyzing environmental and physical factors impacting the attainment of a use and assessing the benefits and costs of attaining a use; (3) changing designated uses; (4) providing for varying levels of aquatic protection; (5) developing site-specific criteria; (6) clarifying the antidegradation policy; (7) eliminating provisions relating to national resource waters; (8) recognizing general policies applicable to state water quality standards; and (9) specifying elements which EPA will review in approving state water quality standards.

NEW TREATMENT METHODS

Due to the complexity of modern industrial manufacturing methods, wastewater has become equally complex and regulations more stringent.

These challenges have prompted new ideas and new techniques to be developed.

It is to the above end that this process was developed. ABCEL [5] is a unique and original formulation that allows for the splitting of emulsions and removal of contaminants in a single step.

Above operates on the principles of adsorption, demulsification and precipitation as well as other chemical reactions. It will react with both organic and/or inorganic pollutants at the same time. It can split emulsions of many types of oil, paints, dyes, cellulose, phosphates, nitrates, nitrites, sulfates, sulfides, chromium III and VI, heavy metals, i.e., copper, iron, zinc, lead, nickel, hexane solubles, acids, latex, cooling emulsions, etc. The chemical reactions that occur during processing cause pollutants to be transferred into a form that can be removed by entrapment in the interstitial sites of the sludge matrix. This, theoretically produces a sludge cake which will not allow the entrapped pollutants to be leached from their tightly bound sites.

Janson, Kenson and Tucker [2] presented a discussion of alternative methods used to treat the typical heavy metal wastewater generally generated from electroplating and surface metal finishing operations. Prior to considering any method of wastewater treatment, it is of prime importance to the manufacturer and his pollution control expert to review the entire operation and reduce by good housekeeping, process operation or modification of the water usage wherever feasible. This important first step will result in water usage reductions that will allow the manufacturers to reduce the volume of wastewater generated. This, in turn, will reduce the size of equipment, capital cost and operational/maintenance costs of the wastewater treatment system.

The EPA is moving forward toward implementation of an ambient water quality based criteria for acceptance by the States to define water quality standards. In the Water Research Strategy FY'84-86 approved by the EPA Assistant Administrator for Research and Development and Water Programs, it is stated that high priority is given to toxicity reduction approach for National Pollution Discharge Elimination System (NPDES) permits [3].

WATER QUALITY STANDARD REGULATIONS

New Water Quality Standards Regulation. A water quality standard defines the water quality goals of a water body, or portion thereof, by designating the use or uses to be made of the water and by setting criteria necessary to protect the uses. States adopt water quality standards to protect the uses. States adopt water quality standards to protect public health or welfare, enhance the quality of water and serve the purposes of the Clean Water Act.

EPA proposed in the Federal Register, revisions to the water quality standards regulation to make fundamental changes in the management of the program. These changes would enable the States to: (1) design a water quality standards program based on priority water quality pollutant problems; (2) select the uses and set criteria consistent with meeting the requirements of the Act; and (3) revise uses based on an analysis of the attainability of uses and the costs and benefits of attaining the uses.

BACKGROUND

The General Pretreatment Regulations of the Federal Government took place on January 31, 1982 (46 Federal Register 4518) [1]. Also regulations for the metal finishing/electroplating industry have been reissued in the Federal Register of January 13, 1982 with the stated date for compliance to be January 28, 1984. These EPA regulations include the maximum discharge criteria for heavy metals. The cited limitations parallel the existing criteria promulgated for the plating/surface finishing industry. The heavy metals limitations can be split into two basic categories; discharges of less than 10,000 gallons per day, and discharges of greater than 10,000 gallons per day to Publicly Owned Treatment Works (POTW). There are explicable formulas for removal credits, however most industrial discharges will probably choose to comply with either of the two discharge schedules listed in Table I and Table II.

TABLE I

LIMITATIONS FOR DISCHARGES MORE THAN 10,000 GALLONS PER DAY TO POTW

Pollutant	Maximum Per Day (mg/l)	Maximum for 4 Consec. Days (mg/l)
Lead	0.6	0.4
Cadmium	1.2	0.7
Chromium	7.0	4.0
Copper	4.5	2.7
Cyanide	1.9	1.0
Gold	1.2	0.7
Nickel	4.1	2.6
Zinc	4.2	2.6
Total Metals	10.5	6.8

TABLE II

LIMITATIONS FOR DISCHARGES LESS THAN 10,000 GALLONS PER DAY TO POTW

Pollutant	Maximum Per Day (mg/l)	Average of Daily Values For 4 Consecutive Days Not to Exceed (mg/l)
CN,	5.0	2.7
Cd	1.2	0.7
Pb	0.6	0.4

A NEW INDUSTRIAL WASTEWATER TREATMENT METHOD FOR REMOVAL OF MULTIPLE CONTAMINANTS

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ABSTRACT

Conventional wastewater treatment methods require multiple steps and expensive equipment. Sludge handling is costly. A new chemical adsorption method removes inorganic and/or organic impurities in a single, 15-minute operation using low-cost equipment and results in a dry, stable sludge. Tests of the water and sludge, after treatment, indicate the removal of pollutants to levels in compliance with regulations.

INTRODUCTION

The U.S. Environmental Protection Agency is charged with implementing the Clean Water Act, Safe Drinking Water Act, and portions of the Marine Protection, Research and Sanctuaries Act. The objective of the Clean Water Act is to restore and maintain the chemical, physical, and biological integrity of the Nation's waters. The objective of the Safe Drinking Water Act is to ensure safety (to human health and welfare) of public water systems (derived from surface and groundwater). The objective of the Marine Protection, Research and Sanctuaries Act is to regulate the dumping into ocean waters of materials that would adversely affect human health and welfare. The Clean Water Act and Marine Protection, Research and Sanctuaries Act give the primary legislative basis for protecting surface water quality, while the Safe Drinking Water Act and Resource Conservation and Recovery Act provide the principal basis for protecting groundwater quality and potable water supply systems.

E-1

Environmental II
Session E

A New Industrial Wastewater Treatment Method for Removal of Multiple Contaminants

Barbara Monick and Alexander Blake
Sweetwater Technologies Corp.
Smithtown, NY

TABLE III CORRELATION OF TEST RESULTS

STUDY IDENTITY AND AS PLATED LEAD FINISH	SOLDERABILITY RESULTS HRS. TO FIRST FAILURE AT 165° ± 5°C	PERCENT CARBON IN PLATED FINISH	OUTGASSING RESULTS LEADS OUTGASSING/ LEADS TESTED		HIGH VACUUM MELT TEST PERCENT PRESSURE INCREASE	MASS SPECTROMETRY 650°F FOR FIVE MIN.		
			HOT IRON	HOT OIL		μg/ g	cm/³ g	VOL. OUT GASSING/ VOL. TIN
AES *G MATT TIN	220	0.036	-	-	-	-	-	-
AES **P BRIGHT TIN	13	0.165	-	-	-	-	-	-
2330 G MATT TIN	-	-	2/80	63/80	-	20.5	0.23	0.8
2330 G MATT TIN	-	-	10/80	64/80	-	34.0	0.34	1.2
2330 P MATT TIN	-	-	0/80	26/48	31	-	-	-
2330 P BRIGHT TIN	-	-	73/80	80/80	-	-	-	-
2330 P BRIGHT TIN	-	0.124	80/80	80/80	224	201	1.60	5.7
2330 P BRIGHT TIN	-	0.041	61/80	73/80	71	52.3	0.40	1.4
RADC P TIN-LEAD	24	0.137	-	80/80	-	-	-	-
RADC P BRIGHT TIN	168	0.157	-	80/80	-	-	-	-
ABOVE FUSED	192	N/A	-	N/A	-	-	-	-
RADC P MATT TIN	1000+	0.013	-	12/80	-	-	-	-
ABOVE FUSED	180	N/A	-	N/A	-	-	-	-
RADC G MATT TIN	1000+	0.018	-	16/70	-	-	-	-

*G = GENERIC; **P = PROPRIETARY

Summary:

Basic Precept:

* Electrolytic tin plating processes have been developed which yie'd deposits of low outgassing levels.

Developmental Principles:

* Generic matt electroplated tins remain solderable ten times longer than generic bright electroplated tins when stressed at the same elevated temperature.

* Intermetallic compound formation, occluded carbon concentration and, to a minor extent, oxide growth interact together to degrade solderability.

* The solderability failure mechanism for generic matt tin was found to be mainly intermetallic formation at the base interface with, to a minor extent, surface oxide growth as a co-contributor.

* The solderability failure mechanism for generic bright tin was found to be co-deposited organic compounds which volatilize during high temperature exposures.

* Deposit analyses show four to five times higher carbon in generic bright tin versus generic matt tin.

* Tests have been developed which are capable of determining conformance to requirements for low outgassing electrolytic tin lead finishes.

* An accelerated manufacturing solderability test at 10 hours/200°C, 20 hours/175°C, or 48 hours/150°C should ensure solderability at 168 hours/125°C (a standard military burn-in).

Conclusions:

* Fusing before burn-in affects solderability time in two ways:

    1. Degrades generic matt tins
    2. Improves generic bright tins somewhat

* The most eloquent statement of the validity of this investigation is the correlation of test results in Table III.

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NOTICE

Publication of this report does not constitute approval by the U.S. Navy of the findings or conclusions contained herein. It is published for the exchange and stimulation of ideas.

TABLE II

Lead Finish	Solderability Results Hours To First Failure	Outgassing Results Leads Outgassing/ Leads Tested	% Carbon In Plated Deposit
A. Tin/Lead Plate	24	80/80	0.1366
B. Bright Tin (as plated)	168	80/80	0.157
*Fused Version	192	N/A	N/A
C. Proprietary Matt (New bath - 3 months)	1000+	12/80	0.0125
*Fused Version	180	N/A	N/A
D. Generic Matt (old bath - 2 yrs.)	1000+	16/70	0.0177

Summary:

Basic Precept:

* Electrolytic tin plating processes have been developed which yield deposits of low outgassing levels.

Developmental Principles:

* Generic matt electroplated tins remain solderable ten times longer than generic bright electroplated tins when stressed at the same elevated temperature.

* Intermetallic compound formation, occluded carbon concentration and, to a minor extent, oxide growth interact together to degrade solderability.

* The solderability failure mechanism for generic matt tin was found to be mainly intermetallic formation at the base interface with, to a minor extent, surface oxide growth as a co-contributor.

* The solderability failure mechanism for generic bright tin was found to be co-deposited organic compounds which volatilize during high temperature exposures.

* Deposit analyses show four to five times higher carbon in generic bright tin versus generic matt tin.

Results:

Data generated in the NAC TR-2330 Study and the RADC Correlation Study on Lead Finishes substantiate that the "Hot Iron Test", the "Hot Oil Test", and the "Carbon Determination Test" all exhibit precision, but the "High Vacuum Melt Test" and the "Mass Spectrometry Test", although feasible, have not as yet been used enough to validly demonstrate the same precision.

Data from two sub-matrixes (solderability and organic content testing) of the RADC Study revealed some significant correlations. Outgassing and organic content results from the five test methods were found to track very accurately to actual device solderability. In addition, empirical results from the test methods can be easily used to identify and distinguish generic matt tins with negligible organics from the higher organic deposits derived from bright tin or certain tin-lead plates.

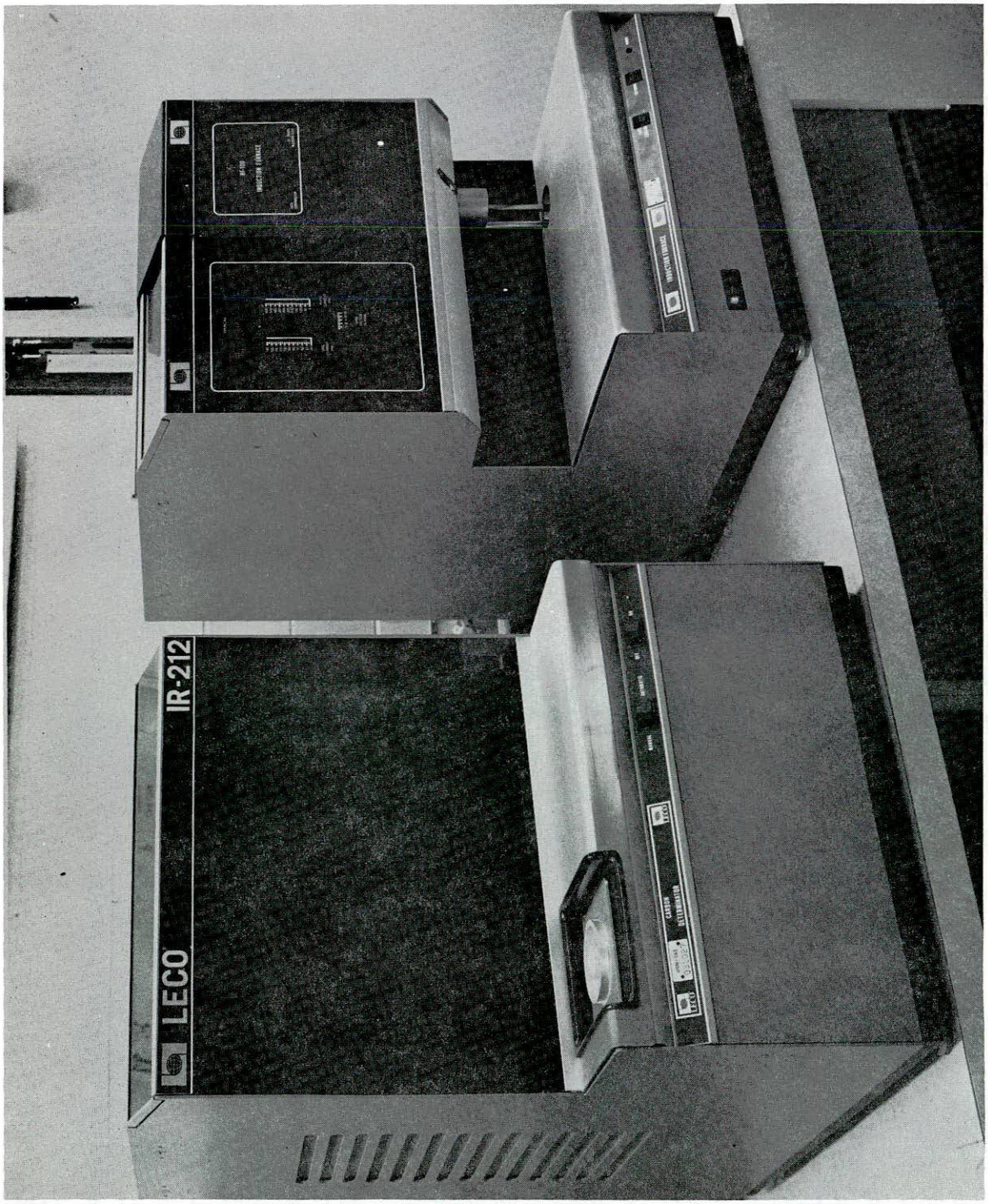
The experimental devices were 16 lead cerflats assembled by a major integrated circuit manufacturer. The devices were subdivided into four plating lots and each lot was plated with a different deposit within the 300-500 micro-inch thickness range. A fused version of two deposits was also evaluated.

The solerability evaluation was done in compliance to the current revision of MIL-STD-883B, Method 2003.2. Units were baked at 165°C $\pm$ 5°C and tested at predetermined time intervals until failure occurred. Results for solderability and organic level testing are tabulated in Table II.

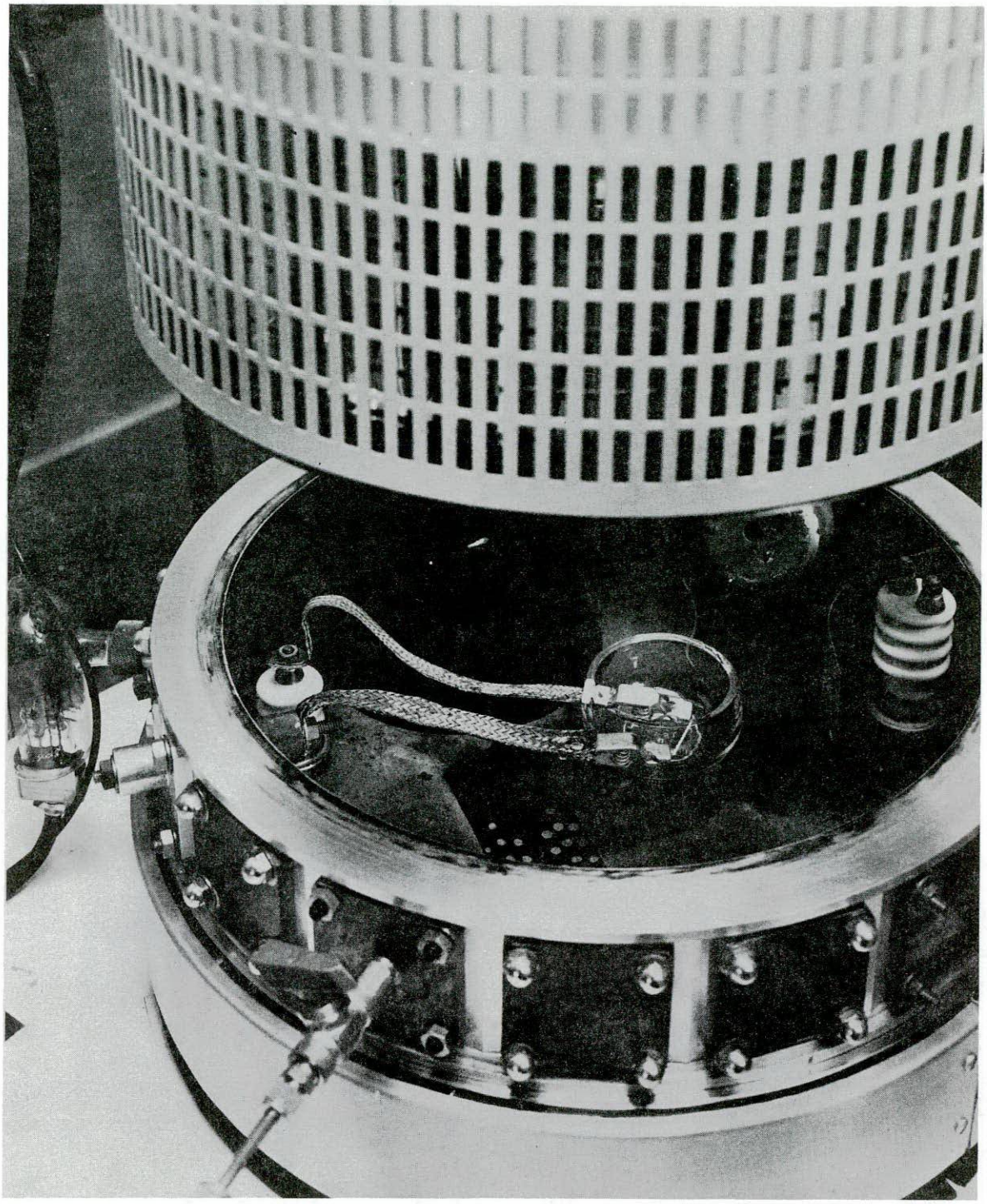
The solderability performance spread between the higher organic finishes (A & B) and the lower organic finishes (C & D) tracked consistently with the order of magnitude spread in percent carbon contents of the deposits. The tin/lead plate had extremely poor solderability in relationship to comparable percent carbon in bright tin. This correlation indicates that another mechanism such as lead segregation during temperature burn-in may also be contributing to failure.

The fused version of the bright tin finish showed slight improvement of solderability performance in comparison to the non-fused finish. In high organic finishes, however, some benefit appears to be derived by subjecting the deposit to elevated temperatures (above 232°C). The contrary was found to be the case in lower organic matt finishes. The fused (reflowed) version of the proprietary matt tin finish showed degradation of solderability by a factor of six in comparison to the non-fused finish (see Table II).

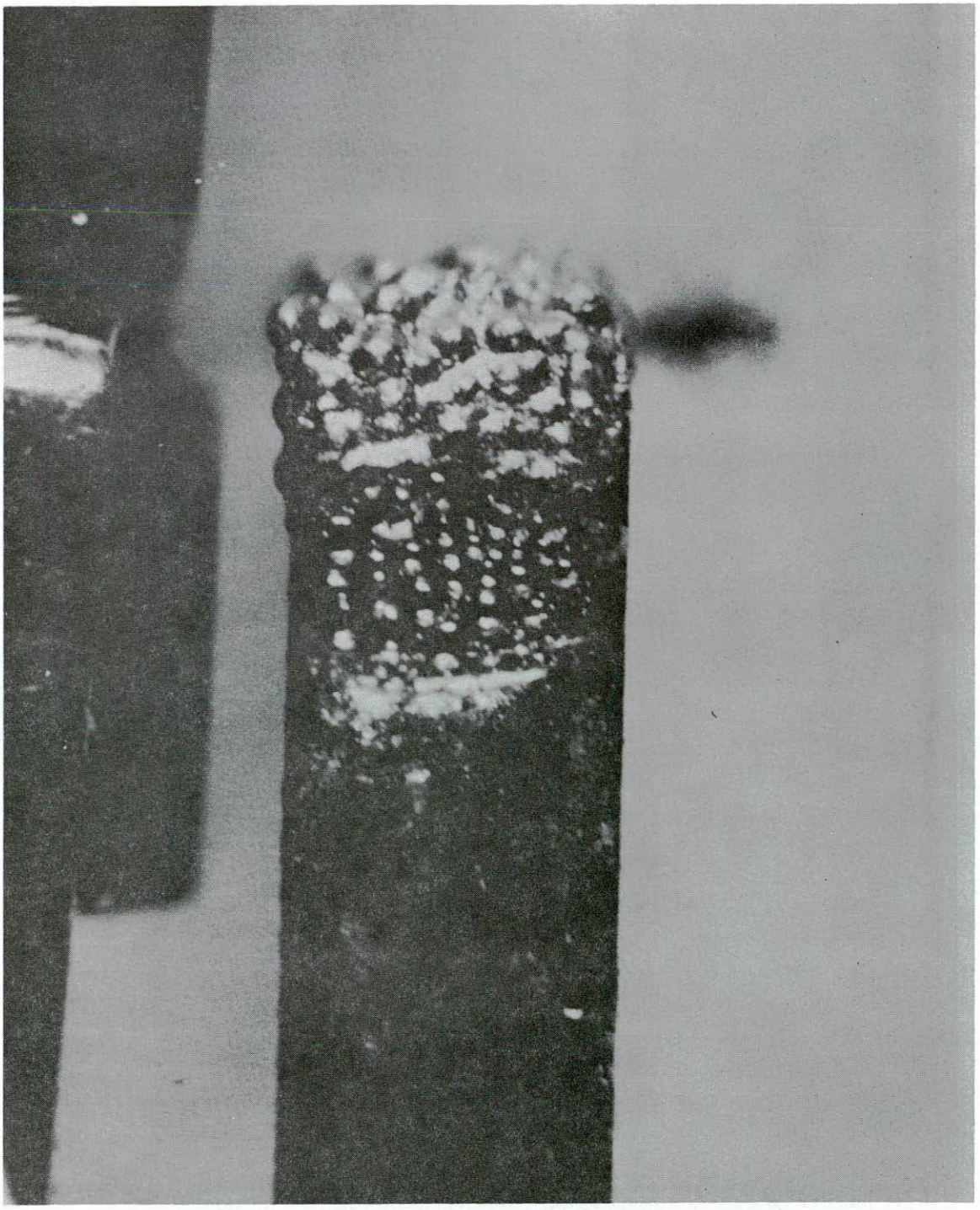
Photograph VIII



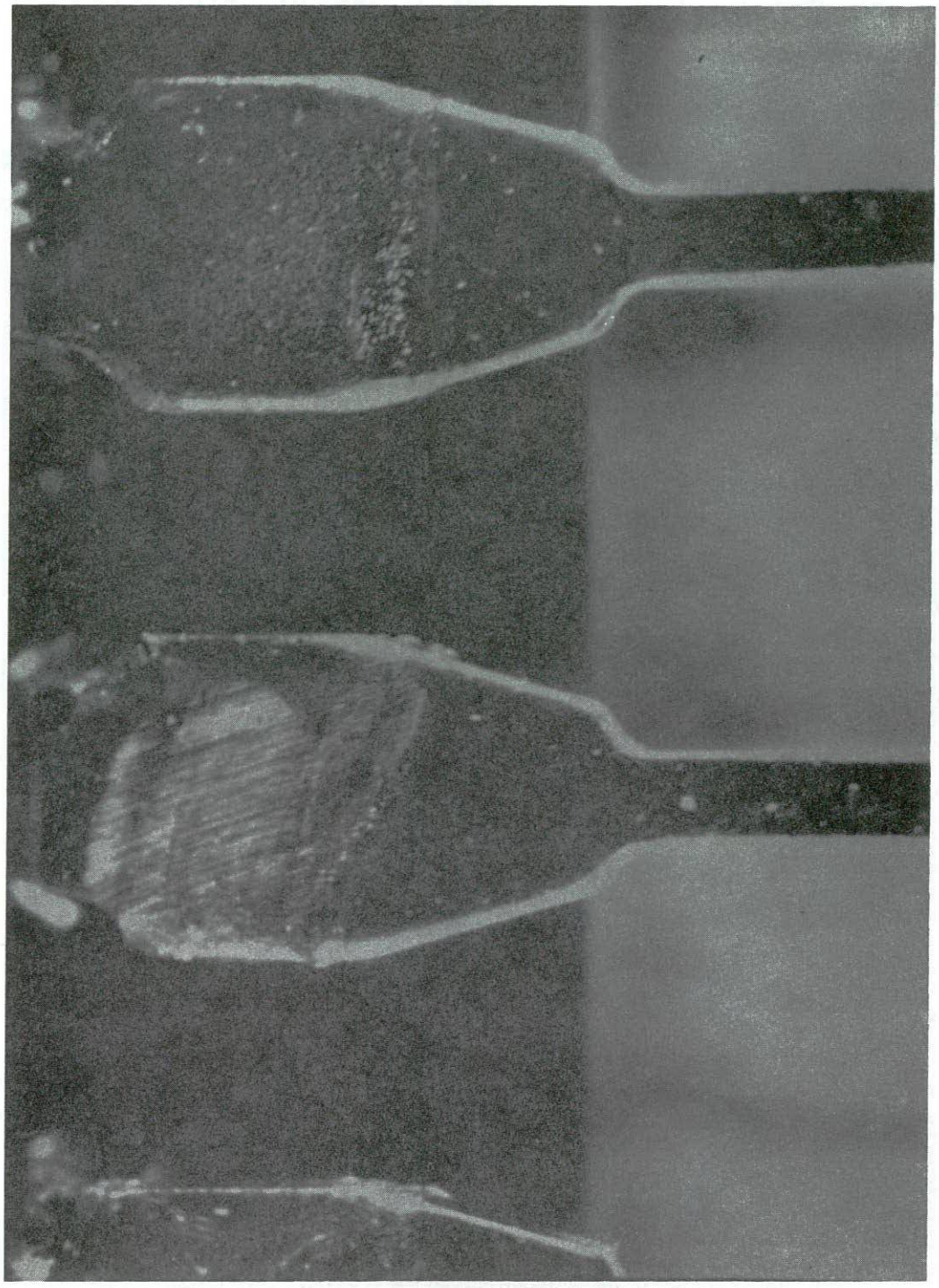
Photograph VII



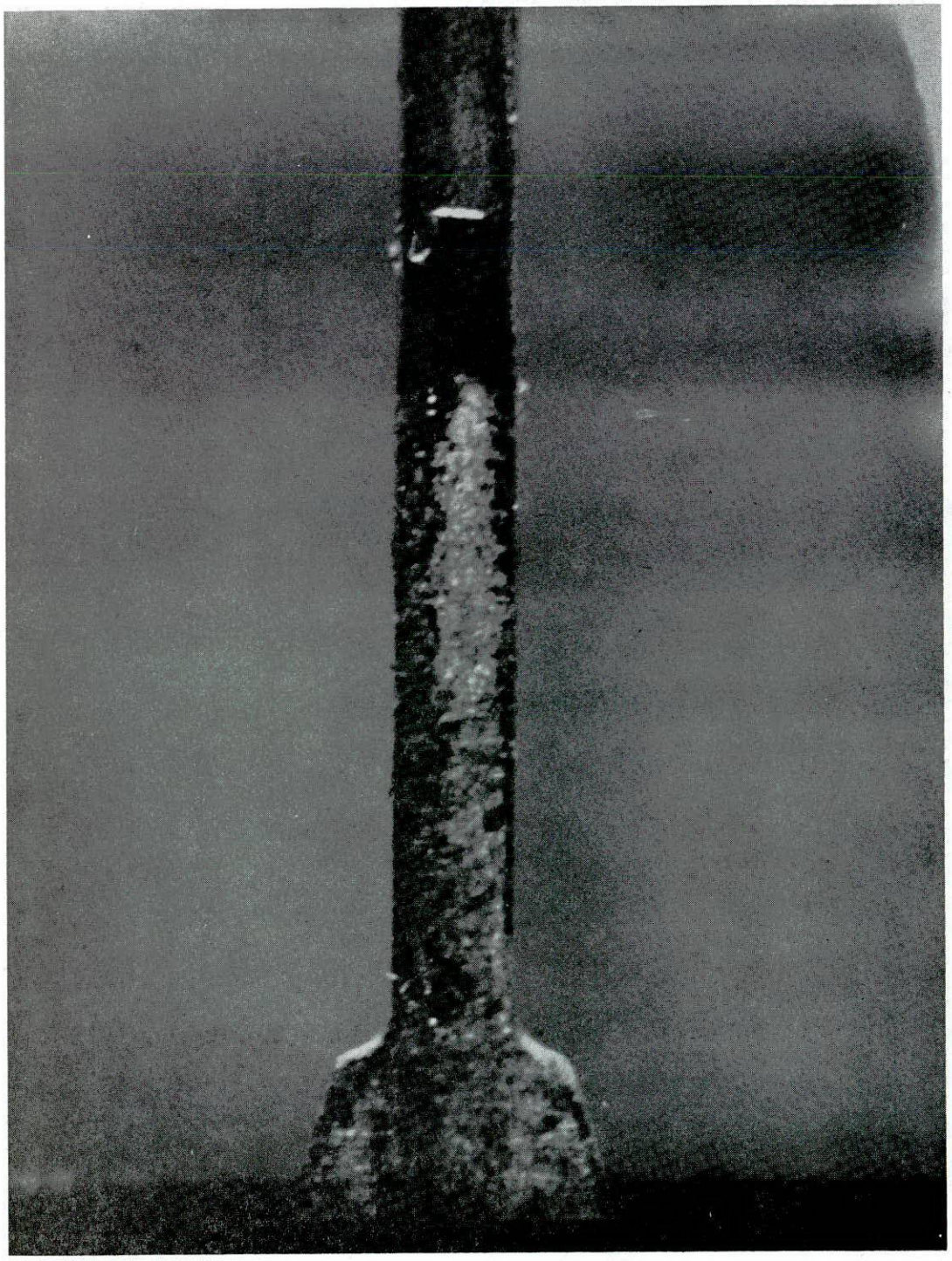
Photograph VI



Photograph V



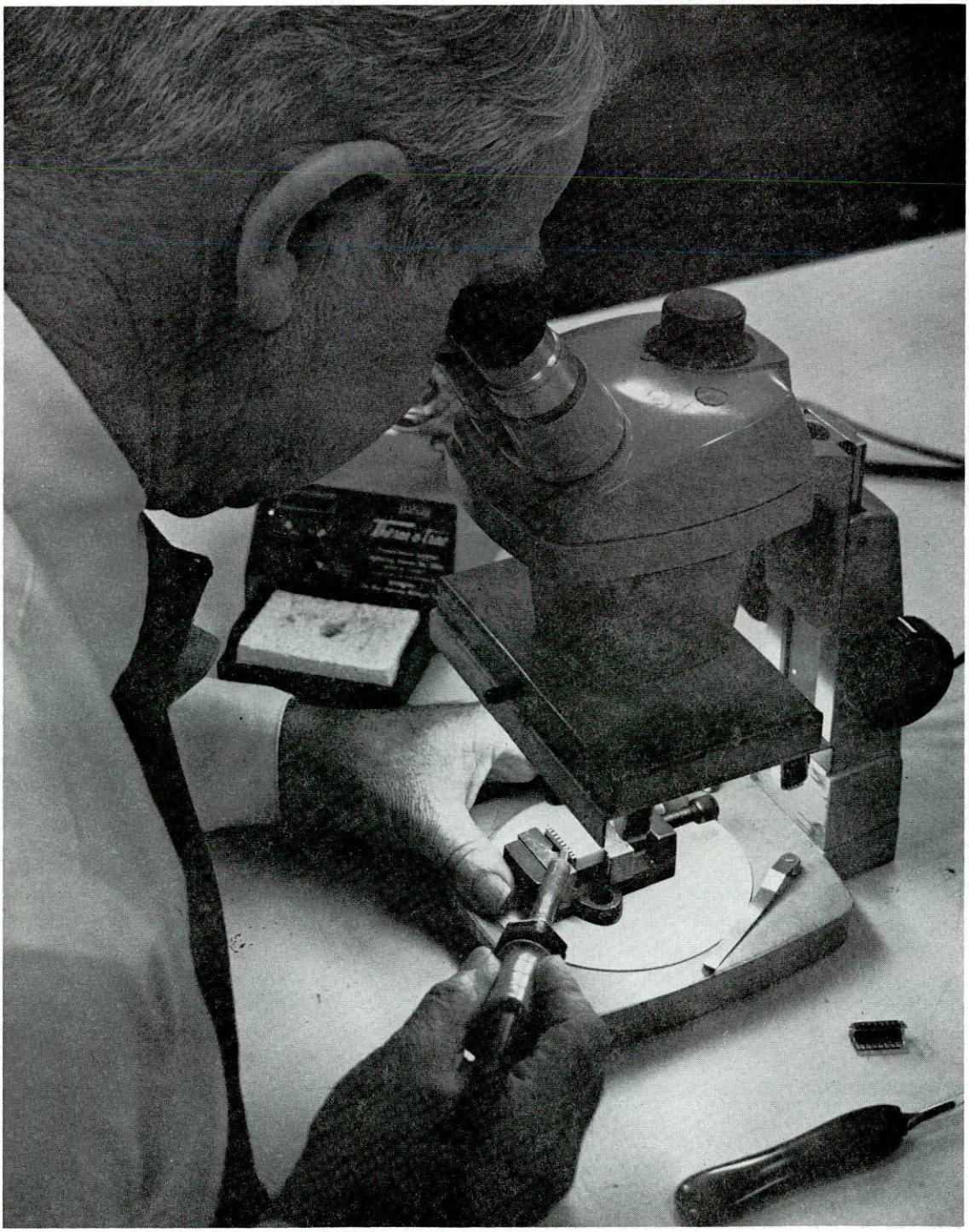
Photograph IV



Photograph III



Photograph II



The "High Vacuum Melt Pressure Test" measures the amount of gas that is evolved at soldering temperatures. The "Mass Spectrometry Test" identifies and quantifies the gases evolved at soldering temperatures. The "Carbon Determination Test" measures the amount of free and combined carbon that has been co-deposited or occluded in the electrodeposited tin. A carbon determination is not an outgassing test, because the organics have been pyrolyzed in an excess of oxygen; however, outgassing test results are predicatable from the carbon determination test results.

Hot Iron Test

The "Hot Iron Test" (see Photograph II) consists of heating the tin plated lead until the electroplated tin melts. The end of the melt zone (melt area adjacent to the unmelted electroplated tin finish) is sliced with a very sharp knife or scalpel and the cut area is examined at 30 diameters for gas porosity (spherical voids).

Hot Oil Test

The "Hot Oil Test" (see Photograph III) is similar to the "Hot Iron Test", with the electrodeposited tin being partially reflowed by immersion in peanut oil that is somewhat hotter than the melting point of tin. The end of the meltzone is examined as in the "Hot Iron Test". The "Hot Oil Test" will detect smaller amounts of outgassing (an indication of the amount of co-deposited or occluded organics) than the "Hot Iron Test" (see Photographs IV, V, and VI).

High Vacuum Melt Test

The "High Vacuum Melt Test" (see Photograph VII) is performed by resistance melting a clean electroplated tin depoist on an alloy 42 lead at a very low pressure. The pressure rise of the system is used to calculate the percentage increase in pressure which is proportional to the volume of gas evolved by the melted electrodeposited tin.

Mass Spectrometry Test

The "Mass Spectrometry Test" is an analysis of the evolved gases from an electroplated tin deposit that has been subjected to 650°F for five minutes. The assay of the evolved gas is usually reported as micrograms of each gas per gram of electrodeposited tin. Using the ideal gas laws, it is possible to calculate the total volume of gases evolved at Standard Temperature and Pressure.

Carbon Determination Test

The "Carbon Determination Test" (see Photograph VIII) is based on the pyrolysis of a metal with an excess of oxygen in an isolatable sytem. The calculation of carbon by measuring the amount of carbon dioxide generated is a reliable method for determining the carbon content of a ferrous metal. In this test method, the percentage carbon found in stripped alloy 42 must be used in calculating the percentage carbon in the electrodeposited tin finish.

Development of Outgassing Tests

Background:

Because of prior solderability problems associated with bright acid tin plated finishes, MIL-M-38510E, 1 December 1981, (Microcircuits, general specification for), prohibits use of bright acid tin plate as a finish for microcircuit leads. Familiarity with the bright acid tin plating process allows adjustment of the plating parameters of a bright acid tin plating bath to produce a matt tin deposit. Such matt tin deposits, however, are subject to the solderability problems characteristic of bright acid tin deposits.

The Naval Avionics Center's Materials Laboratory thought it expedient to investigate methods for detection of outgassing in electroplated tin deposits. The outgassing characteristics of matt deposits from generic bright acid tin baths which are operated to produce matt deposits are very similar to the outgassing characteristics of bright acid tin. Methods were then proposed to differentiate between generic matt tin and a matt tin finish produced by a generic bright acid tin bath.

Procedure:

Fourteen different lots of evaluation packages plated by outside vendors and the Naval Avionics Center were used for development of five test methods. All finishes had been applied to Alloy 42 leads of 14/16 lead ceramic dual inline packages. The fourteen lots of evaluation packages consisted of the following:

a. eight unique lots of bright acid tin plated leads
b. four unique lots of matt acid tin plated leads
c. one lot of furnace reflowed matt acid tin plated leads
d. one lot of hot solder dipped matt acid tin plated leads

Each lot was assigned a code number as received and the typical thickness of the lead finish was determined by metallographic sectioning.

Documentation:

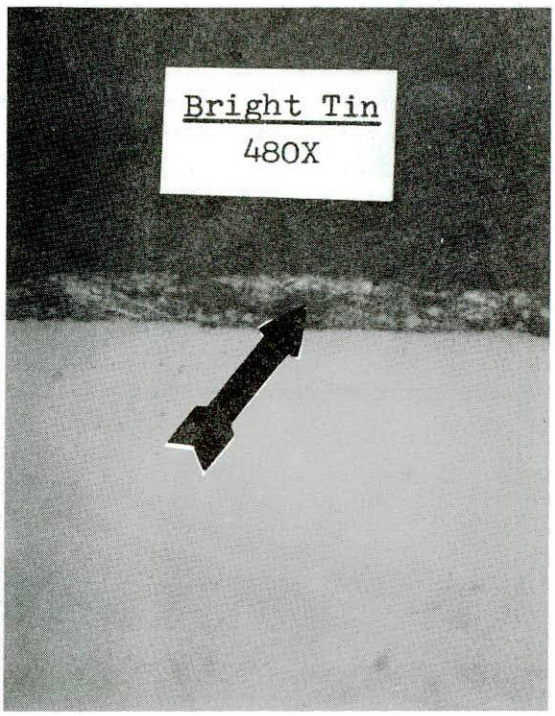
Since development of these outgassing test procedures is documented in NAC TR-2330 "Detection of Outgassing in Electroplated Tin Deposits", available from the U.S. Naval Avionics Center, 6000 East 21st Street, Indianapolis, IN 46218, only a short synopsis of the developed test methods will be detailed. Those interested in evaluating any of these test methods should request NAC TR-2330 on your company letterhead.

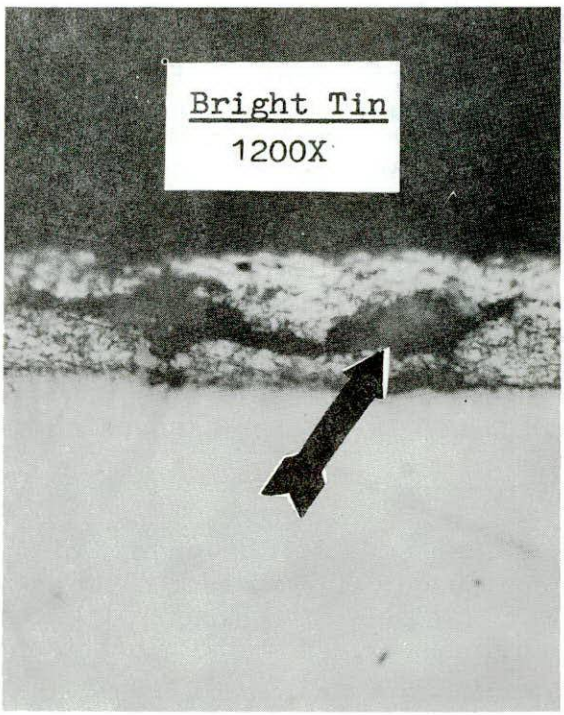
Testing:

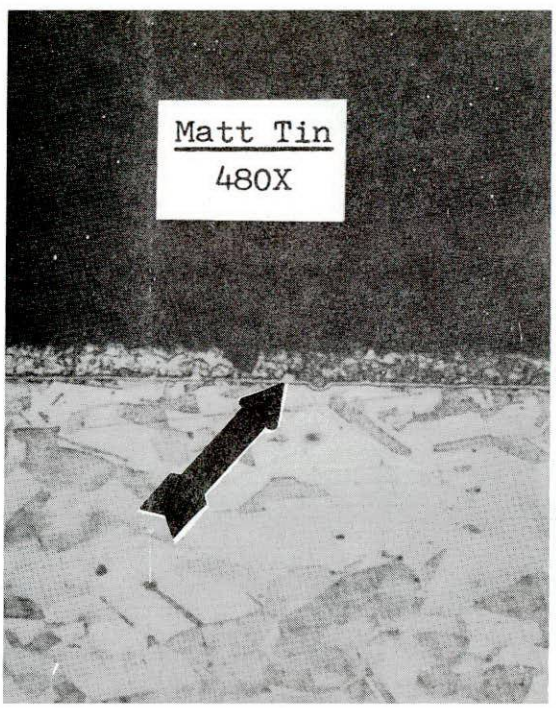
All of the test methods which have been optimized or shown to be feasible share one common limitation -- they are only applicable to electroplated tin deposits which have not been melted (reflowed). The base premise is that co-deposited or occluded organics will, when heated to soldering temperature, outgas. The "Hot Iron Test" and the "Hot Oil Test" each provide static documental evidence that outgassing has occurred.

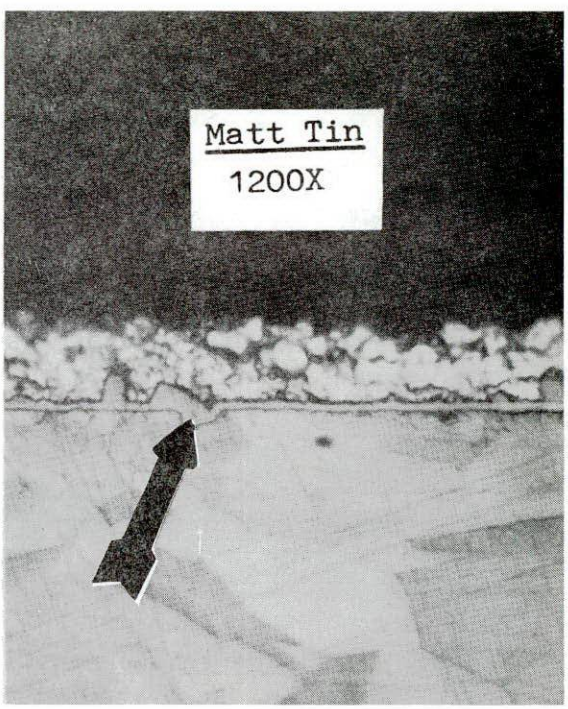
Photo I

SOLDERABILITY FAILURE MECHANISM









The bright tin deposit micrographs (see Photograph I) show numerous voids in the tin plate where entrapped organics volatized during high temperature exposure, resulting in solder joint defects due to outgassing. The tin thickness was measured at 350 microinches. The tin/alloy 42 interface is noticeably contaminated with carbon residues and devoid of intermetallic formation. The solderability failure mechanism for bright tin is, therefore, a function of brightener co-deposition and occlusion, coupled with elevated temperature exposure resulting in organic vaporization within the tin deposit.

On the matt tin deposit micrograph (see Photograph I), a continuous layer of tin-nickel intermetallic (Ni_3Sn_4) can be seen along the entire lead at the tin and alloy 42 interface. A weak nital etch was used to enhance the grain and phase boundaries. These intermetallic compounds form at the interface between coating and base metal throughout the lifetime of a tin plated component by solid/solid diffusion processes.[2] On the top surface of the plating, a tenacious tin oxide layer exists, consuming a minor portion of the free tin. Voids were not noted in microsection views of the matt tin deposit, indicating negligible organic co-deposition and occlusion.

Shorter time to failure of bright tin deposits compared to generic matt tin deposits is attributed to a greater amount of co-deposited and occluded organic compounds in bright tin electrodeposits. A comparison was made by determination of carbon using a standard pyrolysis method for carbon in metals. (See Table I Percent Carbon Found In Electrodeposited Tin).

Generic matt tin electrodeposits exhibit lower carbon contents and outgas less than bright tin electrodeposits when exposed to elevated temperatures. The predominant solderability failure mechanism of generic matt electroplated tin exposed to elevated temperatures is formation of tin-nickel intermetallic compound by solid state diffusion. Bright electroplated tin deposits, however, become unsolderable quickly at elevated temperatures by the mechanism of co-deposited and occluded organic compounds decomposing and outgassing. When bright electroplated tin deposits are microsectioned at the time of first solderability, failure there has not been enough time at temperature to form an appreciable amount of intermetallic compound. Lower organic containing generic matt tin electrodeposits also exhibit less blue tin propensity and fewer adhesion failures than bright acid tin electrodeposits which characteristically contain greater amounts of codeposited and occluded organic compounds.

TABLE I

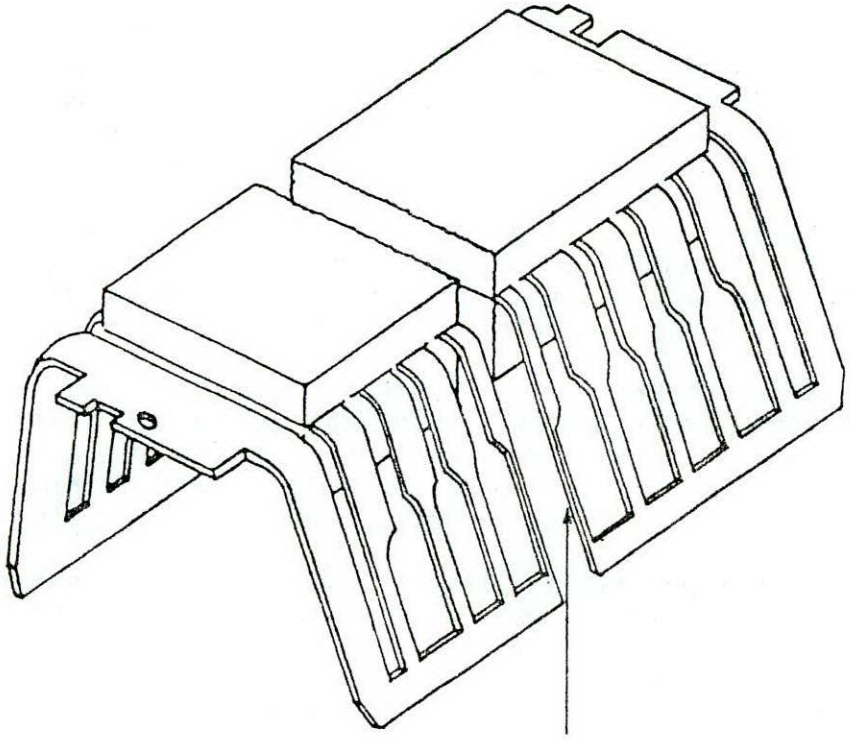
PERCENT CARBON FOUND IN ELECTROPLATED TIN DEPOSITS

Process	Sample #1	Sample #2
Matt Tin	.032	.039
Bright Tin	0.16	0.17

[2] "The Growth Of Intermetallic Compound On Common Basis Materials Coated With Tin and Tin-Lead Alloy", P. J. Kay and C. A. McKay, Transactions of Institute of Metal Finishing, Volume 54, 1976.

Illustration II

POINT OF CROSS-SECTION



Cross-sectioning site

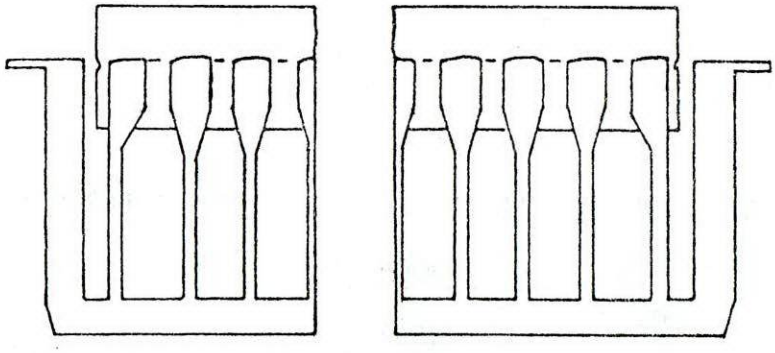
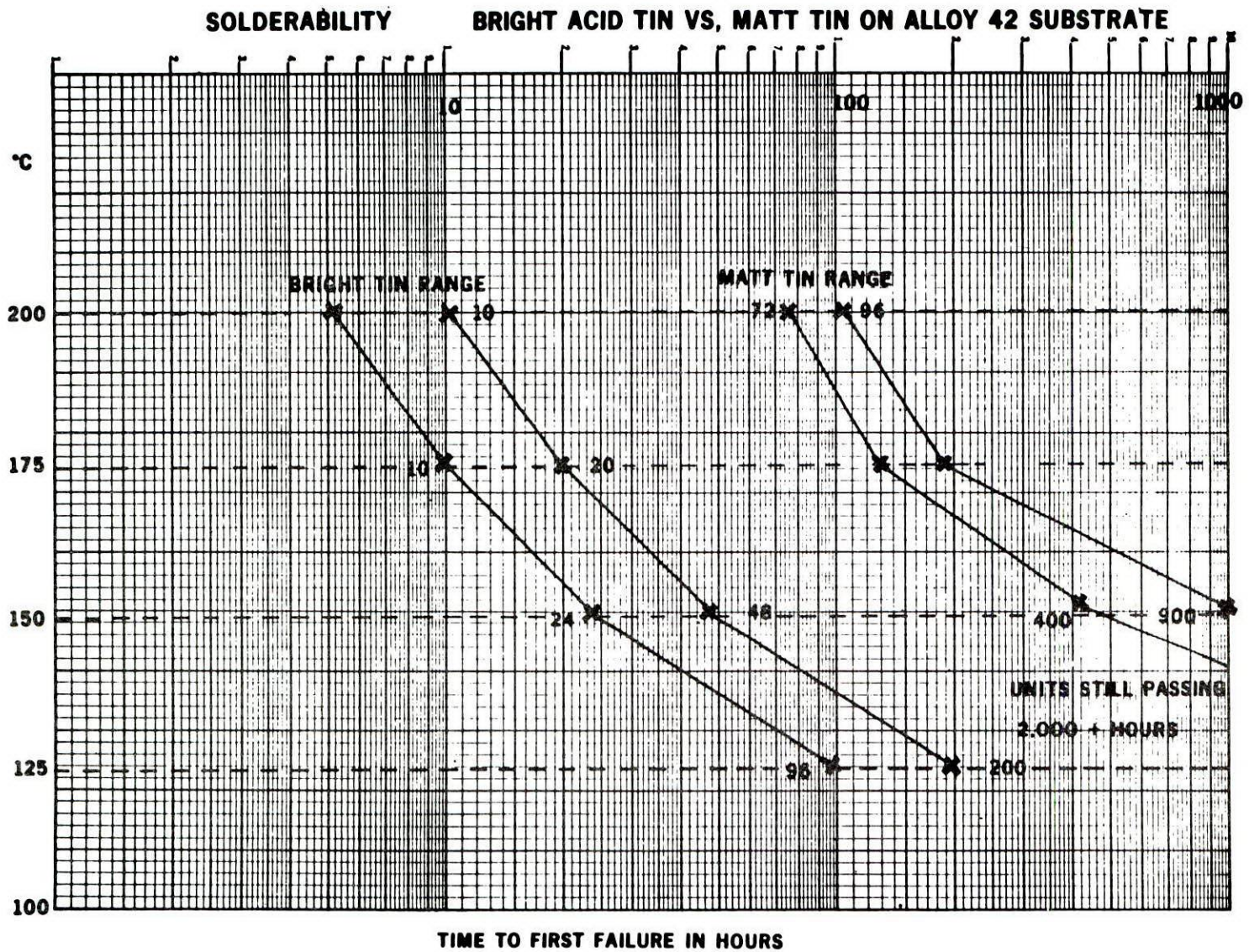


ILLUSTRATION 1.



NEW PROCEDURES FOR PREDICTING SOLDERABILITY PERFORMANCE OF ELECTROPLATED TIN DEPOSITS

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Bance F. Hom, Indy Electronics, Inc., Manteca, California

Historical Background

The "Wren Tin[1]" acid matt tin plating process was developed at the Naval Avionics Center in 1968 and 1969, when bright acid tin plate outgassed during soldering leaving a very porous and cratered deposit at the end of the meltzone. This outgassing caused by volatilization of entrapped organics, could potentially promote electrolytic corrosion of the electronic lead material. The effect of these organics on the solderability of plated tin leads was not known. The matt tin produced by the Naval Avionics Center process adequately resolved the outgassing problem. Over the years since, when long term solderability has been a prime requirement, many manufacturers have adopted a modified version of this tin process successfully.

Matt Tin Advantage: Solderability

One of the key attributes of the matt tin process is excellent solderability after extensive burn-in. (Reference '82 Hom Study, Highlights from Hom/Hobson talk - AES second annual Golden West Regional Conference).

In this study, both bright tin and matt tin solderability on cerdip devices over various temperture and time intervals to simulate device burn-in conditions were evaluated. The solderability testing was done in compliance with MIL-STD-883B, Method 2003.2 using a rosin flux. The criteria for acceptance was 95% solder coverage of the dipped lead below the seating plane. The solderability results were plotted on semilog graph paper, with temperature along the vertical axis in °C and time to first failure in hours along the horizontal axis (see Illustration I). The graphs empirically show that at every temperature interval from 125°C to 200°C matt tin is functionally superior to bright by a factor of almost 10. The graphs (see Illustration I) also show that an accelerated manufacturing solderability test at 10 hours/200°C, 20 hours/175°C or 48 hours/150°C should ensure solderability at 125°C/168 hours (a standard military burn-in).

To delineate the solderability failure mechanism unsoldered units at time of solderability failure (for bright tin at 10 hours/175°C and for matt tin at 188 hours/175°C) were cross-sectioned and evaluated. The leads on both sides of the failed devices were cross-sectioned lengthwise, (see Photograph I). Photomicrographs were taken at 480X and 1200X at the midsection of the leads (see Illustration II).

[1] U. S. Patent 3,585,114 is available from the Office of Naval Research as a royalty free non-exclusive license.

D-6

Electronics I
Session D

New Procedures for Predicting Solderability Performance of Electroplated Tin Deposits

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Indy Electronics Inc.
Manteca, CA

FIG. 7 CURRENT EFFICIENCY vs CURRENT DENSITY RELATIONSHIP FOR A RANGE OF PRORIETARY GOLD ELECTROLYTES

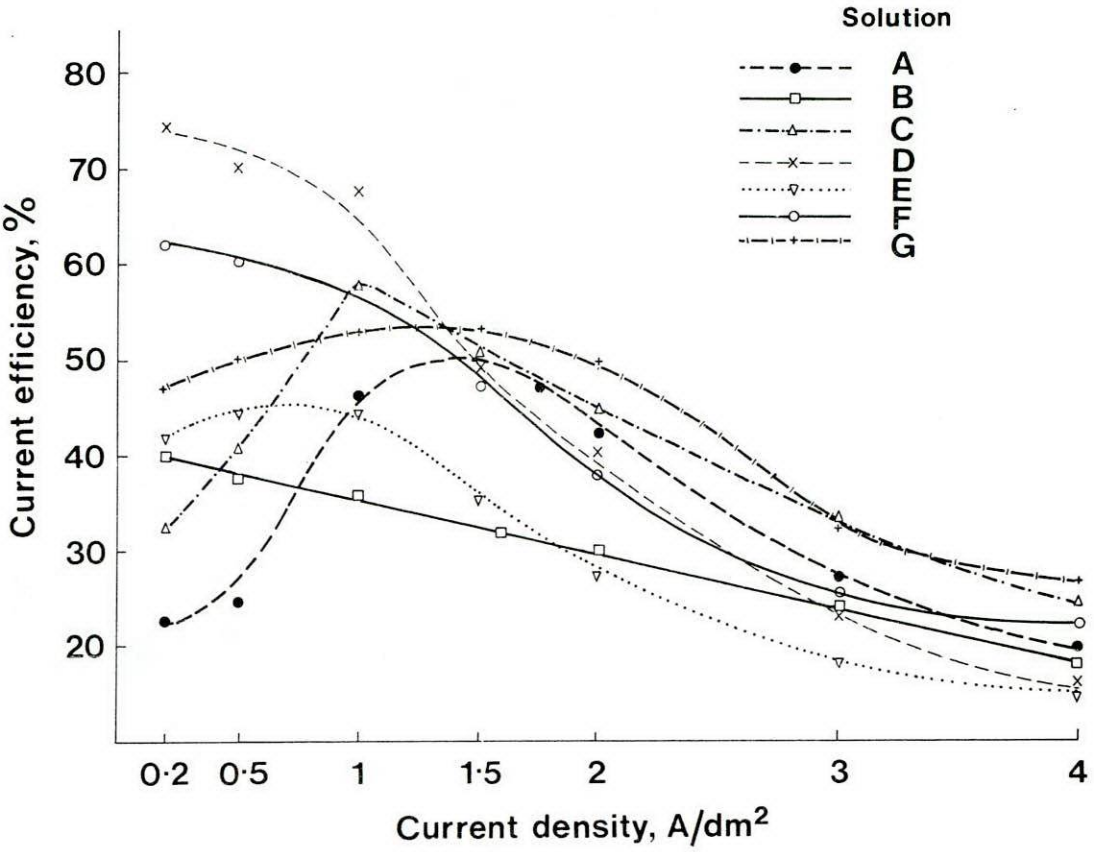


FIG. 5 APPLIED CURRENT DENSITIES TO EQUALISE POTENTIALS AS A FUNCTION OF ROBBER WIDTH. Separate circuit.

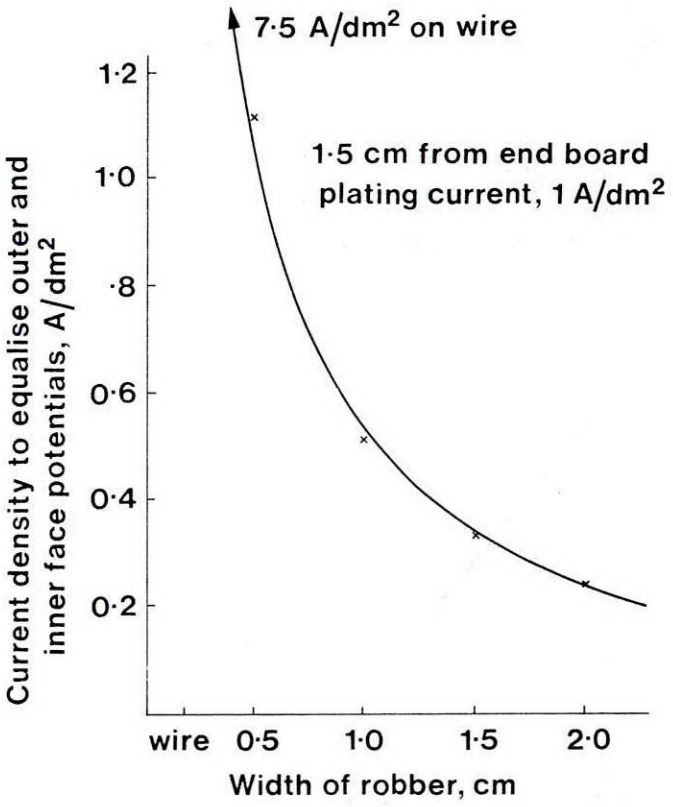


FIG. 6 EFFECT OF APPLIED CURRENT DENSITY ON POTENTIALS. Separate circuit.

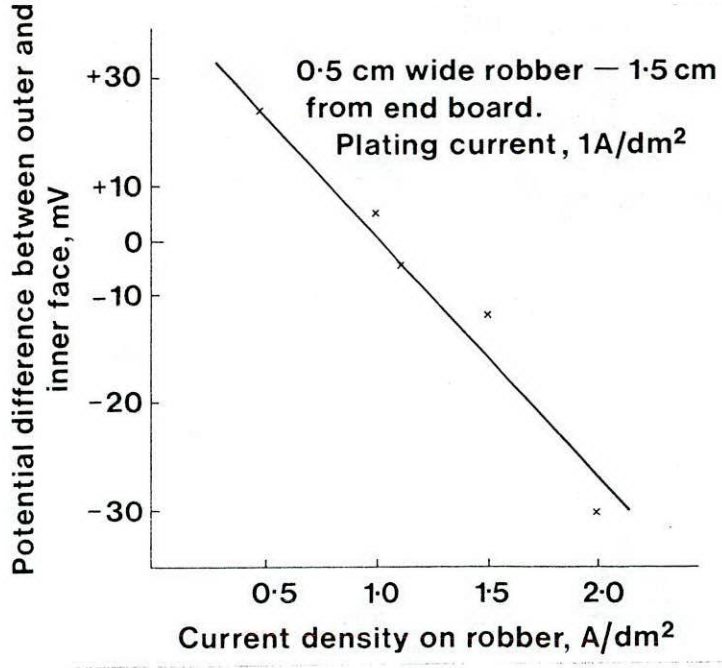


FIG. 3 EFFECT OF ROBBER WIDTH ON POTENTIALS – Same circuit

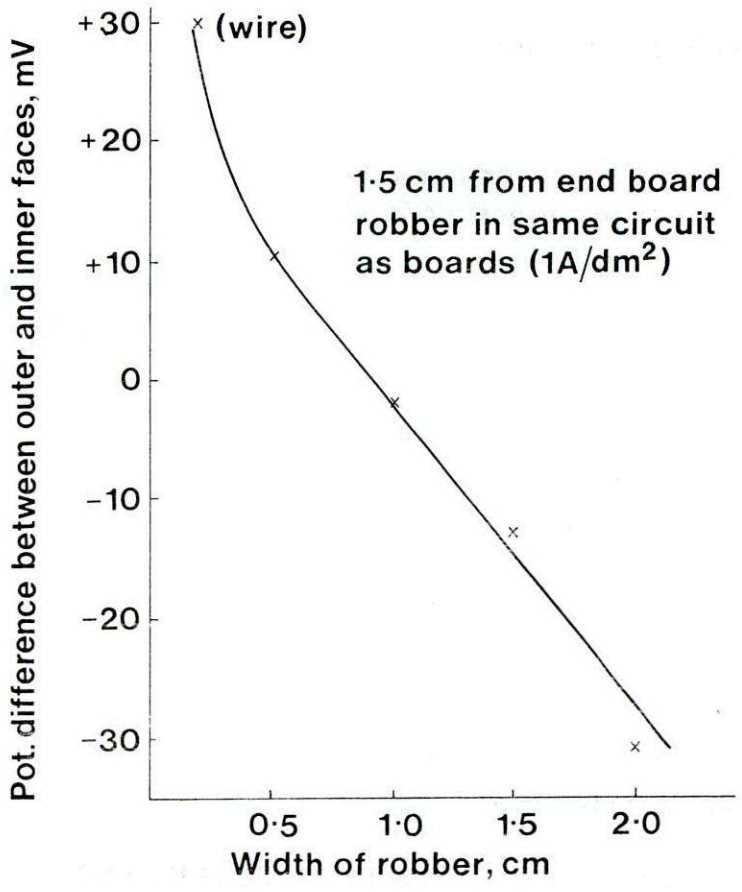


FIG. 4 EFFECT OF ROBBER-BOARD SEPARATION ON POTENTIALS – same circuit

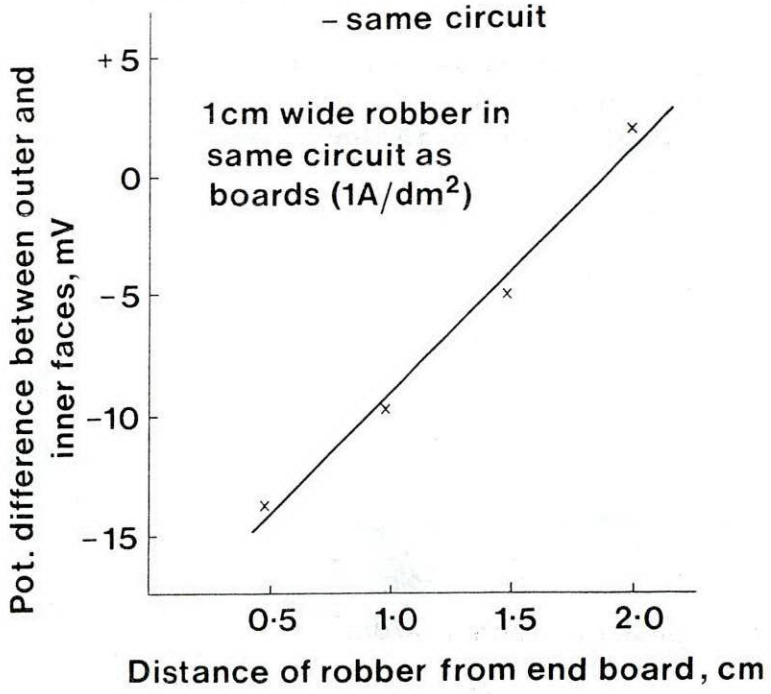


FIG. 1 SIMULATED PCB PLATING FACILITY

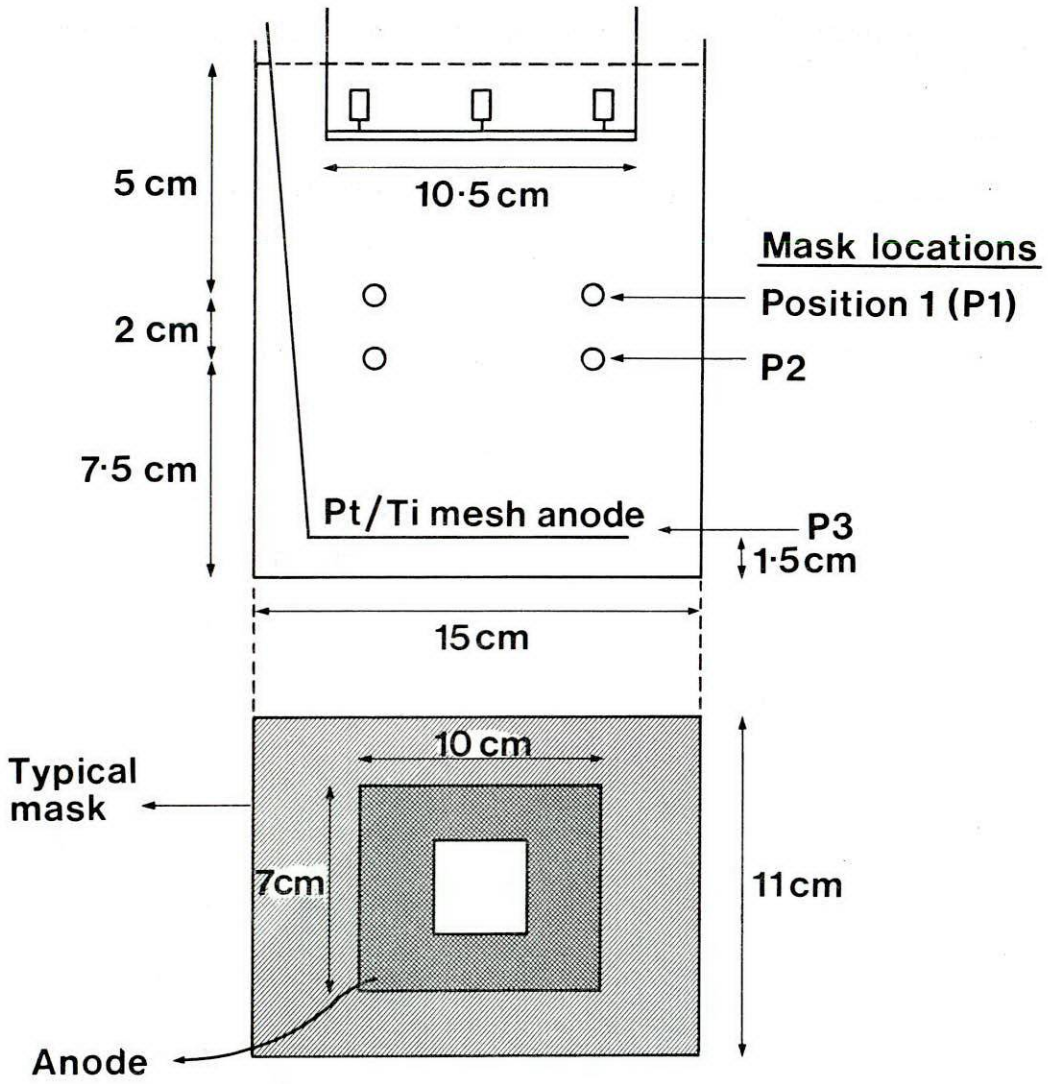
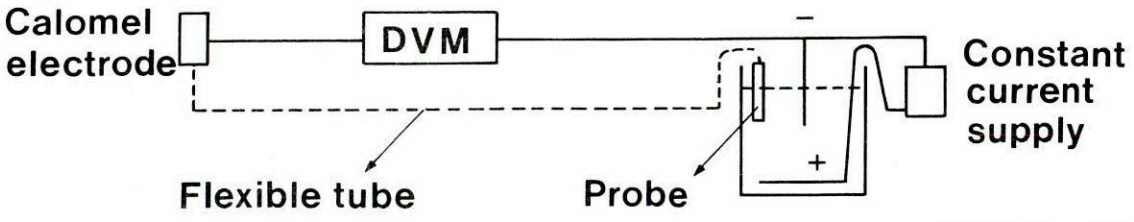


FIG. 2 CIRCUIT DIAGRAM FOR POTENTIAL MEASUREMENTS



Acknowledgement

The author is indebted to the Directors of the Plessey Company for permission to publish this work.

References

(1) J.S. Stevenson, Engelhard Industries - private communication.

(2) "Technology of Electrodeposition", A.T. Vagramyan and Z.A. Solov'eva, R. Draper Ltd., 1961, pp.308.

(3) Plessey Telecommunications Ltd. - private communication.

(4) E.D. Winters, Plating, 1982, 59 213.

curve. The former solutions show an average horizontal variation of 0.73 μm compared to an average of 1.85 μm for the latter two solutions.

These results illustrate the importance of selecting the correct electrolyte to obtain the minimum thickness variation. For example changing from solution A to solution D would provide gold savings of ∿ 20 per cent, under the given set of experimental conditions. On the other hand the earlier work demonstrated that the use of anode masks and/or current robbers could reduce the thickness variations and thereby reduce cost savings in changing the plating solution.

The effects of gold concentration, agitation rate, nickel or cobalt content, pH, temperature and specific gravity have not been considered in the present work. Preliminary investigations have shown that all the above parameters influence the gold distribution and need to be taken into account before the optimum electrolyte can be selected. The question of deposit porosity and brightness in relation to all the parameter combinations also needs to be considered.

Conclusions

The potential probe technique is a convenient method for designing electrode geometries and optimising the size and positioning of anode masks and current robbers. Horizontal masks are effective in reducing potential variations and hence thickness variations across the contacts of a PCB using a stacked arrangement of boards with a bottom anode configuration. The optimum geometry is very critical for the bottom anode mode of operation. Masks are not effective in influencing vertical distributions. Reductions in current density and increasing the depth of board immersion in the solution improve the potential variations in all directions. With stacked boards the major potential increase occurs on the outer faces of the stack. Conventional masks cannot overcome this adverse distribution. An alternative approach to the use of anode masks would be to utilise anodes constructed from thin strips of material, which are mutually insulated. Switching the appropriate segments could then cope with a range of cathode sizes.

Current robbers are an effective means of overcoming the end face problem. The optimum size, position and applied current density have been derived to equalize the outer-inner face potentials.

The shape of the variation of current efficiency with current density curve of the electrolyte is another important factor having a major influence on distribution. The efficiency characteristics of a range of proprietary gold solutions have been determined and shown to exhibit significant differences. A decreasing efficiency over the plating current density range is the most desirable, such that the plating rate varies little with current density. Thickness variations are in general agreement with the efficiency data, and gold savings of up to 20 per cent can be achieved between different electrolytes.

sity levels. A more informative method of presenting the data is to plot current efficiency X current density (or plating rate) against current density, the flatter the curve the more uniform the metal distribution.

The thickness distribution on a PCB test piece (7 contacts on each side of 1.1 x 0.35 cm) was evaluated for some of the proprietary solutions at a current density of $1A/dm^2$. The results (average of 3 readings) are presented in Table 8, the thicknesses being normalised to a minimum of 2.50 µm.

TABLE 8: GOLD THICKNESS VARIATIONS IN DIFFERENT SOLUTIONS

$1A/dm^2$. Normalised to 2.50 µm. 14 contacts.

No mask.

Solution	A		B		C		D		F		G	
Pad position	T	B	T	B	T	B	T	B	T	B	T	B
Thickness, µm	3.59	4.26	2.79	2.82	2.93	3.41	2.62	2.84	2.64	2.96	2.62	2.92
	2.83	3.22	2.60	2.78	2.70	2.97	2.57	2.78	2.55	2.80	2.57	2.91
	2.50	3.68	2.50	2.73	2.70	2.97	2.61	2.79	2.53	2.77	2.52	2.84
	2.54	3.38	2.50	2.79	2.50	3.12	2.50	2.82	2.62	2.78	2.52	2.85
	2.61	3.23	2.55	2.75	2.53	3.19	2.58	2.77	2.50	2.70	2.60	2.90
	3.08	3.61	2.66	2.76	2.59	3.31	2.54	2.77	2.63	2.78	2.64	2.80
	3.95	4.62	2.98	3.11	2.60	4.05	2.95	3.18	3.00	3.19	3.01	3.25
	3.37	3.95	2.73	2.73	3.27	4.07	2.63	2.91	2.62	2.87	2.75	2.99
	2.65	3.37	2.56	2.81	2.81	3.37	2.58	2.81	2.50	2.72	2.51	2.86
	2.65	2.88	2.60	2.79	2.72	3.12	2.53	2.80	2.53	2.79	2.50	2.83
	2.61	3.26	2.66	2.70	2.55	3.19	2.55	2.88	2.50	2.59	2.56	2.75
	2.77	3.35	2.55	2.75	2.67	3.09	2.56	2.85	2.51	2.70	2.57	3.01
	3.10	3.52	2.59	2.82	2.70	3.27	2.59	2.86	2.58	2.85	2.67	2.72
	3.95	4.19	3.07	3.00	3.02	3.44	3.04	3.22	2.79	3.07	3.25	3.38
$\bar{x}$, µm	3.31		2.74		3.07		2.75		2.72		2.80	
σ, µ	0.57		0.16		0.42		0.19		0.18		0.24	
max.-min., µm	2.12		0.61		1.57		0.72		0.69		0.88	
T = 2 mm from top of pad B = 2 mm from bottom of pad.												

The data of Table 8 show the superior distributions obtained with solutions B, D and F and to a lesser extent G, in both the horizontal and vertical directions. This is in agreement with the efficiency characteristics (Figure 7), solutions B, D and F operating on the decreasing portion of the curves and G in the flat plateau region. The other two solutions (A and C) were operated in the region of the efficiency maximum or even on the ascending part of the

Current efficiency.

The potential probing work has demonstrated that electrode geometry is important in improving the deposit distribution. Another very important factor which is solution dependent is the relationship between current efficiency and current density. The efficiency versus current density (0.2 - 4A/dm^2) relationship for a range of proprietary cobalt and nickel hardened gold electrolytes is shown in Figure 7. The solutions were operated under the manufacturers recommended conditions of temperature and pH. Under the given experimental conditions all solutions show a decreasing efficiency characteristic above 1 - 1.5A/dm^2, with varying rates of change. Below 1A/dm^2 solutions A, C, E and G show an increase in efficiency with increasing current density, the first two solutions having steep initial slopes. On the other hand solutions B, D and F exhibit a decrease in efficiency over the whole current range. It may be concluded that the latter three solutions should be the most suitable for reducing gold thickness variations, particularly if it is required to operate below 1A/dm^2. The potential measurements showed that it was beneficial to reduce current density to improve the distribution. The maxima in the efficiency curves were found to be dependent upon the agitation rate, increased rates shifting the maxima to higher current densities. Higher agitation rates than used in the present experimental work would normally occur under production conditions. Changes in efficiency and the position of the maximum are illustrated in Table 7 under controlled agitation conditions, with rotation of a cylindrical cathode (low efficiency solution)(3). Similar effects have previously been reported in the literature (4).

The conclusion that can be drawn from the effects of agitation is that agitation should be maintained uniform over the cathode and that since current density varies over a component the agitation level should be in the region where the efficiency varies little or decreases with increasing current density.

TABLE 7: VARIATION OF EFFICIENCY WITH AGITATION AND CURRENT DENSITY

Agitation, r.p.m.	Current density, A/dm^2		
	0.25	0.75	1.2
	Current efficiency, %		
20	32.6	35.1	24.8
40	19.4	39.6	36.2
60	20.6	40.5	36.2
80	15.5	32.0	40.6
100	-	31.6	39.4

Care needs to be taken in interpreting efficiency curves since a sharp decrease in efficiency with current density often leads to an increase in poro-

are used as burners, with reclamation of the gold. This leads, in production (20 board stack), to a 10 per cent reduction in board throughput. Therefore consideration was made into the use of current robbers to overcome the end face problem. The robbers were placed parallel to the end contacts and extended the full length of the board. The effects of robber width, distance from the board and applied current density were studied and the results are summarised in Figures 3-6. With the robber at a fixed distance from the board and in the same circuit (Figure 3) the potential difference between the outer and inner faces of the end board decreases with increasing robber width, giving negative values (i.e. a higher potential on the inner face) at > 1.0 cm for a separation of 1.5 cm. Figure 4 shows the potential difference sensitivity for variations in separation for a given robber, indicating the need for accurate positioning. A more controllable process is obtained if the robbers are placed in a separate electrical circuit. Figure 5 shows that the current density required on the robbers to equalize the inner-outer face potentials decreases with increasing robber width, e.g. $7.5A/dm^2$ on the wire and $0.5A/dm^2$ on the 1 cm wide robber. The above current densities represent applied currents of 0.3A and 0.1A respectively and therefore the lower current on the larger robber would reduce the frequency of gold reclamation. For a given robber and separation a linear relationship is observed, Figure 6, between the applied current density on the robber and the potential difference. Adoption of robbers in production would give an increase in board throughput, but the probe technique would be necessary to establish the optimum geometry.

TABLE 6: POTENTIAL DATA ON STACKED BOARDS (NO MASK)

Position	Potential, mV				
	Pad 1	5	10/11	15	20
Board 1, right hand (outer face)	1241	1232	1226	1223	1233
Board 1, left hand	1210	1185	1175	1180	1195
Board 2, right hand	1196	1185	1181	1186	1204
Board 2, left hand	1205	1195	1190	1196	1210
Board 3, right hand	1213	1192	1184	1192	1204
Board 3, left hand (outer face)	1238	1236	1237	1246	1248

In the above work all the robbers were maintained in a constant vertical position, with the top of the robber being level with the top of the pads. In this situation no improvement in the outer face vertical potential difference was observed, typically $\sim$ 50 - 70mV. The vertical variation could be reduced to 20-30 mV by positioning the robber towards the bottom of the pads. However, if the robber extends beyond the bottom of the board it will adversely affect the potentials on the inner faces. Therefore it is preferred to use a narrow robber (in a separate circuit), e.g. 1cm rather than 2cm, located towards the bottom of the pads but not extending beyond the bottom of the boards.

Stacked Boards.

In the case of the stacked boards (3 boards) the anode masks again influenced the potential variations (Table 5). The optimum mask size and position appeared to be different for 3 boards than for the single board experiments, the actual optimum size and position not being determined. The small 1 x 1cm mask in fact worsened the distribution. Again inversion of potential occurred with certain combinations. Column 3 of Table 5 (variation between boards) represents potential differences between pads at a given location on the 3 boards (e.g. all the 6 centre pads or 6 end pads) averaged between the various locations measured. In this series of experiments the horizontal variation through the stack was affected to a different extent to that in the across board horizontal direction, for a given mask condition.

TABLE 5: EFFECT OF ANODE MASKS ON POTENTIALS FOR STACKED BOARDS

Board separation 2.5cm. Current density $1A/dm^2$

Mask	Potential Variation, mV		
	Across board, average 6 sides	Average Variation between boards	Max. - Min.
No mask	22	56 (15)	73 (38)
1 x 1cm., position 1	31	74 (21)	93 (46)
2 x 4cm., position 1	12	59 (21)	68 (29)
4 x 4cm., position 1	28	53 (11)	77 (41)
4 x 4cm., position 2	19	61 (12)	73 (28)
The figures in brackets neglect the outer two faces			

The detailed potential measurements for the run without the mask (Table 5) are presented in Table 6. Even in the absence of a mask a slight inversion in potential is observed.

The data of Tables 5-6 show that the majority of the potential change occurs on the outer two faces of the stack. Therefore masks of the type considered will never significantly improve the distribution on the outer faces in relation to the inner layers. Further extensive potential profiling was carried out utilising vertical masking with and without the conventional horizontal masks. Detailed shaping of the masks enabled potential variations to be reduced in the vertical direction as well as horizontally. However, the complexity of the jigging arrangements and the effect of the masks on the solution flow pattern produced a non-viable production technique and further work was curtailed on this aspect.

Current robbers.

Table 5 demonstrated that with stacked boards the main problem on thickness distribution arises on the two outer faces. In practice the two end boards

TABLE 2: THE INFLUENCE OF THE PLATING RAIL ON POTENTIAL VARIATIONS

	Vertical Potential Variation, mV
Rail stopped-off	50 - 60
Rail plated	25 - 30
Rail plated	100 (pad top→rail)

TABLE 3: EFFECT OF IMMERSION DEPTH ON POTENTIAL VARIATIONS

Current density 0.75A/dm^2 No mask

Condition	Average potential variation, mV	
	Horizontal	Vertical
Solution level with pad top	20	70
Solution 0.5cm above pad top (standard)	10	65
Solution 1.5cm above pad	5	59

Table 4 shows that reducing the plating current density reduces the potential variation in the horizontal and vertical directions, in both cases a linear relationship is observed. However, any reduction in current density would have to be compatible with the subsequent increased plating time. Also efficiency effects may be more favourable at higher current densities for certain electrolytes (see current efficiency section).

TABLE 4: EFFECT OF CURRENT DENSITY ON POTENTIAL VARIATIONS

Current density, A/dm^2	Average potential variation, mV	
	Horizontal	Vertical
0.25	2	16
0.5	6	33
1.0	16	64
1.5	22	99
2.0	29	131

In the absence of a mask the potential variation in the horizontal direction shows a typical U-shaped profile with most of the change occurring towards the ends of the board. All the masks studied reduced the horizontal variation, with the 4 x 4cm mask in position 2 giving the smallest change. Under ideal geometric conditions with parallel electrodes filling the cross-sectional area of the cell a uniform distribution would be expected. However, in normal practice with the electrodes not filling the cell section a build-up of deposit would occur at the edges (as observed). On the other hand a point anode close to the centre of a board would be expected to give a build-up on the centre pads rather than the ends. Therefore one would predict an optimum position for a given size anode or mask (the mask acting as the effective anode) to equalize the two effects and yield a uniform horizontal distribution. If one considers the schematic potential profiles across the boards (Table 1) the inversion in potential is apparent under some of the conditions, the closer the mask to the board the greater the effect. Differences in profiles between mask positions 1 and 2, which have a separation of only 2cm, suggests that the positioning of a mask is very critical. The profiles exhibiting a maximum and minimum reflect the importance of centrally positioning the cathode over the mask. The mask produced only small improvements in the vertical direction. Typical bottom to top variations (over 1.5cm length) of $\sim$ 50mV indicated that this distribution is more significant and also more difficult to influence than the horizontal direction. Again a flat profile was found over the central region of a pad, the minimum in potential in the centre reflecting the influence of the solution interface in concentrating the current. A semi-quantitative relationship between cathode potential and current density was obtained by plotting the potential at points of known current density on a Hull Cell panel. This gave a linear plot of potential against log current density with a slope of 160mV/decade, i.e. a 50mV change for a doubling of current density. Using this relationship the calculated thickness variations were found to be in general agreement with actual thickness values, confirming the validity of the technique. For example a typical across board variation of 20mV would predict a 3.25µm maximum on a 2.5µm minimum, while the use of a mask to halve the variation would reduce the maximum to $\sim$ 2.9µm (neglecting efficiency effects).

The observed vertical variation raises the question of if the current rail should be stopped-off. This is illustrated in Table 2, which shows that plating the rail significantly improves the pad distribution; the rail acts as a current robber, but is itself plated with excessive thicknesses. This gold can however be reclaimed. The efficacy of stopping-off needs to be equated with the improved pad distribution, reclamation costs and taping costs. Under optimum conditions it is normally found to be advantageous to stop-off.

Potential variations as a function of immersion depth show, Table 3, that increasing the depth of board immersion improves both the horizontal and vertical distributions, particularly across the board. This confirms that the solution interface acts effectively as a "mirror", concentrating the current flow. This improvement was shown not to be influenced by the minor changes in the anode-cathode separation.

sheeting provided the anode masks, with variable openings, and were assessed at the two levels shown in Figure 1 and also when positioned directly on the anode. Current robbers in the form of copper strips or wire were positioned opposite the contact face of the outer boards of the stack and operated either in the same electrical circuit as the boards or in a separate circuit.

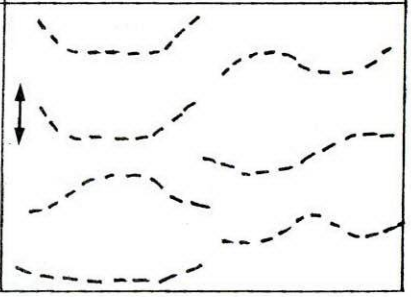
Cathode potentials were measured with respect to a calomel electrode positioned outside the plating cell and connected to the solution via a flexible remote junction probe (2mm diameter). The probe was filled with saturated KCl and fitted with a ceramic frit at the end. Potentials were measured close to the pads (1mm separation), in varying positions, and recorded on a high impedance voltmeter. The circuit diagram is shown in Figure 2. Potentials were equated to current density by monitoring potential variations along a Hull Cell panel at points of known current density. Potential variations are independent of the gold electrolyte but thickness variations are solution dependent, based upon different current efficiency characteristics. The current efficiency - current density relationships and actual thickness distributions were determined for a range of proprietary acid hard gold electrolytes (Co-Au and Ni-Au). Efficiency was determined by a weighing technique based on sheet cathodes centrally positioned between vertical anodes. Gold thickness was measured by a beta back-scatter method.

Results and Discussion

Single Boards.

Average values of potential variations in both the horizontal and vertical directions for a single board and the influence of various masks are presented in Table 1. In the case of the 2 x 4cm mask the board was positioned along the short length of the mask. A plating current density of $1A/dm^2$ was used. The vertical variations represent potential differences between the bottom and top of the pads and those in the horizontal direction the difference between the maximum (board edge) and minimum (centre pads).

TABLE 1: POTENTIAL VARIATIONS OVER A DOUBLE-SIDED BOARD

Mask	Average potential variation mV		Potential profile across board
	Horizontal	Vertical	
None	22	69	
1 x 1cm., position 1	17	-	
1 x 1cm., position 2	16	-	
1 x 1cm., position 3	17	-	
2 x 4cm., position 1	18	42	
4 x 4cm., position 1	15	52	
4 x 4cm., position 2	11	57	
4 x 4cm., position 3	16	48	

current distribution, having a positive or negative effect on the primary distribution.

(a) Potential - current relationship
(b) Solution conductivity
(c) Current efficiency - current density relationship

and the factors which influence these parameters (composition, temperature, pH, specific gravity etc.). For a given electrolyte and plating conditions the metal distribution can be improved by optimising the geometry. In the case of side anodes, the anode width is typically 1/3 to 1/4 the width of the cathode (the actual width being dependent upon the anode-cathode separation). In the bottom anode configuration, where the anode is exposed to the edges of the work rather than the total area to be plated, a much more complex relationship holds. Shielding effects between the stacked boards also affect the distribution. However, as a rough guide the width of the anode should be approximately 1/4 the width of the cathode and its length is usually 1/2 to 2/3 the distance between the outer boards (1,2).

The utilisation of a bottom anode configuration enables a high work load to be employed for a relatively small volume of solution. An initial assessment of a bottom anode arrangement showed large gold thickness variations in both horizontal directions, i.e. across a given board and also across the stack of boards. Thickness variations outside specification were also observed in the vertical direction along the length of the contact pads.

The present paper considers improvements in the gold distribution on PCB's in terms of geometric factors using a bottom anode arrangement. It is known that the size and positioning of the anode is very critical but changes in the anode size cannot be easily made for changes in board dimensions. Anode masks are normally employed which can be more readily changed than the anode. Therefore the role of anode masks and also current robbers have been considered. A potential probe technique to monitor potential variations over edge connectors during deposition was employed. Variations in potential were equated to variations in current density and with a knowledge of the current efficiency versus current density relationship of the electrolyte the thickness variations could be estimated. Later work studied the efficiency - current density relationship for a range of proprietary acid hard gold solutions and the influence on the thickness distribution. The probe technique can be used to rapidly assess the performance of different cell geometries without the need for carrying out complete plating runs. Off-line experiments can however only be used as guidelines for production, there being no substitute for carrying out the potential measurements under the actual production conditions.

Experimental

The simulated PCB plating cell ($2\frac{1}{2}$l solution) is diagrammatically illustrated in Figure 1. Short samples of edge connectors (10.5cm wide with 20 pads on each side of 1.5 x 0.3cm) were used as cathodes and a board separation of 2.5cm was used for the stacked board experiments (X3 boards). Rigid plastic

GOLD DISTRIBUTION ON PRINTED CIRCUIT BOARD EDGE CONNECTORS

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Abstract

A potential probe technique has been employed to monitor the variations in cathode potential across PCB edge connector contacts during gold plating using a bottom anode configuration, with the objective of improving the metal distribution. Distribution in both the horizontal and vertical directions has been considered. The effects of geometry, anode masks, current robbers and current density have been evaluated. Anode masking was found to be the most effective practical method of improving distribution and current robbers to overcome the end board problem with stacked boards. Potential variations are however independent of the gold electrolyte and depend only upon the cell and electrode geometries. The current efficiency versus current density relationship is the most important solution factor in minimising thickness variations and work is reported on the efficiency behaviour of a range of proprietary gold solutions and their effect on distribution.

Introduction

The gold plating of double-sided printed circuit board (PCB) edge connector contacts can be carried out in two basic modes, namely:-

1. Side anodes with the PCB situated centrally between the anodes. This can be operated in a manual, automatic or continuous linear mode.

2. A stacked arrangement of boards with a bottom horizontal anode configuration.

The achievement of a uniform distribution of current (and hence thickness) over the surface of an electrode is very difficult in practice, but minimising such variations is particularly important with gold on economic grounds.

The factors which affect metal distribution may be divided into two main categories, namely:-

1. Geometric factors which determine the primary current distribution. These include the shape and size of the electrodes and plating cell and their relative separations and orientation.

2. Electrochemical and electrical factors which determine the secondary

D-5

Electronics I
Session D

Gold Distribution on Printed Circuit Board Edge Connectors

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to prevent the possibility of water spotting. The optimum way of accomplishing this would be with an oiless blower furnished with the machine as standard equipment. This would prevent the possibility of oil from a plant air compressor getting on the plated fingers and staining them and at the same time not tax the plant air supply.

In the beginning of this discussion, manual load and automatic unload was recommended. The reason for this is that the automatic unload should be designed such that it will return the plated board to the operator at the load end of the machine for reinsertion into the machine so the second edge may be plated or stacked in the case of a completely plated or single edge panel. Depending on the speed the machine is being run at, the operator can also be taking measurements of the plated metal and removing any plating tape that may have been required during the process. Utilizing an automatic load and unload as is presently available on the market today requires an operator to load the loader so it can automatically load the machine and an operator to unload the unloader so it can automatically unload the machine. For example, running at 6'/minute with a 12' long panel and a tray that holds 50 panels would require both the automatic loader and unloader to be filled and emptied approximately every 8 minutes. Utilizing a system described above would virtually require only <u>one</u> <u>operator</u>.

There are other factors that have not been previously covered that must also be considered in the selection process of a machine. Other things that are recommended are: all digital meters on the rectifiers, a digital speedometer, liquid level sensors that are reliable and in-tank filter systems that enable the carbon treatment of the solution while the machine is still running. Lastly, there should be independent rectifiers for the front and back sides of the panels for both the nickel and gold plate sections to allow for better control of the plating thickness and a soft, dense <u>brass</u> brush should be used for making DC contact to the panels as they run thru the machine.

Do not underestimate your company's need for an automatic tab plating machine if you wish to remain competitive in the PC board market. If your competitor is plating his tabs on an automatic machine, he is probably plating them with more accuracy, more consistency and using less gold to do the same job as you and therefore, he has a more desirable product at a lower price. If your company uses as little as 25-35 oz. of gold/month, you can easily justify the purchase of an automatic tab plating machine.

adjusted to accommodate the agitation in the cell of the machine purchased. The current density at which the tabs are being plated at is of concern since the gold is being "blasted" on at high current densities and could effect the deposition, grain structure, porosity and tolerance of the plated metal. A maximum tolerance of ±5% of the plated thickness measured anywhere on the panel is not unreasonable to expect on a standard panel with today's technology. The proper use of squeegees or wipes at the exit end of this cell is as important here as it is for the nickel cell to minimize the gold dragout. Platinum clad anodes should also be utilized here for the same reasons as stated for the gold strike cell. High speed plating baths as marketed by most chemical suppliers can be used here and are normally run at 1 to 2 oz/gallon. Of course, again, for economic reasons it is preferred to use a bath that requires only 1 oz/gallon and still yields the desired results. Depending on the solution used and the machine cell design, the current density this bath will be run at will vary from 60-300 ASF.

The dragout/reclaim rinse is a necessary part of the process cycle but again, with the proper utilization of squeegees and wipes at the exit end of the gold plating cell and a 1 oz/gallon gold solution, the importance of this station can be minimized although, still required. The dragout that can be expected from the machines on the market today will vary from 1/4 - 5 ml/ft^2 of plated material. With possible dragouts of this concentration, it is recommended that the solution be run through an electrolytic reclaim unit first, then a resin column recovery unit prior to being dumped down the drain. Running the solution through an electrolytic recovery unit gives the plater a much more accurate account of the amount of gold being sent to the reclaimers and can extract as much as 90-95% of the gold from the dragout solution. Most of the additional gold in the solution will be recovered by running it through the resin column unit 2-3 times. The dragout solution should be changed periodically after running it through the resin column to prevent possible staining of the gold plated fingers.

The rinse after the gold dragout is primarily for the purpose of removing any remaining solution that can cause staining on the gold fingers when dried. The necessity for this rinse can be minimized by periodically changing the dragout solution and again the proper utilization of squeegees or wipes at the exit end of the dragout cell. Instead of a cold water rinse as is normally used here, a hot water rinse should be used. This would assist in removing any residue on the gold plated fingers and aid in the drying process.

Drying should be accomplished by using a high pressure, oiless, warm air blow-off since the drying needs to be accomplished quickly and the water blown off the gold plated fingers

The rinse after nickel plate and prior to gold can be a tap water or D. I. water rinse again depending on the purity of the water available. However, again to be safe, a D. I. water rinse should be used.

You will notice that the recommended process cycle did not include an acid activator after nickel plate as is normally used in a hand line and some automatic machines. This step is not required since the speed an automatic machine is normally run at (from 1-12'/minute) does not allow the panel tabs time to become passive. What this additional step will do is provide for the very real possibility of dragging acid into the gold baths, add cost to the machine and provide another bath in the machine that must be maintained. It has been proven on many occasions with machines in the field that an acid activator is not required here and also that the machines with an acid activate after nickel are more trouble than they are worth.

The gold strike is used primarily to help prevent possible contamination of the gold plating bath and provide a good base needed for passing porosity tests. The need for this step to prevent contamination of the gold bath can be minimized with the proper utilization of squeeges or wipes at the exit end of the nickel cell and a good rinsing after nickel. Another point to be concerned with here is that the anodes should be a platinum clad material rather than plated. It has been proven that platinum clad anodes will last 4-5 times longer than plated anodes. Although initially more expensive, the minimizing of the down time involved in changing them when the platinum wears off and the rejects that can result in using an anode without platinum far exceeds the initial cost advantage. Another factor is that the machine be flexible enough to allow this cell to be used as a plating cell (by switching of valves, etc.) if a gold strike is not required and additional speed or gold thickness is desired. Depending on the solution used and the machine cell design, the current density this bath will be run at will vary from 5-20 ASF. High speed plating baths as marketed by most chemical suppliers can be utilized here and are normally run a 1/2 to 1 oz/gallon. Of course, being able to run this bath at the lower concentration of gold and still be able to achieve the desired results is preferred from an inventory standpoint.

The gold plating step is one of the most important processes in the machine. Points of concern based on the machines on the market today, are the appearance of the plated gold and the current density the gold is being deposited at. The appearance of the plated gold does not normally have any effect on the functioning of the PCB but does however, effect the esthetics of the part which could be of primary concern to a job shop plater. The appearance of the plated gold is a result of current density, agitation and/or the formulation of the bath. Most high speed plating baths can be used here and the current density

as the surface they are being plated onto. The activating and cleaning of the fingers is of secondary importance since activation will take place further down the line and if any solder is left on the panel when it reaches the scrubber, it will probably be smeared into the copper. The scrub brushes used should be a very fine or super fine silicone carbide, self-cleaning type brush. Very little pressure at approximately 800-1000 RPM should be used to prevent scratching or scoring of the tabs. Since scrub brushes are expensive, the design of the scrubber, should be such that a sufficient amount of adjustment is available to insure maximum feasible wear of the brush.

The rinse after scrub is used to remove any residue left from the brushes such as bristles or fibres.

The activator solution should be a non-proprietary solution of 20-25% sulfuric acid and water. The length of time in this cell is of primary importance since too long in this solution can cause attack of the copper fingers and dull the surface therefore affecting the appearance of the plated metals and defeating the main purpose of the scrubbing. Therefore, the length of this cell is of primary importance to the machine designer and must be sized based on the speed range of the machine.

This next rinse prior to nickel plating can be a tap water or D.I. water rinse depending on the purity of the water available to the machine. To be safe, a D.I. water rinse should be used.

Nickel plating is probably the single most troublesome step in the process to both machine manufacturers. To eliminate most of the problems normally experienced, soluable nickel anodes in the form of SD rounds or NI shot should be used here in conjunction with a sulfamate nickel bath. Without the use of soluable anodes, the control of the pH, specity gravity and metal concentration in the bath will be an on-going battle that the plater or chemist normally loses. Depending on the solution used and the machine cell design, the current density used in this step will vary from 200-800 ASF. The current density however, is not a key factor as many people feel. What is important, is the deposition rate of the metal and the sizing of the length of the cell based on the speed the machine is to be run at to yield a required thickness. This is important since the use of soluable nickel anodes will reduce the allowable current density and therefore the thickness that can be achieved at a given speed in a given length of cell. A machine originally designed to run with insoluable anodes cannot be converted to run with soluable anodes and yield the same thickness at a given speed as it was originally designed for. Of secondary importance is that the bath needs to be run at the saturation point with boric acid and the reservoir tank in the machine should be made with a compartment that will easily allow for the addition of boric acid when needed.

further towards the end of this discussion. The primary thing to be concerned with during the loading process is that the machine be capable of accepting boards loaded end to end (i.e. no gap between panels) to eliminate the high current density area on the leading and trailing edges of each panel. This in itself is a considerable cost savings if only the cost of the gold saved is taken into account. However, an additional factor to be considered is the increased production that can be realized by not having a space between each panel. For example, at 6'/min., based on an 8 hour day, a 3" gap between panels can mean a loss in production of approximately 576 twelve inch panels per day or approximately 1.6 million linear feet of material per year.

The stripping process should utilize a non-proprietary stripping solution such as a solution of 35% hydrochloric acid and water. To this can be added other chemicals to limit the attack of the copper and extend the life of the solution, although they are not necessary. The advantages of a non-proprietary stripping solution is the cost (approx. 65¢ to 70¢/gal, vs. $7.00 to $8.00/gal. for a proprietary stripper) and the fact that you minimize the undercutting that can take place with a proprietary chemical stripper. The amount of attack the copper can be controlled by varying the current density based on the thickness of SnPb being removed and the speed the machine is run at. The life of the solution can be extended and/or the strength increased by adding 1/4 - 1/2#/gallon of common table salt to the bath.

The rinse after stripping is required for the same reason every other rinse is required in a plating process. On occasion, a neutralizer is used here to de-activate the stripping solution; however, it is not required. Points to be concerned with about all the rinses are that they be at least 1/8" higher than the highest plating height and a sufficient amount of water necessary to properly rinse the panel is available. What is meant by this is that, spray rinses, although not required at every station should be used throughout the machine since overflow type rinses cannot compare with the effectiveness of a spray rinse. Since water is costly to bring into a plant and in some cases even more costly to dispose of, recirculating type rinses should be utilized throughout the machine. With recirculating type rinses, the water usage for the entire machine can be as low as 1/2 - 2 GPM.

The primary purpose of the mechanical scrubbing process is to brighten up the surface to be plated and secondarily to activate and clean the fingers. It should not be used for the purpose of leveling the copper, removing nodules, or to correct other prior defects in plating or manufacture. The brightening or polishing of the surface to be plated is important since the luster and brightness of the plated metal will only be as good

automatic tab plating machine would be configured and the best approach, in the author's viewpoint, to the plating of fingers (tabs) on a printed circuit board on an in-line automatic continuous tab plating machine.

The process cycle that should be used is as follows:

Manual Loan
Reverse Current Strip
Rinse
Mechanical Scrub
Rinse
Acid Activate
D. I. Rinse
Nickel Plate
D. I. Rinse
Soft Gold Strike
Hard Gold Plate
Dragout/Reclaim Rinse
Hot Rinse
Blow-off/Dry
Automatic Unload

Before we get into each step in the process cycle, let's look at one of the most important and expensive steps in the preparation of the panel required to its being inserted into the machine. That being, first and foremost, with the machines available on the market today, the fact that the panel must be taped above the fingers to insure a good demarcation line, prevent contamination of plating baths and to prevent attack on other areas of the panel that are not being plated. The amount of tape required according to the machinery manufacturers varies from 3/4" to 1-1/2" wide. Although the necessity for fume tape is eliminated, this is still a considerable cost factor and a necessary evil with the machines presently on the market. It has been estimated, that taping a panel for gold tab plating can add as much as $1.00 to the manufacturing cost of the PCB. A factor in the size of tape required is the accuracy of the shearing of the panel on the bottom edge. Since both machines available rely on the bottom edge of the panel for positioning during the loading process, the "line of plating" above the fingers will be directly parallel to the sheared edge of the panel. To exaggerate this point, if the panel were sheared at a 1° angle in relationship to the top of the fingers, it would result in a difference of .420" over the length of a 24" panel. Therefore, in this case, a minimum of .420" tape would be required just to insure a straight line on the top of the fingers and on top of this, you would have to add the minimum width of tape recommended by the machine manufacturers to prevent attack of areas not plated, contamination of baths, etc. It is not realistic to expect the PC manufacturer to hold the shearing of the bottom edge of the panel in relationship to the top of the fingers to within .010/.020". Therefore, the optimum here would be the ability to run without plating tape on a machine that would use some other part of the panel for reference for loading other than the bottom edge.

You will notice that manual loading was recommended in the process cycle, not automatic loading. This will be pursued

AUTOMATIC PCB PLATING MACHINERY

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In a matter of only a few years since their introduction to the industry, Automatic Tab Plating Machines have become a necessary piece of capital equipment for PCB/PWB manufacturer. Although relatively new to the industry, a multitude of field experience has been gained and many miles have been logged on the existing design machines. Sufficient time has elapsed to warrant a study being made of available machines and technology. The results of this study allows the "good features" of existing machines, field experience and new technology to be combined to enable one machine to be developed that will truely be a turn-key, state-of-the-art type machine. The following summarizes a study made of the existing machines and available technology and outlines the optimum methods that should be used to plate PCB tabs in an automatic machine.

Up until approximately 8-10 years ago, the manufacturing process of a PCB could have been described as closely fitting the shape of a venturi tube. That is, the capacity at the beginning of the process was large, got progressively smaller as it reached the nickel/gold tab plating step and again got progressively larger after nickel/gold tab plating. This was changed when an Automatic Printed Circuit Board Tab Plating Machine was developed and introduced to the Printed Circuit industry as a joint venture between a large chemical company and a small manufacturing concern. The first machine was slow, inaccurate, costly and in general had more than its share of problems. However, after being redesigned a number of times it was responsible for revolutionizing the technique of selectively plating tabs and over the years has evolved into a very necessary piece of capital equipment for the PC manufacturer. This was mainly due to the increased production capabilities of the machine and the gold cost savings. Since that time, two additional machines for the purpose of automatic tab plating have been introduced to the market place. Two of the three machines now available have been widely accepted in the industry for a various number of reasons. Both machines that have been accepted have their pros & cons and the decision as to which machine to purchase has been primarily a judgment call, usually by a capital equipment engineer. The following is how the optimum

D-4

Electronics I
Session D

Automatic PCB Plating Machinery

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machine. The true stresses and strains were calculated using the equations[7]:

$$\sigma_T = \frac{(P-P_o)a^2 \exp[-2\bar{\delta}]}{4ht_o}$$

$$\bar{\delta} = \frac{4h^2}{3a^2}$$

where σ_T is the true stress, P is the gas pressure to bulge the specimen, P_o is the initial gas pressure, a is the specimen radius, $\bar{\delta}$ is the true significant strain and h is the bulge height. The results of these tests are listed in Table 1. Again the reproducibility is good. It is seen that the tensile strengths are significantly lower than those measured for the same material in the new machine. The lower strength can probably be attributed to the observation[7] in smaller samples that the strength increases as the cross-sectional area decreases. The reason why the ductility which was also somewhat lower when measured by the bulge tests was probably due to the fact that there was no necking. It can be seen from Table 1 that the values of the true strains at the maximum load, i.e., before necking occurred, and the true strains from the bulge test are about the same.

The results of this study show that consideration should be given to using tensile specimens of the same thicknesses and width as the elements on printed-circuit boards. The spin off from an AES Research Project is also illustrated. The new machine can also be used for the determination of the low-frequency fatigue properties of electroless copper by simply reversing the motor which turns the fine-threaded screw by which the load is applied.

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Acknowledgements

Mr. S. Delehanty prepared the substrates and Messrs. D. Karabag and L. Smith plated the samples. Mr. C. C. Nee performed the bulge testing. The support of the AES Research Board which led to the development of the new tensile machine is also acknowledged. Dr. Paunovic participated in this study as a member of the AES Project 38 Committee.

TABLE 1

TENSILE TEST RESULTS

Test with New Machine

Sample No.	Tensile Strength MPa	Tensile Strength Kpsi	% Elongation	True Strain at Max. Load (%)
1	211	31	9.1	7.1
2	197	29	9.2	7.9
3	210	31	7.1	4.7
4	197	29	7.2	5.3
5	210	31	6.4	4.3

Bulge Tests

Sample No.	True Stress at Fracture MPa	True Stress at Fracture Kpsi	True Strain at Fracture (%)
6	116	17	3.8
7	129	19	4.5
8	116	17	3.1

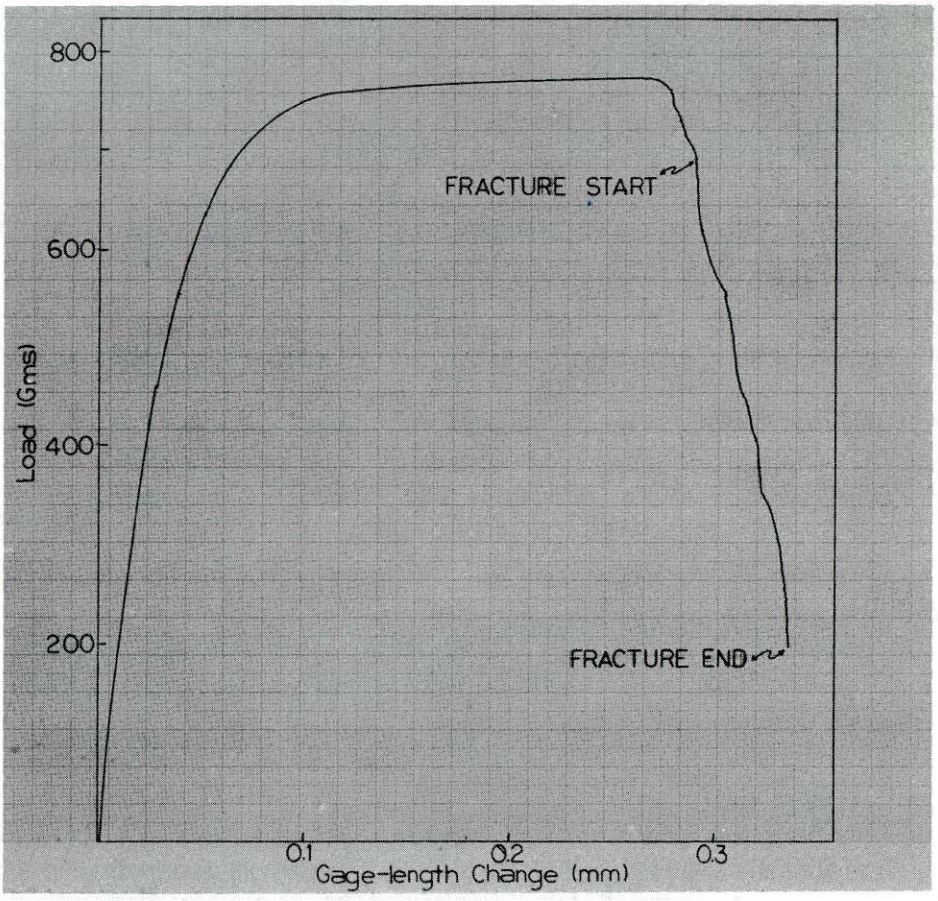

Figure 3 Graph of Load vs Uncorrected Gage-Length Change

Electroless copper from a proprietory solution of the EDTA-formaldehyde type was plated onto expoxy-glass substrates in a way that the deposits could be readily stripped[4,5] for subsequent testing. Such a stripping method is recommended in the IPC standards[1]. The substrate was made catalytic by first coating it with adhesive to bind the subsequently laid-down layer. This layer, which was the catalytic one, was composed of a cured epoxy resin containing 20% TiO_2 pigment, phthalocyanine blue colorant and a 15% clay carrier containing the 0.1% palladium catalyst. By the use of photoresist and a mask having the shape of the tensile specimen and its supporting frame, electroless-copper deposits were plated which did not have to be cut to size or subsequently finished in any way. The tensile specimen and its supporting frame are shown in Figure 2. The purpose of the supporting frame, which is the stripe of deposit to the left of the dotted line in Figure 2, was to facilitate handling and mounting in the testing machine. This stripe was cut prior to testing after the tensile specimen had been mounted in the grips.

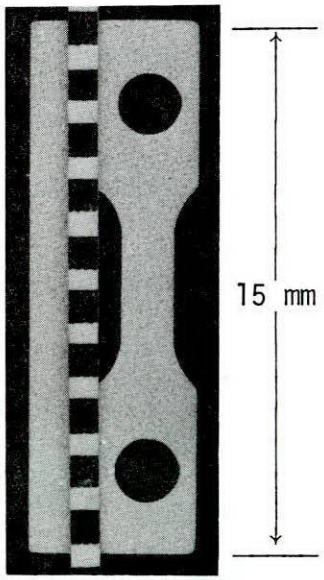

Figure 2
Tensile Specimen

The results of tensile tests are presented in Table 1. It is evident that the reproducibility of the tensile strength for Samples 1-5 is very good. The reproducibility of the ductility, i.e., % elongation is also quite good for the type of material and specimen tested. A typical graph of applied load vs uncorrected gage-length change is shown in Figure 3. In the calculation of the strains, the gage-length changes had to be corrected for the stiffness of the machine. A rise is seen in Figure 3 to a maximum load, which divided by the original cross-sectional area is the tensile strength. After the maximum load, fracture begins and ends as indicated on Figure 3. The drop in the load beyond the maximum is due to a local decrease in the specimen thickness, i.e., necking, which preceded the beginning of fracture. In order to calculate the true stress, i.e., the load divided by the actual cross-sectional area, the minimum specimen thickness was measured by means of a scanning electron microscope. Assuming that the cross-sectional area at fracture was the minimum thickness times the original specimen width, the true stress was calculated to be 388 MPa ($\sim$54 Kpsi). The true stress at fracture was actually greater than 388 MPa because part of the specimen had already fractured so that the width and therefore the cross-sectional area was smaller than the one used in the calculation. The electroless-copper deposits were therefore stronger than their tensile strengths indicate. However, as discussed elsewhere[3], the fracture stress of a deposit attached to the substrate lies between the tensile strength and the true fracture stress.

An alternate method of measuring the mechanical properties which is not burdened with some of the problems of specimen size is bulge testing. Bulge tests[6] were performed to compare their results with those obtained with the new machine. Samples 5.5 cm square were plated on the same substrates at the same time as the tensile specimens which were tested in the new

TENSILE TESTING OF PRINTED CIRCUIT BOARD ELEMENTS

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The integrity of electroless-copper deposits on printed-circuit boards depends on their mechanical properties. The determination of the mechanical properties presents problems, particularly the tensile-specimen configuration. IPC standards[1] specify specimen width of 1/2". Therefore for a typical foil thickness of 25 μm (1 mil), the width-to-thickness ratio is 500. ASTM Standard E8-77[2] specifies a maximum width-to-thickness ratio of 8. On a typical printed-circuit board, the width-to-thickness ratio is about 50. For thin deposits, it is not possible to attain a ratio of 8. However, it would seem that the ratio in test specimens should be closer to 50 than to 500. As the gage length also has to be scaled, specimens with a width-to-thickness ratio of 50 are very small and difficult to test with conventional instrumentation. In order to investigate the mechanical properties of electrodeposits under AES Project 38, a tensile machine which can test very small specimens had to be designed and built.

This small, compact machine is shown in Figure 1. It is described in greater detail in a paper[3] being presented at this conference in the Research Session. The purpose of this presentation is to demonstrate the applicability of the instrument in Figure 1 to the tensile testing of electroless copper for printed-circuit boards and to compare the results with those from another method.

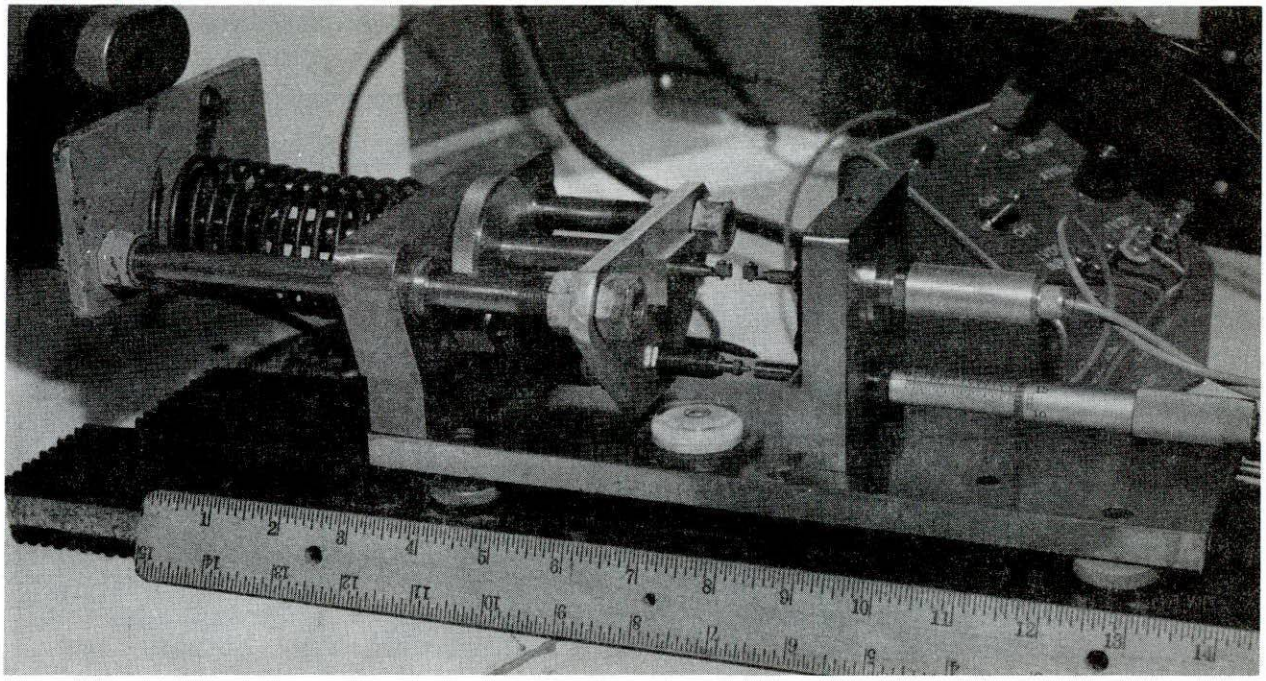

Figure 1. Tensile Testing Machine

D-3

Electronics I
Session D

Tensile Testing of Printed Circuit Board Elements

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P-t-h interconnection in UDEL® polysulfone

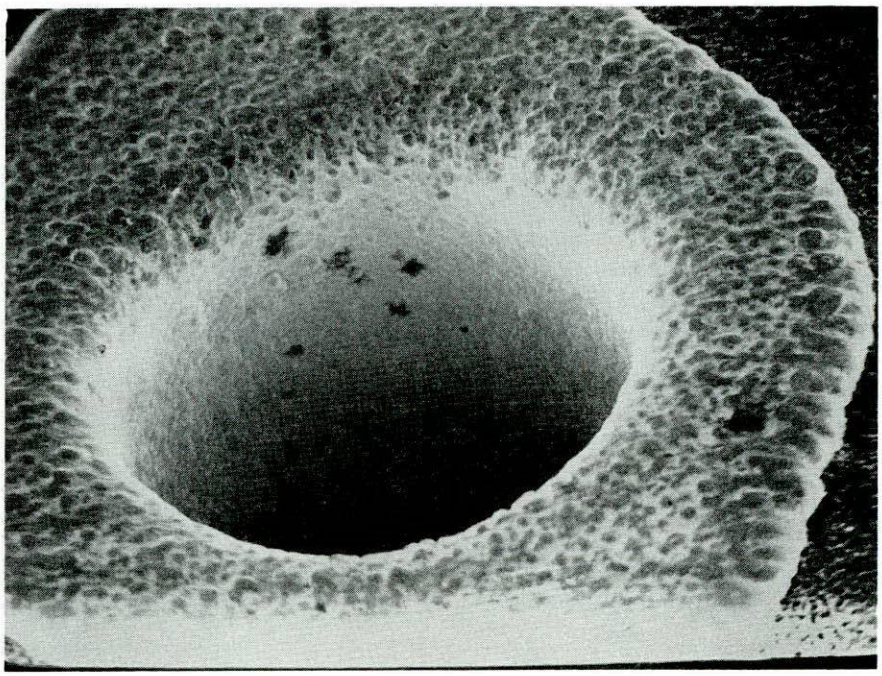


Figure L

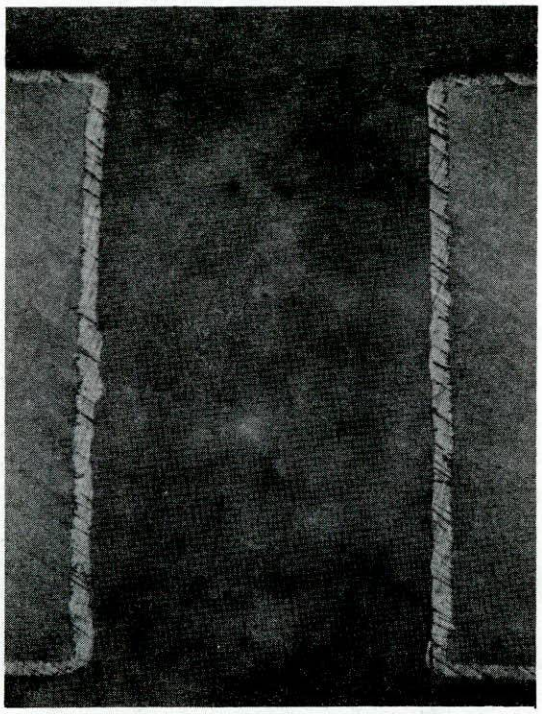


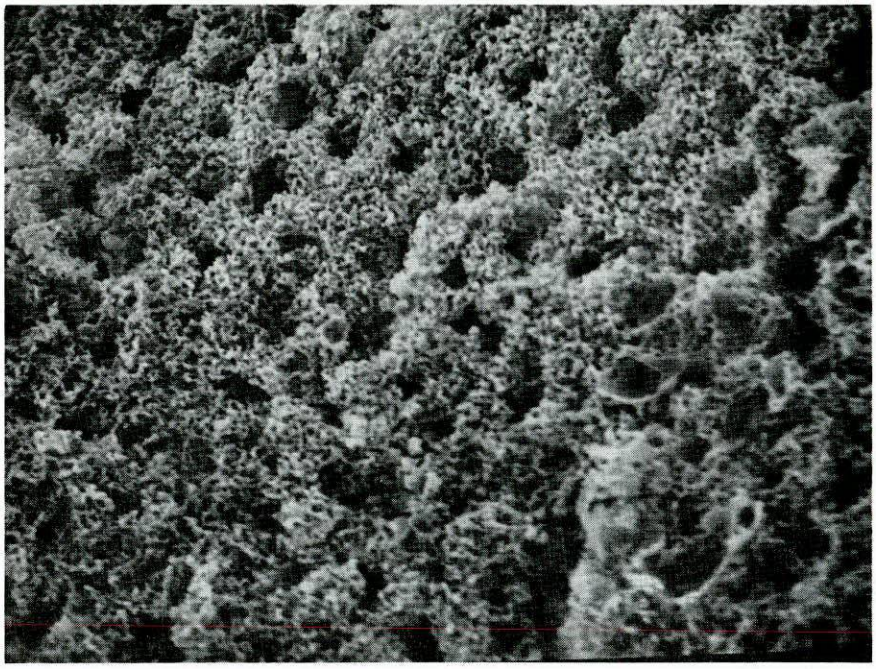
Figure M

Adhesion promoted UDEL® polysulfone



(50x,40°)

Figure J



(700x,30°)

Figure K

Ultem 1000 Substrate
Proper adhesion promotion at 200x, 30°

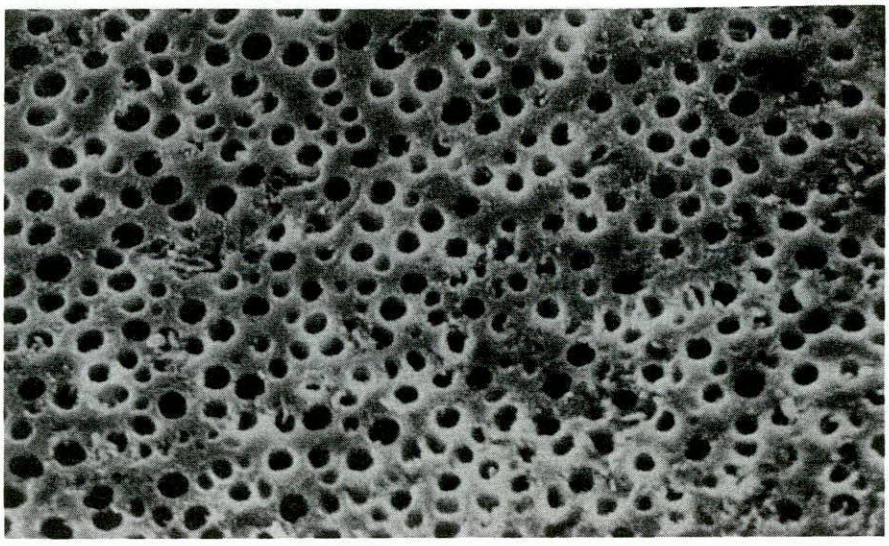


Figure I

Ultem 1000 Substrate
Over adhesion promotion at 200x, 30°

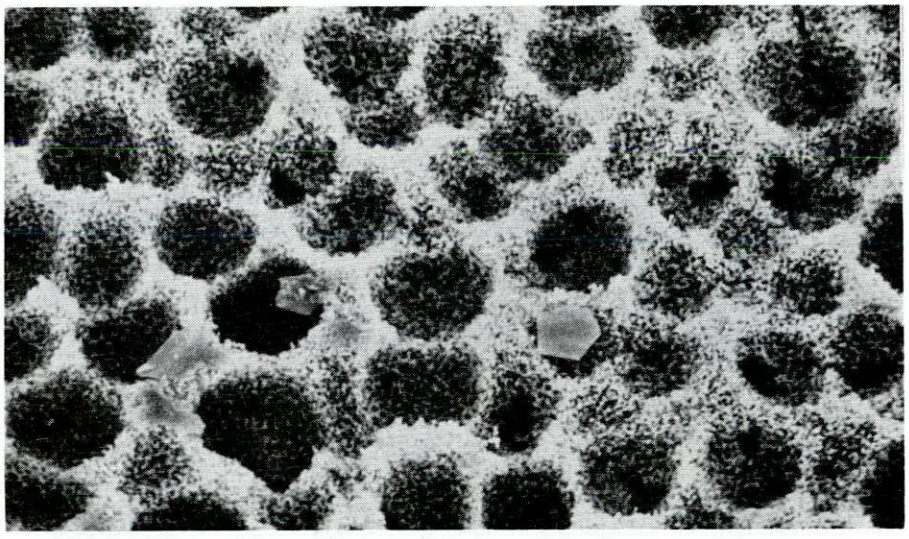


Figure G

Insufficient adhesion promotion at 200x, 30°



Figure H

Drilled hole in UDEL® polysulfone (50x,30°)

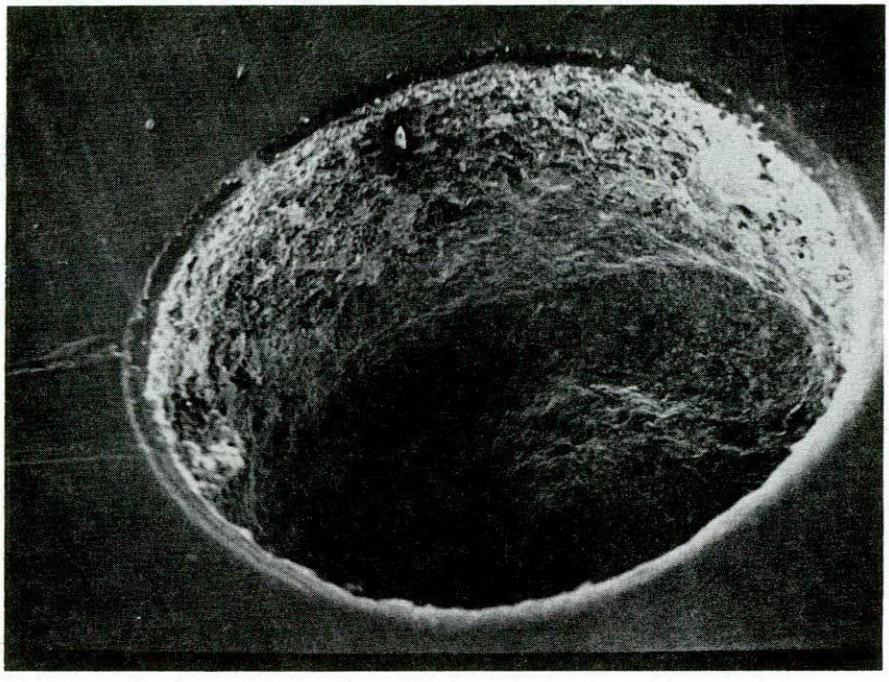


Figure F

Typical Sheet Extrusion Line

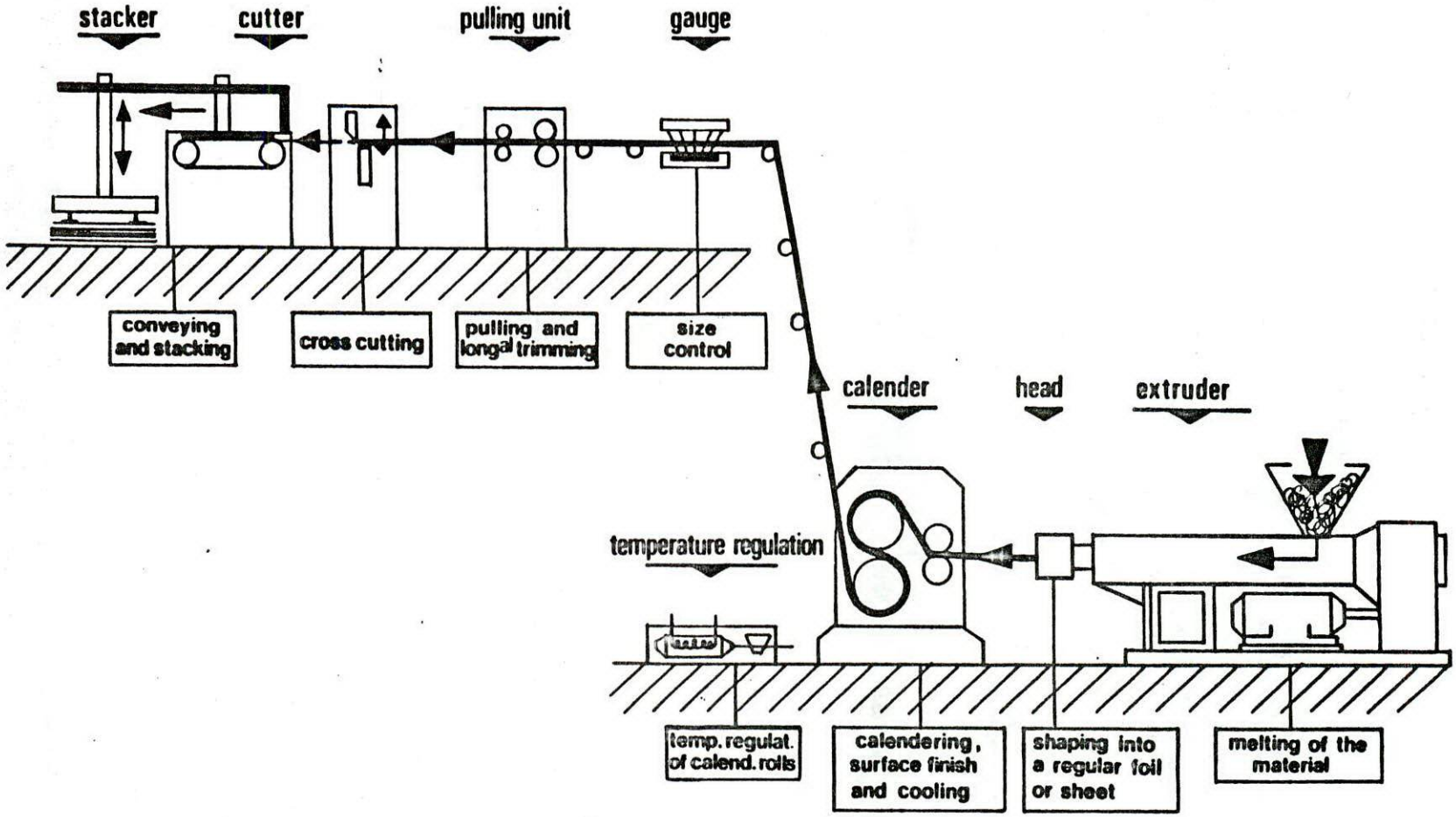


Figure E

DIELECTRIC CONSTANT OF UNREINFORCED PSF/PEI vs FREQUENCY, AT 50% RH

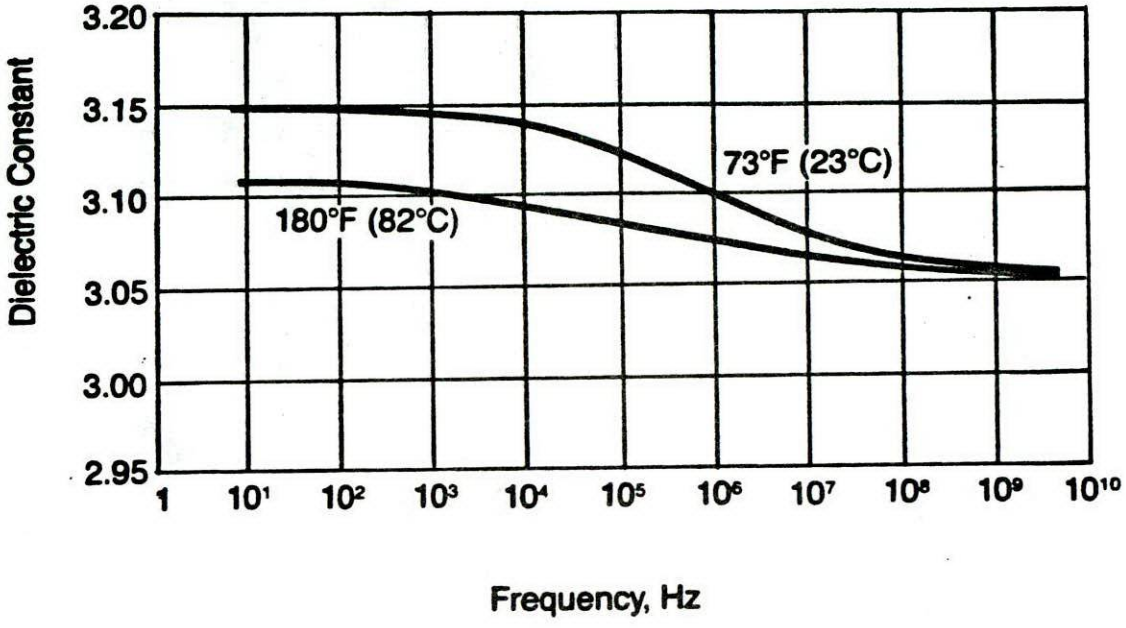


Figure C

DISSIPATION FACTOR OF UNREINFORCED RESINS vs FREQUENCY @ 73°F (23°C), 50% RH

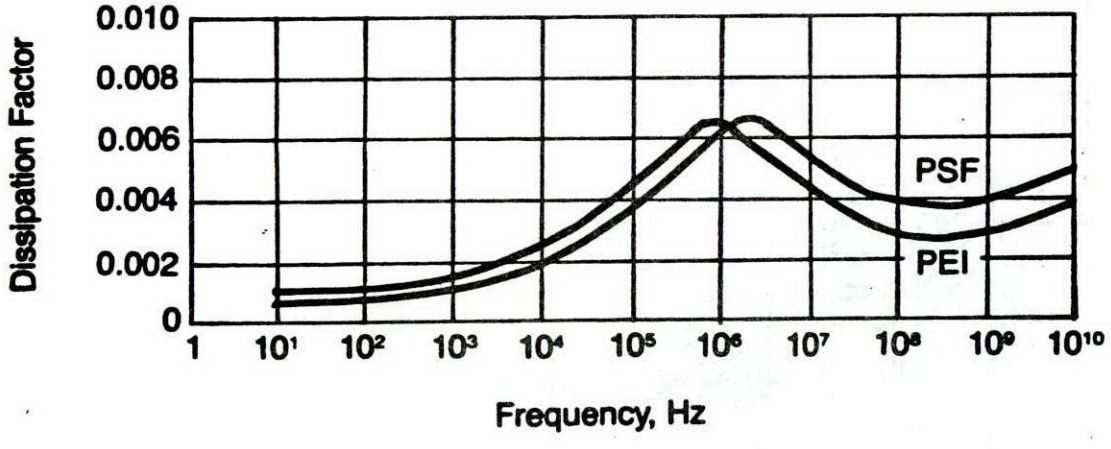


Figure D

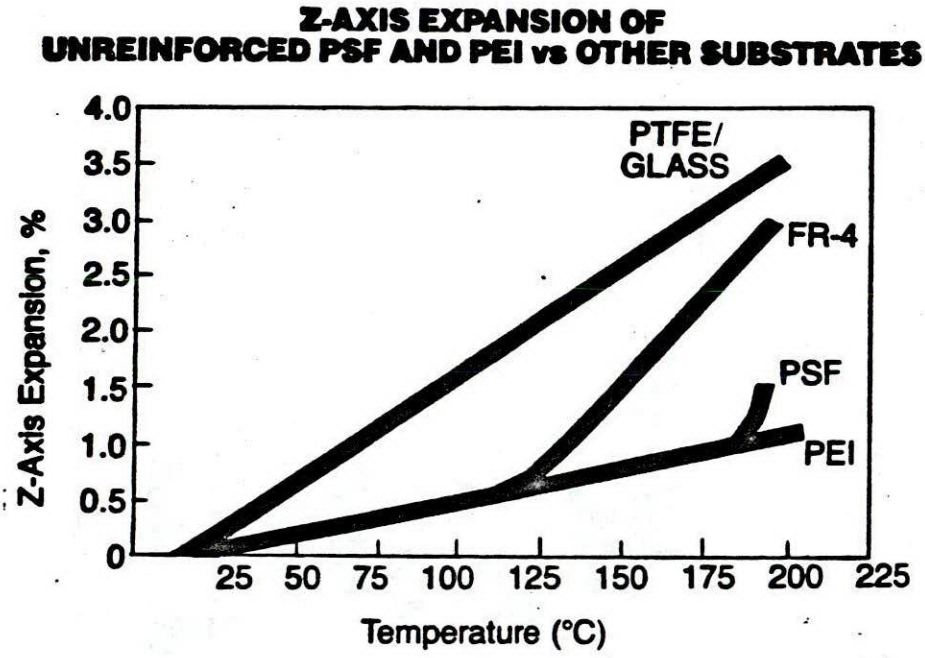


Figure A

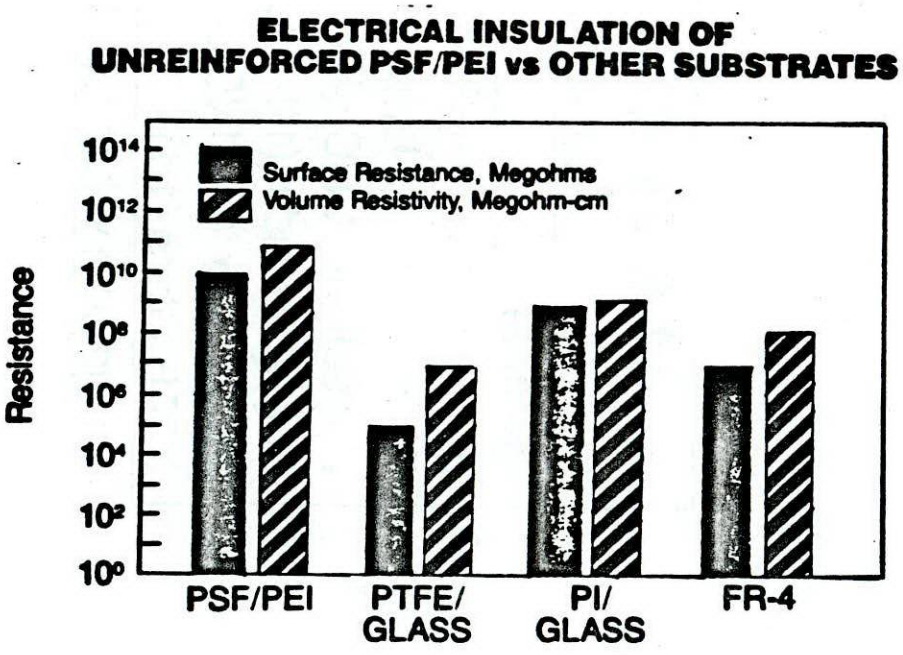


Figure B

TABLE II

COST COMPARISON ($/FT²) for .060" MATERIAL	
Material	**Cost**
Epoxy-glass (1/1-FR-4)	$2.40 (average)
Polysulfone (1/1-Udel)	$14 to $18
Polysulfone, UNCLAD	$2.10 to $3.40*
Polyetherimide, (1/1-Ultem)	$16 to $20 (est.)
Polyetherimide, UNCLAD	$2.60 to $4.00*
PTFE-Glass (1/1)	$25 to $35
*In medium volumes, Westlake Plastics	

TABLE I

THERMAL PROPERTIES OF PSF & PEI				
Property	**PSF**	**Unreinforced PEI**	**20% G.R. PEI**	**FR-4**
Heat Deflection (HDT) @ 264 psi	174°C	200°C	209°C	—
Glass Transistion (Tg)	190°C	217°C	217°C	120°C
U.L. Max. Temperature	150°C	170°C	170°C	125°C

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In addition, experience has shown that adequate pre-heating is vital to assure complete removal of all flux vehicles prior to exposure in the molten solder. Odd shaped geometrics or large boards may require some degree of stiffening of support as part of the transport mechanism to avoid sag while passing over the wave.

Conclusion

Semi-additive thermoplastic circuits can offer performance advantages for a variety of product applications. These benefits become even more significant when economic factors are taken into consideration. Although the techniques for producing printed wiring boards on extruded or injection molded substrates is relatively new, the semi-additive technology is well established with over fifteen years of production history on unclad laminate base substrates.

The development of UDEL Polysulfone and ULTEM Polyether-imide materials with semi-additive circuit plating will result in a greater market penetration of fine line, high resolution circuit boards.

Essentially, the test boards passed extremes of cycling temperature, thermal shock, hot oil immersion, thermal aging and plated through hole bond strength retention. Similar testing of ULTEM 1000 circuits is planned.

Additionally, PCK has been granted Underwriters Laboratories printed wiring board process "Recognition" on UDEL Polysulfone grades P1700 and P1720 (reference: file #E-76278) as follows:

Minimum Line Width: 0.010"

Maximum Unpierced Area:

P1700-2.0 inch dia. @245°C/5 secs.
0.5 inch dia. @260°C/5 secs.

P1720-2.0 inch dia. @260°C/5 secs.

Maximum Operating Temperature - 140°C

Minimum Thickness: 0.060"

Submission of the ULTEM PEI is now in process with similar ratings anticipated.

Soldering Recommendations

Since the processing of thermoplastic extruded additive circuits is in its infancy, experience relating thereto is being acquired at a rapid rate. PSF and PEI are known to be attacked by chlorinated hydrocarbons, aromatic hydrocarbons, some alcohols and highly polar materials. Also, non-ionic surfactants should be avoided. Since these are present in some commercial fluxes and aqueous cleaners, formulated products should be evaluated carefully and suppliers' literature consulted before using such products.

Experience has shown Alpha Metals Inc. Type OA (organic acid) water fluxes are compatible with both PSF and PEI. Alpha types 709 and 2883 have produced excellent results at pot temperatures ranging from 460°F to 500°F, with line speeds ranging from 10 to 20 FPM. For applications requiring Freon post cleaning, Alpha Type 881 yielded comparable performance to the water soluble materials. Fully activated rosin fluxes (Type RA) are suitable; however, they tend to lack sufficient activity for soldering at slightly reduced pot temperatures and increased line speeds associated with the non-glass filled thermoplastic grades. Super activated rosin fluxes such as Alpha RSA 942 may be considered in certain applications.

- Electroplated Copper - A 10% thicker plating deposit is advised if subsequent metal etch resists are not used.

- Optional Overplates - If required, overplating of tin-lead or nickel-gold can be used; however, a copper-only board may be manufactured without plating a metal etch resist.

The following illustrates the relationship between the total build-up of copper on a circuit conductor and the background electroless flash that has to be etched.

	Surface	Background	Ratio (S/B)
Conventional 1 oz.	2.7 mil	1.4 mil	1.92
Conventional ½ oz.	2.0 mil	0.7 mil	2.84
Semi-Additive (unclad)	1.3 mil	0.1 mil	13.00

The higher comparative thickness ratio of semi-additive permits the elimination of overplate etch resists while preserving the integrity of plated conductors and holes.

- Strip Plating Resist - The equipment-stripping mediums and procedures are identical to the subtractive process. Remember, semi-aqueous and fully-aqueous resists are highly recommended.

- Quick Etch of Copper Flash - The thin background electroless copper only requires a "quick etch", thereby reducing the cost and quantity of etchants with increased through-puts. Etching a maximum of 0.1 mils produces no observable undercut of the conductors, resulting in accurate fine line patterns.

A typical plated-through hole interconnection is shown topographically in Figure "L" and cross-sectionally in Figure "M".

Final secondary operations such as solder masking, nickel-gold plated contact fingers and nomenclature (legend) markings are compatible with PSF and PEI. Thermally-cured masks such as PC-501, as well as UV curable systems, have been used to produce semi-additive thermoplastic boards with excellent results.

Physical Properties

In-house quality control, independent laboratory and customer testing has shown semi-additive thermoplastic circuits to be of good quality. To date, several environmental evaluation tests have been performed on PSF, grade P1720. This program and its results were reported on at the Fall 1981 IPC meeting in Dallas, Texas (IPC Technical Paper TP-382).

- Adhesion Promotion and Copper Reduction - to ensure a strong bond between the substrate and the electrolessly deposited copper, it is necessary to pre-treat in an oxidizing solution. This step is commonly referred to as "Adhesion Promotion, Pretreatment or Conditioning". The oxidizing agent is an acidic chrome solution.

The Adhesion Promotion process sequence encompasses:

Solvent Swell
Conditioner
Acid Predip
Adhesion Promoter
Dragout Rinse
Neutralization
Water Rinse

In-process quality control testing of a chemical and topographical nature ensures the reliability of the process. Examples of an adhesion promoted ULTEM substrate are shown in the photomicrographs of Figures G, H, and I. Hole walls replicate the surface topography by virtue of the homogeneous nature of the extruded substrates. Figure J illustrates a UDEL Polysulfone adhesion promoted drilled hole. The microporous (etched) texture is uniform throughout the hole wall as shown in the SEM photograph of Figure K at 700X magnification.

The panel is then catalyzed by depositing either a noble metal, usually palladium, or a non-noble metal complex on the surface and on the hole walls. This step is common to conventional (subtractive) circuit board manufacture.

The final step in this sequence is to deposit a micron thin layer of electroless copper on the surface and in the holes. The copper should be thick enough to withstand subsequent imaging and plating operations. Typically, 25 millionths to 100 millionths of an inch are deposited.

Copper reduction consists of the following steps:

Cleaner Conditioner
Activate and Rinse
Accelerate and Rinse
Electroless Copper

- Screen or Photoprint Plating Resist - The methods, materials and equipment required in this step are common with subtractive circuit manufacture. However, these thermoplastics are attacked by chlorinated hydrocarbons; consequently, semi-aqueous or full-aqueous resists are recommended in lieu of methylene chloride strippable products.

catalysts and electroless copper (or nickel) platings adhere with great tenacity. Finally, after etching, peel strengths commonly exceed quoted 6 lbs/inch minimum values, averaging 10 to 12 lbs. on both the surface and in the hole walls.

The essential step to achieving strong plating-to-substrate is in the "adhesion promotion" (surface treatment) chemistry which creates a microporous topography on the surface and in the drilled holes, providing anchors for subsequent electroless metallization.

Process

The semi-additive process is composed of a sequence of manufacturing operations starting with the selection of the appropriate base material, proceeding through surface pre-treatment, electroless and electrolytic plating and concluding with a quick etch of the background electroless copper.

The following is the entire manufacturing process from the raw material stage to the finished product. Each of the individual manufacturing steps will be highlighted to detail their procedure.

- Stress Relief - extruded materials require heat treatment to relieve internal stresses induced during their fabrication. This is normally performed by baking the sheets in a convection oven at the temperatures at or just below the resin's heat deflection temperature (HDT). Typical baking times of 3 to 6 hours are recommended by the resin suppliers depending upon the sheet thickness. Furthermore, fixturizing between metal platens is suggested to avoid heat-induced distortion. An alternative to this lengthy procedure has been developed wherein the extruded unclad sheets are exposed to either an infra-red or microwave radiation (Frisch et.al., Patent No. 4,339,303).* This new technique eliminates both the need for elaborate fixtures while shortening exposure times to between 15 to 20 minutes.

- Form Pattern and Pilot Holes - thermoplastics require more attention to avoid overheating. Heat dissipating entry and back-up foil has been found to yield acceptable results with good quality, smear and burr-free holes. Figure F illustrates a typical drilled hole in PSF sheet.

  Subsequent to drilling, the sheets are resubjected to the stress relief process. This step is essential since the materials will be exposed to stress cracking agents during the following adhesion pretreatment steps.

* Assignee is Kollmorgen Technology Corporation

conventional epoxy-glass and PTFE-glass laminates. Plated-through hole reliability is enhanced by the reduced change in thickness versus temperature profiles of PSF and PEI.

The key electrical properties for printed wiring board applications include excellent volume and surface resistivities, as well as a low dissipation factor and stable dielectric constant over a broad frequency and temperature range, as shown in Figures B, C and D.

Although not directly interchangeable with conventional microwave substrates, both the UDEL and ULTEM offer improved characteristics over higher loss materials like epoxy-glass (FR-4) or polymide-glass. Furthermore, where design proves compatible with PSF and PEI, significant economic benefits may be realized. Cost savings become particularly important with higher volume commercial and consumer products.

The economic factors for considering polysulfone and polyetherimide become even more attractive when comparing differences between clad and unclad sheeting. Because semi-additive plating does not require a pre-clad base material, "as extruded" sheet products are used, thereby eliminating secondary "off-line" lamination processes which add unwarranted additional cost to bare substrates.

As shown in Table II, PSF and PEI offer economic advantages over conventional PTFE-glass, while approaching FR-4 prices.

Manufacturing Thermoplastic Sheets

The reason for the economy of engineering thermoplastics is the extrusion processes. Unlike laminates which are fabricated in batch quantities, extrusion is a continuous process wherein resin, supplied as a solid plastic pellet, is heated in a chamber to its melt viscosity (600°F to 800°F), forced through a narrow opening or gap in a die in continuous film or sheet until finally being sheared into full-sized sheets or panels and stacked for delivery. A complete extrusion line is illustrated in Figure E.

Tight tolerancing is routinely achieved on the order of ±0.003"; however, ±0.002" is obtainable. Custom extruders such as Westlake Plastics, Lenni, Pennsylvania and Rowland Inc., Berlin, Ct., have production experience in processing high quality UDEL and ULTEM sheets.

Semi-Additive

Plating directly onto "as fabricated" thermoplastic sheets has been routinely accomplished by semi-additive techniques. With proper pre-plate chemical treatment, conventional plating

consumption of plating and etching chemicals.

Materials

Two thermoplastic resin systems are commercially available that meet the general criteria for printed wiring board fabrication including:

- Compatibility with PTH "additive" chemistry
- Machinable on existing equipment
- Plating adhesion ≥ 6.0 lbs/inch
- Wave and hand solderable

Of the two materials, the first to be available was UDEL® Polysulfone, marketed by Union Carbide Corporation (PSF). Standard grades being made are: P1700 and P1720 (unfilled) and P8000 (mineral filler).

The second material to date proven suitable is available from General Electric Co. under the trade name ULTEM® Polyetherimide (PEI). As is the case with PSF resins, ULTEM is offered in an unfilled grade (1000) and 20% glass reinforced alternative (2200).

Both of these materials are classified under the general heading of amorphous thermoplastics. This means that they have no crystalline form. They do not have a melting point. Rather they gradually become softer and softer until, finally, they are recognized as being a liquid. Their characteristics allow them to be processed on conventional extrusion equipment.

Because of their improved thermal characteristics, the PSF and PEI resins are known as "high temperature" engineering grade thermoplastics as their heat deflection (HDT), and glass transition (Tg) temperatures are far greater than for conventional thermoplastic resin materials like polycarbonate and ABS.

It is these features that result in the ability of UDEL and ULTEM plated products being suitable for mass soldering procedures.

Furthermore, the Underwriters Laboratories Inc. has extended "Recognition" ratings to these materials for maximum operating temperatures in excess of that assigned to the more commonly used circuitry substrates such as epoxy-glass (FR-4). Table I shows the thermal ratings for the UDEL and ULTEM materials.

An added performance benefit of the high Tg values is the low thermal expansion coefficient at elevated temperatures. As shown in Figure A, their Z-axis expansion is lower than for

ENGINEERING GRADE THERMOPLASTICS & ADDITIVE PLATING

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The primary support base for essentially 100% of all printed wiring boards for almost thirty years has been thermo-setting resin-laminated plastic sheets. Regardless of the resin chemistry; i.e. phenolic epoxy or polyester, the common link between all these materials is the use of reinforcement fabrics such as cellulose paper or woven glass cloth and their batch processing steps of resin impregnation, slitting, stacking, laminating and final trimming. All told, there are at least five discrete operations required to fabricate a "C"-staged rigid sheet or panel.

As an alternative approach to batch techniques, continuous processes have been considered as potential methods to improve on the efficiency and economy of press laminating. However, these concepts have had limited commercial success.

Recent break-throughs in the development of engineering grade, high temperature thermoplastic resins, suitable for printed circuit applications, have generated considerable interest because of their non-lamination manufacturing methods. Being hot melt processable resins, thermoplastic sheets may be produced by either "in-line" continuous extrusion or injection molding techniques. Regardless of the process used, modest to significant price reductions may be realized over conventional premium grade laminate materials. For applications requiring dielectric properties that are superior to that of epoxy-glass laminates but sensitive to the higher costs of PTFE-glass RF or microwave substrates, the low loss characteristics of selected speciality thermoplastics offer performance at economical savings. Also for products requiring base substrates thermally stable over a broad temperature range, high temperature thermo-plastics again present alternatives to the more costly poly-imide-glass type laminates.

Finally, in addition to the economic benefits realized in manufacturing thermoplastic substrates, their inherent unclad "As Fabricated" construction is ideally suited for PC metal-lizing by semi-additive plating methods. Fine line, high density patterns with reliable plated through hole intercon-nections can be produced at additional savings as compared to the subtractive or conventional approach. Semi-additive circuits differ from their subtractive counterparts in a variety of features including; minimal to no undercuts of conductor traces, rework capability during fabrication (recycle drop-outs) and lower manufacturing costs due to reduced

D-2

Electronics I
Session D

Engineering Grade Thermoplastics & Additive Plating

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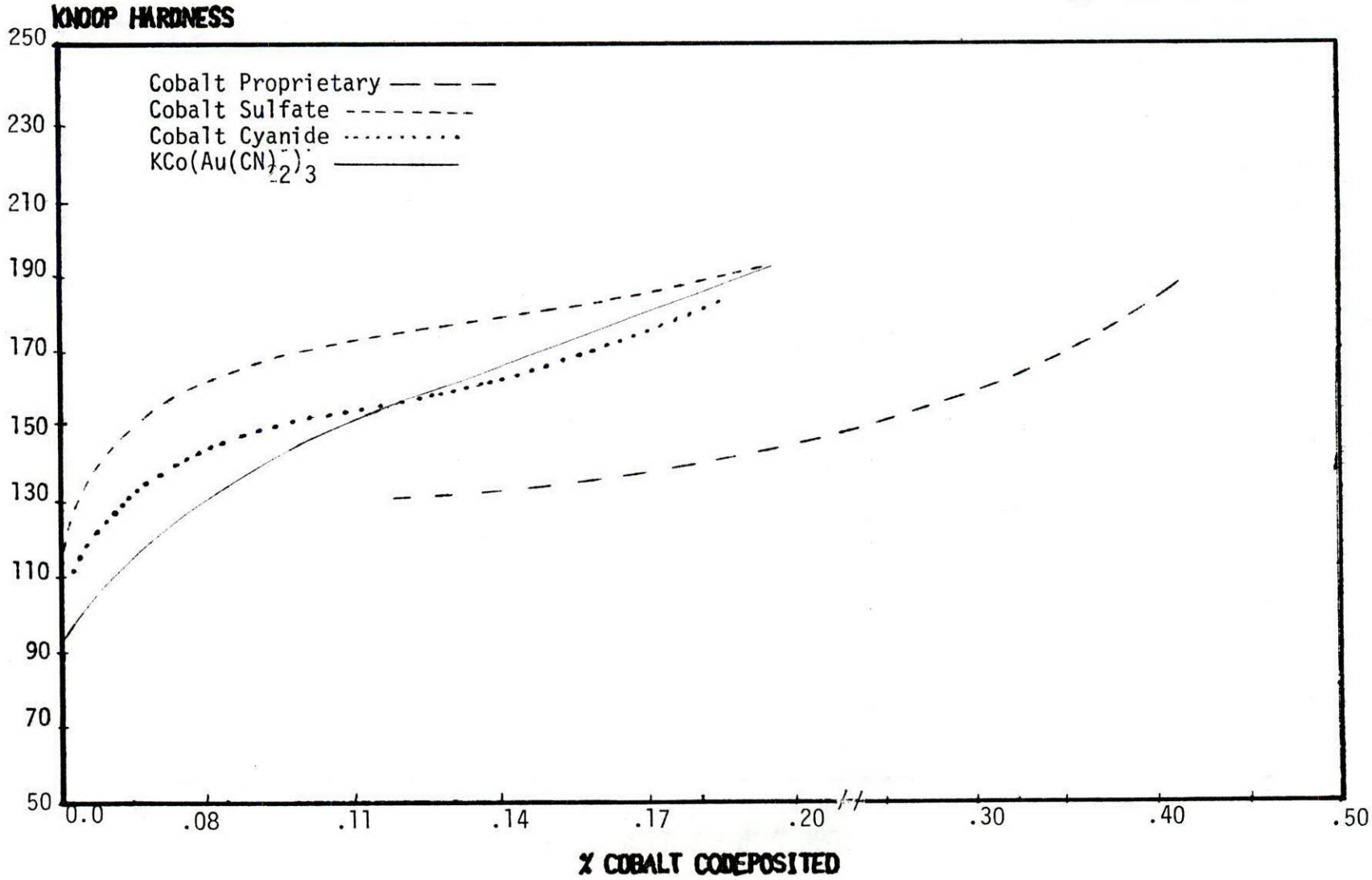
KNOOP HARDNESS VS. % Co IN DEP

Figure 3



CATHODE EFF. VS. Co IN SOL'N

Figure 2

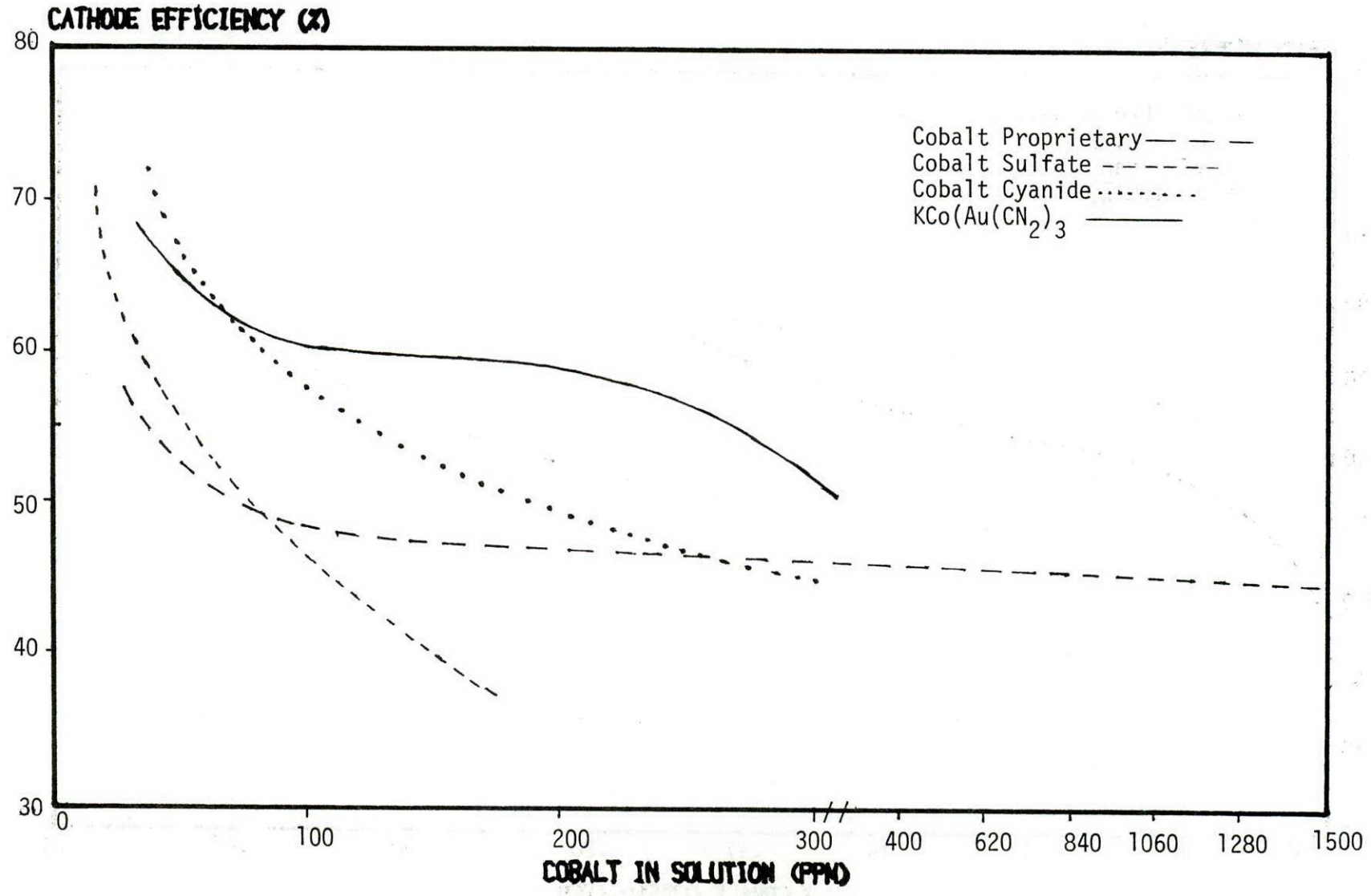


Figure 1

% CO CODEPOSITED VS. Co IN SOL'N

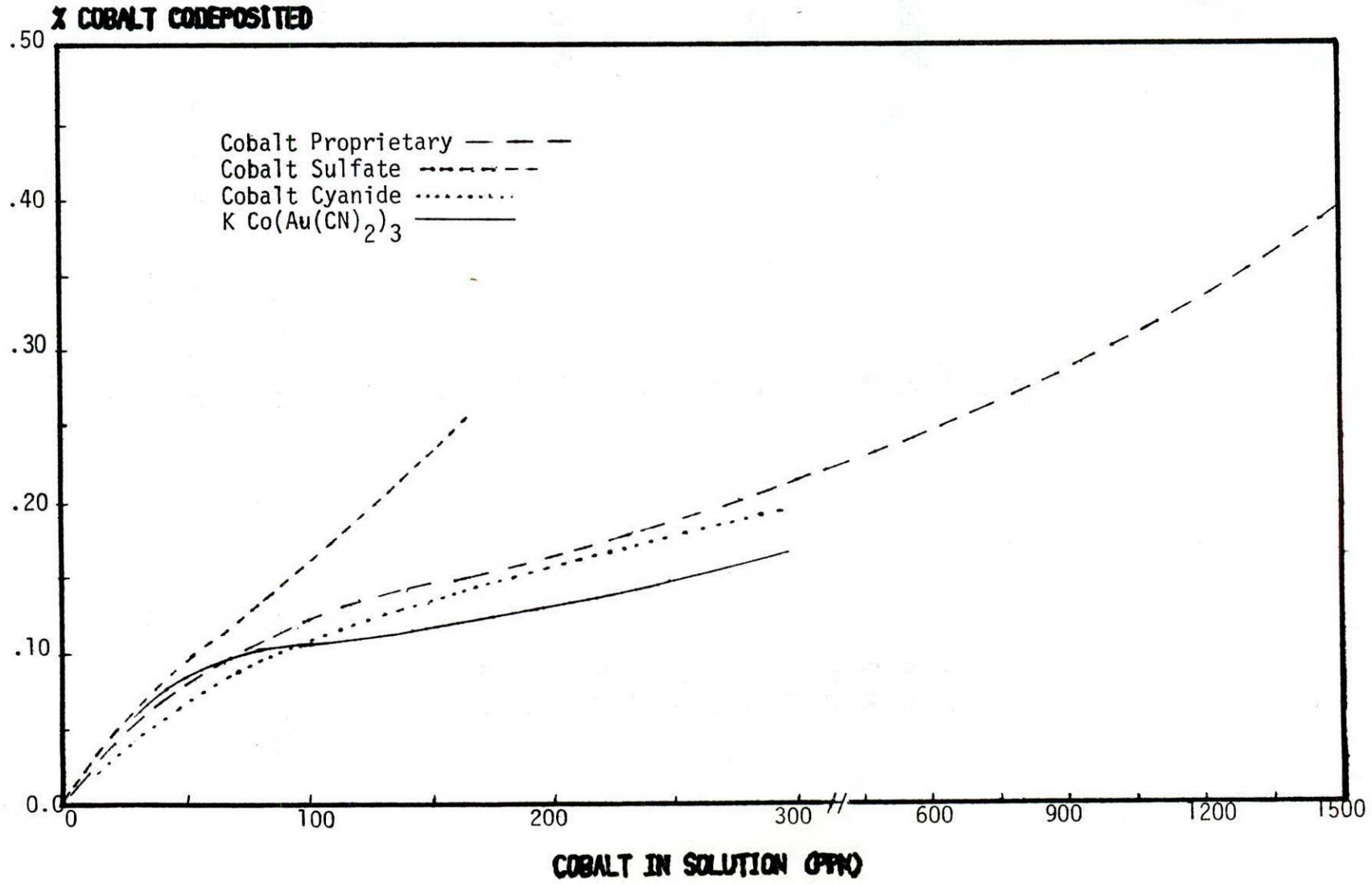


Table 3

Knoop Hardness vs. % Co in Deposit

Cobalt	Knoop Hardness	% Co in Deposit
Proprietary	130	0.12
	135	0.16
	138	0.19
	156	0.31
	160	0.33
	180	0.40
Cobalt Sulfate	141	0.05
	175	0.09
	188	0.13
	187	0.16
	195	0.20
Cobalt Cyanide	143	0.07
	152	0.11
	162	0.14
	181	0.16
$K\ Co(Au(CN)_2)_3$	138	0.09
	156	0.10
	160	0.12
	157	0.14
	168	0.16

Table 2

Cathode Efficiency Vs. Co in Solution

Cobalt	PPM Co	% Efficiency
Proprietary	100	46
	200	50
	400	47
	800	46
	1000	47
	1500	40
Cobalt Sulfate	16	71
	32	60
	64	52
	100	47
	125	43
Cobalt Cyanide	50	67
	100	58
	150	52
	300	46
$K\ Co(Au(CN)_2)_3$	50	63
	100	60
	150	60
	200	61
	300	49

Table 1

% Cobalt Codeposited Vs. Co in Solution

Cobalt	% Codeposit	PPM Co
Proprietary	0.12	100
	0.16	200
	0.19	400
	0.31	800
	0.33	1000
	0.40	1500
Cobalt Sulfate	0.05	16
	0.09	32
	0.13	64
	0.16	100
	0.20	125
Cobalt Cyanide	0.07	50
	0.11	100
	0.14	150
	0.16	300
$K\ Co(Au(CN)_2)_3$	0.09	50
	0.10	100
	0.12	150
	0.14	200
	0.16	300

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Conclusions

1. For weak complexes, cobalt in deposit is much more dependent upon cobalt concentration in solution.

2. As cobalt concentration in solution is increased, cathode efficiency decreases and this trend is more pronounced in electrolytes containing weak complexes of cobalt.

3. Deposit microhardness increases as cobalt concentration in solution (and thus in deposit) increases.

4. All variables appear to be less critical when using stronger cobalt complexes.

It was decided to investigate the influence of cobalt complex and its concentration on cathode efficiency, cobalt in deposit, and deposit microhardness.

The electrolyte used throughout was:

Gold as potassium gold cyanide	8.0 g/l
Potassium citrate	100 g/l
Citric acid	76 g/l
pH	4.2
Temperature	35°C
Current density	10 A/ft^2

Cobalt was introduced as either the sulfate, cyanide ($Co(CN)_2$), cyanoaurate or as a proprietary complex. Deposits containing up to 0.2% by weight cobalt were aimed for and the influence of cobalt concentration in solution is presented in Tables 1, 2, and 3 and on Figures 1, 2, and 3.

It should be noted that complex D, potassium cobaltous trisauricyanide, is only sparingly soluble in water, however, it dissolves slowly in an electrolyte. It must be assumed that a chemical change occurs under these conditions and that cobalt is present as citrate, cyanide, and a low concentration of potassium cyanauroate.

Results

As expected, cobalt concentration in solution influences cobalt in deposit much more when the complex is weak. Stronger complexes can be used over a much larger concentration without significantly changing deposit composition. Conversely, cathode efficiency remains almost unchanged by cobalt concentration in solution for stronger complexes. Naturally, this means that cathode efficiency is generally higher at low concentrations of weak complexes. When cobalt concentration is kept constant, other variables such as current density, solution pH, and temperature all influence codeposition of cobalt and cathode efficiency to a greater degree with a weak cobalt complex.

Deposit microhardness increases as cobalt concentration is increased, in line with higher deposit levels of cobalt. Again, the trend is less marked for stronger cobalt complexes than for weaker ones. Since all the deposits are of a similar nature, it is possible to apply a general comment - as deposit microhardness increases, ductility decreases. It is not safe to assume that wear resistance improves with harder deposits since the type of wear can change (adhesive wear versus abrasive wear). Much work has already been published on testing this property of gold deposits.[11]

Role of Cobalt in Acid Gold Plating Systems

by Alan Blair
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Introduction

The role of cobalt in acid hard gold plating systems has been the object of considerable study since they were first introduced in the late 1950's.[1]

The introduction of these processes marked the most significant change in the technique of electrodepositing gold since Wright and Elkington's work around 1840.[2]

Gold's physical and chemical properties make it an ideal material for certain electronic uses, particularly in its electroplated form. Its electrical and corrosion resistant properties were augmented by wear resistance when transition metals, such as cobalt, were co-deposited at levels of 0.1-0.3% in deposit. This codeposition causes spectacular changes in deposit character and electrolyte performance. Deposits are transformed from dull, equi-axed or columnar structures into bright, laminar ones and cathode efficiency is significantly decreased, becoming much more current density dependent.

Analysis of these deposits soon revealed that other elements, such as carbon, were codeposited with the transition metal, and so-called "polymer" was isolated.[3]

Carbon inclusions were determined to have eminated from the cyanide ligand in potassium gold cyanide and were found to be located near cobalt inclusions within the deposit[4]. Eisenmann[5] suggested the presence of cobalt cyanoaurate in these deposits and other workers,[6,7,8] have studied this possibility more closely. The hypotheses presented appear to explain both the inclusion levels of the various elements involved and the modification of grain growth.

On a more practical plane, studies have been performed to establish the influence of the chemical form in which cobalt is introduced to the electrolyte and the ultimate influence this has on the deposit.[9]

The object of this paper is to extend this last mentioned work and to present a more complete illustration of this chemical influence within a simple citrate system.

Experimental

Previous experiments[9] have indicated that cobalt, when introduced to a citrate-based electrolyte, will produce hard deposits unless the cobalt complex used has a very high stability constant (e.g., $K_3Co(CN)_6$; $K_1 = 10^{-32}$.

D-1

Electronics I
Session D

Role of Cobalt in Acid Gold Plating

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- The copper plated onto the base metal can be classified as non-hazardous for disposal purposes and may be sold or reclaimed.

- Equipment has been developed that offers low maintenance, and low capital and operating costs.

SUMMARY

Conventional methods of removing the copper from metal finishing waste streams prior to discharge, generate large quantities of hazardous sludge with associated disposal problems. Newer technologies recently introduced provide economical recovery of the copper which may be used for other purposes, but not for reuse in the bath. The resulting copper-depleted rinse solutions can then be discharged with other treated metal finishing wastes to POTW or receiving waters as required. Of these newer technologies, selective electrochemical displacement appears to be the best approach in terms of operational efficiency and cost.

DISCUSSION

The main disadvantages of current waste treatment methods for copper removal are the following:

- Calcium or iron displacement produces large amounts of hazardous sludge which should be disposed of in classified landfills. The costs for hazardous landfill are increasing daily, and even though the calcium or iron displacement methods are very effective on treating certain electroless coper waste streams, it can be seen that in the future processes which produce large amounts of sludge will actually become a liability to the companies using them.

- Sodium borohydride and sodium hydrosulfite when used to effect copper removal, both prove to be costly from the chemical and process viewpoint, as well as producing a sludge which has to be disposed of in an environmentally acceptable manner.

- ISX is an effective copper removal method but only becomes cost effective as compared to other known methods for final polish water containing less than 10 mg/l of copper.

- The recycle of the copper complex using ion exchange is presently only applicable to copper Quadrol solutions; it is not effective on dilute streams, and has an extremely high operating cost due to the complexity of the process and the equipment that has been developed.

- Destruction of the complexing agent is not economical for small quantities of rinse, and it is not effective on all copper complexes.

- Removal of the copper by ion exchange is not an effective method on all electroless copper streams and the regenerant still requires further processing to remove the copper.

- Removal of the copper by electrowinning requires equipment that has a high capital cost. Also, the efficiency of the electrowinning process is very low at very low concentrations of copper.

The advantages of copper removal using selective electrochemical displacement are:

- Selective electrochemical displacement is effective on any copper containing stream.

- It is a simple direct copper removal method.

The results were achieved on a solution of electroless copper rinse water* with an initial copper concentration of 58 mg/l at a flow rate of 5 GPM, at a pH of 4, and an ambient temperature. Six pounds of copper was removed in the forty-hour period.

When the copper concentration exiting the lead canister exceeds 4 mg/l; its media is replaced and the flow through the canisters is alternated to make this the second canister in the series.

The copper plated base metal is classified as non-hazardous and the media can be either sold or disposed of as scrap metal.

The effluent from this process still contains complexor and must be segregated from other plant waste streams until they have been treated prior to discharge.

The equipment** for this process is shown in Figure 10. The unit is skid mounted, prepiped and prewired for easy installation. The only hook-ups that have to be made are electroless copper waste waters, city water for intermittent flushing of the canisters and a line to take away the effluent from the equipment; also required is an electrical hook-up to the panel of 440 volt, 3 phase power.

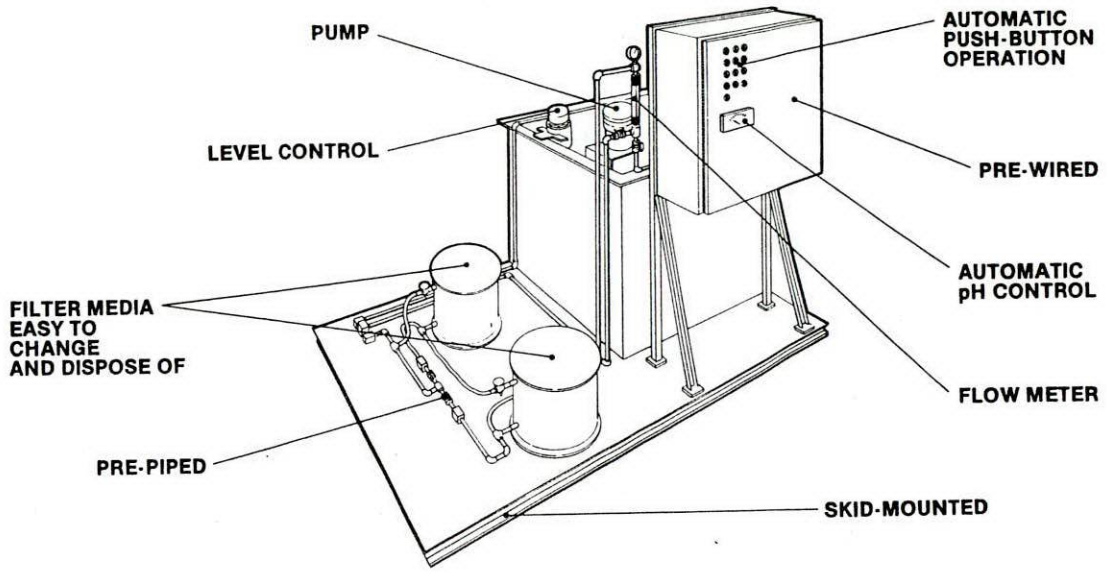

FIGURE 10. Apparatus to Remove Copper from Copper Containing Complexed Solutions[14]

*UDIQUE® 820
**CUPRATROLLER™

The process is shown schematically in Figure 9.

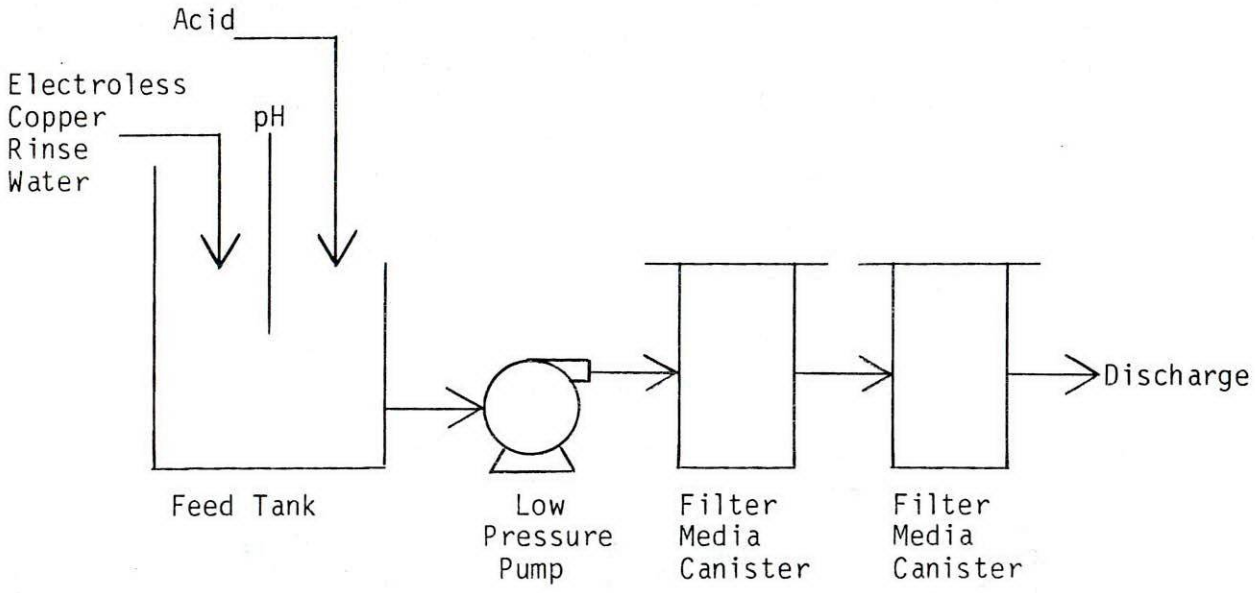

FIGURE 9. Schematic of Copper Removal Process

The electroless copper containing rinse water flows into a feed tank in which the pH is adjusted by the addition of acid to the optimal level for selective electrochemical displacement. The residence time allowed in the feed tank permits adequate blending. The pH adjusted rinse water is then pumped through a pair of filter media containing canisters in which the copper is selectively removed from the solution and replaced by a metal complex. The use of the canisters in series is alternated to optimize the removal media use. The majority of the copper is removed in the first canister and the stream is polished in the second canister. Removal rates of greater than 90% are achieved in each canister.

Field results to date indicate that copper is removed to a level of less than 1 mg/l from an initial level of 100 mg/l from solutions such as, EDTA copper, Quadrol copper, Tartrate copper, pyrophosphate copper, ammonium persulfate etch, and peroxide sulfuric copper etch.

The results are summarized in Table III.

TABLE III. Summary of Field Results.

Time In Service	8 Hours	40 Hours
Canister #1	0.5 mg/l	1.5 mg/l
Canister #2	0.05 mg/l	0.05 mg/l

This result appears to agree with the expectation based on the respective chelating constants[11], shown in Table II.

TABLE II. Relative Strength of Chelating Constants for Copper with Chelating Compounds[11]

CHELATING COMPOUND	CHELATING CONSTANT k
EDTA	$10^{18.8}$
Iminodiaceticacid	$10^{10.55}$
Tartaric Acid	$10^{9.9}$

The efficiency for copper separation from Quadrol is greater in an acidic solution, pH=2.7-7.0, than it is in an alkaline solution. When the resin is exhausted, it is regenerated with dilute sulfuric acid, which redissolves the copper retained on the resin. Thus copper bearing acid solution can then be treated by conventional hydroxide precipitation, or the copper can be plated out and the acid recycled to be used in the next regeneration sequence. As with most ion exchange procedures, copper removal is extremely sensitive to process variables such as pH, flow rate, copper loading and temperature.

An alternative method of removing copper from the copper complex is by plating out the copper. A variety of processes have been developed to plate out the copper either as a copper sheet, Stewart et al[12], or as a non-complexed copper containing solution, DasGupta et al[13]. However, the effluent as a result of these processes normally has a copper concentration of between 10-50 mg/l. We have developed a method by which the copper is selectively removed from a solution containing copper in a complexed form, Arcilesi et al[14]. The mechanism of the removal is shown below.

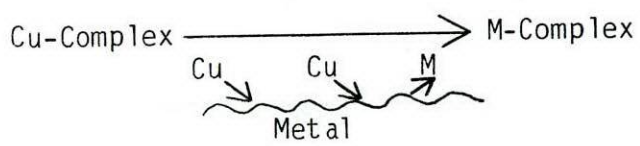

FIGURE 8. Selective Electrochemical Displacement Mechanism

EDTA or Quadrol, prior to copper precipitation using lime, yielded less than 60% removal of the copper from an initial concentration of 50 mg/l copper to 22.4 mg/l for the EDTA and 16.7 mg/l for the Quadrol based solutions, respectively.

The addition of UV activation to the ozone oxidation process has been investigated by Prengle and Mauk[8], who found that promising oxidation of the organics occurred. Macur et al[9], further discussed the ozone/UV destruction of EDTA. This method is currently in commercial use. However, it is important, during the ozone/UV process, to remove the copper as it is released from the complex. If this is not done, the released copper will selectively initiate the ozone degradation and thus no oxidation of the EDTA will occur. In general, oxidation of the organic complex is not a practical method of treating an electroless copper waste stream.

PROPRIETARY COPPER RECYCLE AND REMOVAL TECHNIQUES

Ion exchange can be used as a method to remove copper from a complexed solution, thus rendering the solution depleted in copper and able to be discharged directly. Development of suitable ion exchange techniques has been delayed because the specialty resins required to remove the copper have only recently been available for industrial use.

The resin used to remove the copper has to be a powerful chelator which will selectively remove copper from the copper-chelate complex in the electroless copper effluent. A process has been recently developed by Courduvelis et al[10], and Whalen[11], using a resin with an iminodiacetic acid functional group.

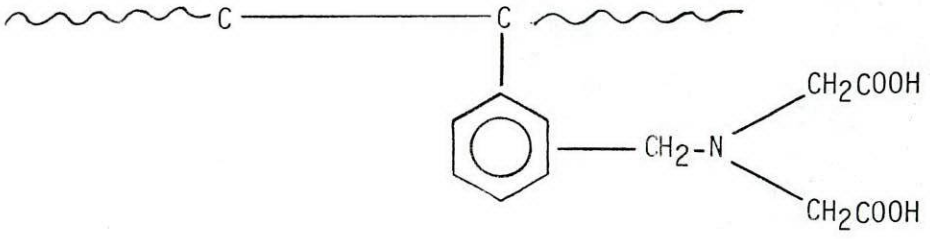

FIGURE 7. Polystyrene Bearing Iminodiacetic Acid Functional Groups[11]

This resin has been found to remove copper from a variety of chelators such as carboxylic acid and alkanolamine type chelators.

However, no separation of copper takes place in the presence of ethylenediaminetetracetic acid (EDTA), and other amino acid type chelators.

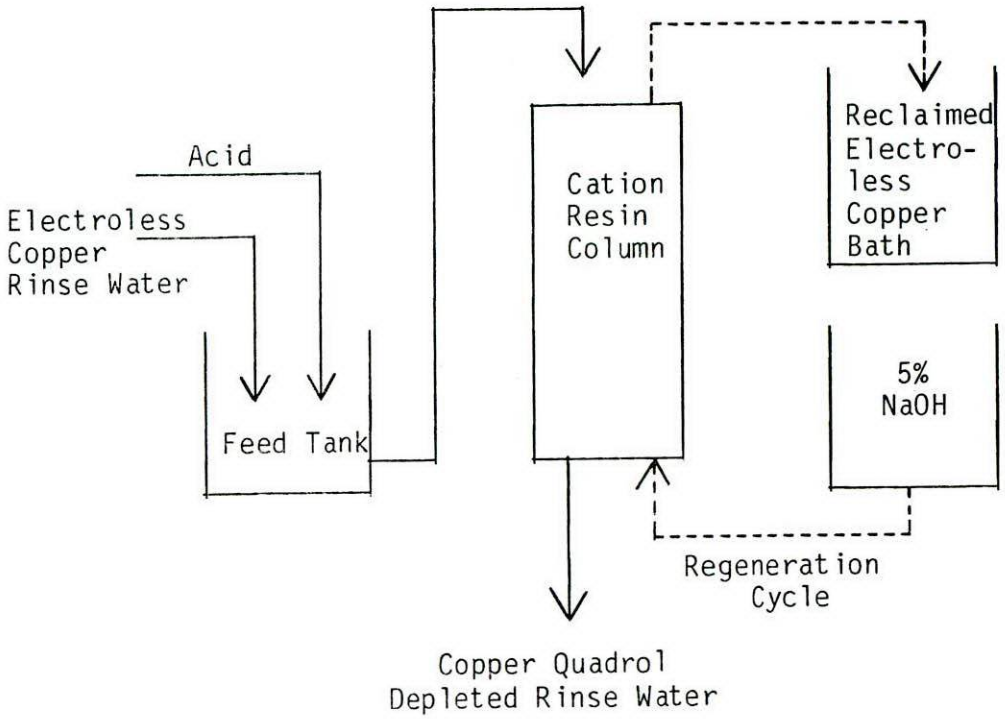

FIGURE 6. Schematic for Copper-Quadrol Recovery[6]

An alternative method of regenerating the Cu-Quadrol complex is to pass sulfuric acid over the loaded resin, and then wash the copper complex from the resin, using water. The process is used mainly to reclaim Cu-Quadrol from concentrated solutions and not from rinse water. The Cu-EDTA-type complex does not protonate on pH change; thus, this process is not applicable. If the pH of an EDTA-Cu bath is lowered to a pH of 2.5, the EDTA-Cu complex dissociates and the EDTA separates to form a lower layer. The EDTA can be thus recovered and reused to replenish the bath EDTA concentration. The resulting supernate is an acidic solution containing large amounts of copper and small amounts of EDTA. Depending upon the degree of copper removal required, the solution should be segregated from other plant effluents so that it can be treated, using techniques discussed previously.

TECHNIQUES INVOLVING DESTRUCTION OF THE COMPLEXING AGENT

If the organic complex is destroyed by oxidation techniques, the copper-containing stream may then be mixed with other plant effluent streams for conventional treatment. Cullivan[7] has investigated the economics of using either chlorine or ozone to oxidize large quantities of organic containing effluents. However, this survey was for large quantities of organic containing wastes. For electroless copper containing wastes it would prove uneconomic. Work carried out in our laboratory, using sodium hypochlorite to oxidize the

RECYCLING TECHNIQUES

Conventional recycling techniques such as evaporation, reverse osmosis or electrodialysis, cannot be used to concentrate the dilute electroless copper effluent stream to give a concentrate which can be returned to the electroless copper bath. This is because changes in bath chemistry can be anticipated on reconcentration, which could initiate copper deposition, thus rendering the recovery equipment inoperative. Also, the electroless copper bath is extremely sensitive to contaminant build-up. The return of recovered concentrate back into the bath will be accompanied by the return of recovered contaminants, and operation of the bath will become increasingly difficult.

Currently, only one technology exists which can successfully recycle the copper-complex to the bath. This process is detailed by Zeblisky[6] and is only applicable for alkanolamine and copper-alkanolamine type complexes such as (ethylenedinitrilo)-tetra-2-propanol, triethanolamine, ethylenedinitrilotetraethanol, nitrilotri-2-propanol, etc. which can protonate and therefore have a net positive charge. At high pH values, these complexes will deprotonate and become species with no electrical charge, as shown in Figure 5.

$$\underset{\text{pH}<7.3}{\text{Cu-Complex}^{+2}} \rightarrow \underset{\text{pH 7.7-10}}{\text{Cu (Complex-H}^{+})^{+1}} \rightarrow \underset{\text{pH}>10}{\text{Cu (Complex-2H}^{+})^{0}}$$

FIGURE 5. Effect of pH on Copper Complex Charge

The free ligand also reacts in a similar way. Therefore, the complexed copper and ligand in an alkanolamine type electroless copper bath such as (ethylenedinitro)-tetra-2-propanol can be removed and recovered from waste electroless copper solutions using a cationic exchange system. The pH of the waste electroless copper bath is lowered to form the cationic copper-complexor species. The copper-complexor is retained on a cationic exchange resin and then reclaimed from the resin, either by using standard resin regenerating techniques or by raising the pH of the resin bed with hydroxide. Raising the pH of the resin bed reclaims the copper complex by converting the complex to a zero charged species and releasing it from the ion exchange resin in a form suitable for additions to an electroless copper bath. This process is shown schematically in FIGURE 6.

The high pH, calcium substitution treatment procedure and the iron substitution procedure reduce the copper concentration to an acceptable level for discharge. However, large amounts of sludge which require disposal are generated.

The copper has also been removed from the complex by using strong reducing agents such as sodium hydrosulfite, Kamperman[2], or sodium borohydride, Jula[3]. Sulfide precipitation of the copper is also discussed by Scott[4] and Anderson and Weiss[5]. Starch-based products, such as Insoluble Starch Xanthate, have been developed by Wing[1] and are presently commercially available. All these processes, however, generate a sludge that has to be disposed of in an environmentally acceptable manner.

Tests carried out in our facility (shown in Table I) indicate that these methods produced only partially acceptable results for copper removal from solutions containing initially 50 mg/l of copper.

TABLE I. Copper Removal from EDTA or Quadrol Complex Using Sodium Hydrosulfite, Sodium Borohydride and Insoluble Starch Xanthate

TECHNOLOGY	EDTA* mg/l	QUADROL* mg/l
SODIUM HYDROSULFITE	7.2	0.46
SODIUM BOROHYDRIDE	14.0	2.4
INSOLUBLE STARCH XANTHATE	.7	.31

*Initial copper concentration 50 mg/l.

TREATMENT USING ADVANCED TECHNOLOGY

As a result of more stringent government regulations regarding disposal of hazardous materials, and the increased emphasis on zero discharge, several new approaches to the treatment of electroless copper-containing rinse waters have evolved. It is convenient to classify these approaches as follows to facilitate discussion of the technology issues involved:

1. Recycling of the copper-complex back to the bath.
2. Destruction of the complexor so that the copper can be removed by conventional techniques.
3. Removal of the copper by proprietary techniques.

TREATMENT USING CONVENTIONAL TECHNOLOGY

Electroless copper treatment methods, used traditionally in industry to remove the copper, generate voluminous amounts of sludge, require costly capital expenditure and are labor-intensive. The treatment of electroless copper-containing rinse wastes of either EDTA or Quadrol have been thoroughly discussed by Wing[1]. Wing and his co-workers found that these complexes can be treated with calcium hydroxide, calcium oxide, calcium chloride or calcium sulfate at a pH of 11.6 to 12.5. In work done at our facility, we found that to effectively reduce copper to a concentration of less than 1 mg/l from an original concentration of 50 mg/l, a large excess of calcium is required (up to 15X stoichiometric excess). This is because the equilibrium constant, k, for the equation:

$$Ca^{2+} + Cu\ EDTA \overset{k}{\rightleftharpoons} Ca\ EDTA + Cu^{2+}$$

$$\xrightarrow{\text{Excess Ca}}$$

FIGURE 3. Equilibrium Equation for EDTA-Cu-Ca

was found to lie between 5.6 and 14.0 (with a mean of 10), thus providing a rough measure of the amount of calcium required for adequate copper displacement.

This calcium treatment is not effective for Quadrol-copper complexes. The copper displaced from the complex precipitates from the solution as copper hydroxide.

Another effective method of displacing the copper from the EDTA or Quadrol complex is to lower the pH to between 2.7 and 5.0 and add ferrous sulfate or ferric chloride. The reduction in pH weakens the copper complex bond and facilitates the substitution of the copper for iron. Approximately one gram of ferrous sulfate or ferric chloride was added per 50 mg. of copper present, indicating a 7X stoichiometric excess of iron is necessary to displace the copper. The pH was then raised to 9.0, using lime or caustic, and the precipitated copper hydroxide filtered from the solution.

$$Fe^{2+} + Cu\text{-}Complex \rightleftharpoons Fe\text{-}Complex + Cu^{2+}$$

$$\xrightarrow{\text{Excess Fe}}$$

$$\downarrow OH^-$$

$$Cu(OH)_2\downarrow$$

FIGURE 4. Equilibrium Equation for Copper Removal Using Iron

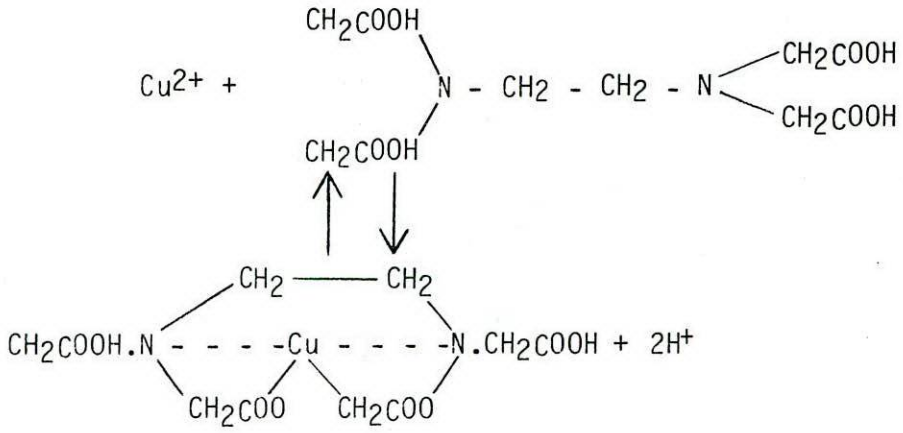

FIGURE 1. EDTA-CU Chelated Complex Mechanism

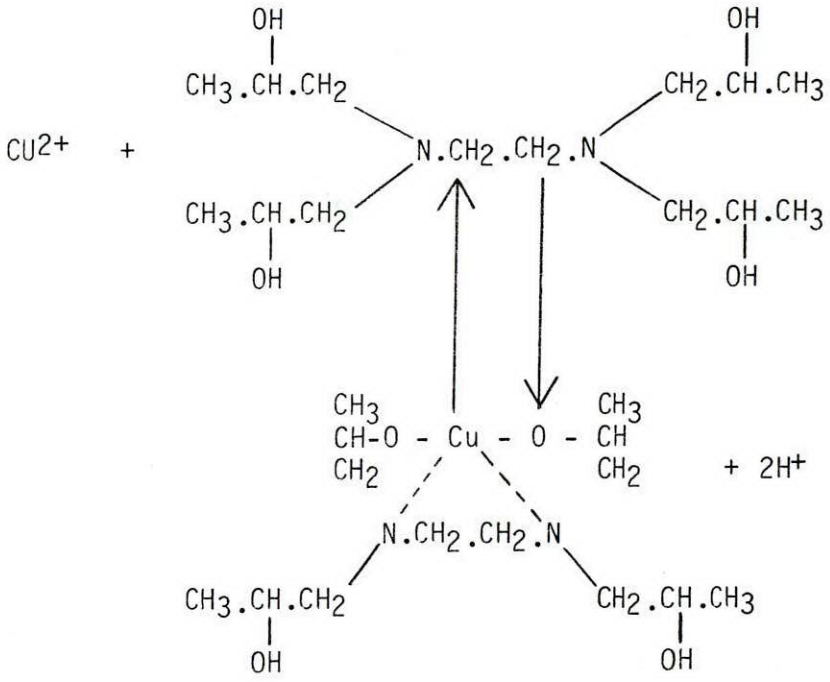

FIGURE 2. Quadrol-Cu Chelated Complex Mechanism

The complexing agent, because of its nature, will complex with cations in other effluent streams. Thus it is obligatory that the electroless copper effluent stream be segregated from other plant wastes and treated separately to remove the copper. The concentration of the copper in the stream is usually too high to be suitable for direct discharge. Restrictions usually do not apply regarding the discharge of organic chelators, since these organic compounds are biodegradable in the presence of light.

BACKGROUND

The advantages of using electroplated plastics over their metal counterparts include more freedom in part design, reduced weight, lower raw material costs and the elimination of costly surface preparation operations such as polishing and buffing.

Although many plastics can be plated, adhesion varies widely. Only those which provide the best adhesion are used for electroplating applications. The basic electroplating cycle for plastics is divided into two stages. The first stage is called the preplate cycle. The purpose of this cycle is to provide an adherent, conductive metallic film on the surface of the plastic part so that the second stage, electroplating the decorative or functional finish, can be added by conventional electroplating technology.

The last step of the preplate cycle is to cover the surface with a thin layer of nickel or copper. This layer is deposited autocatalytically from an electroless solution, which contains the nickel or copper salt, a reducing agent, a complexing agent, a stabilizer and a pH buffering system. The chemistry of this electroless solution is such that the copper or nickel is reduced spontaneously as the catalyzed plastic surface contacts the solution, and a very thin uniform metallic coating is then formed. In many applications, a copper deposit is preferred to a nickel deposit due to its superior adhesion, ductility, corrosion performance under both wet and dry conditions, and its electrical properties.

The nature of the electroless copper plating solution is such that the copper ion is held in solution by the complexing agent until a catalyst initiates the action of the reducing agent. Hence, any solution going to waste treatment that is pulled out of the bath through surface tension, or lost due to spills or bath dumps, will contain the metal ion tightly held in solution by the complexing agent. The complexing agent is used in molar excess to ensure that the metal ion is not reduced, and thus precipitate out of solution under normal operating parameters.

The two principal complexing agents predominantly used in electroless copper solutions are EDTA (ethylenediaminetetraacetic acid) or Quadrol (N,N,N',N'-tetrakis (2-hydroxypropyl)-ethylenediamine) as shown in FIGURES 1 and 2.

COPPER REMOVAL FROM METAL FINISHING WASTE SOLUTIONS

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The presence of complexing agents in waste solutions increases the difficulty of removing heavy metals, such as copper. This fact is of vital importance to the metal finishing industry because of the growth in the use of printed circuit boards for consumer products and telecommunications equipment, and to the growing utilization of plated plastics for shielding electronic enclosures such as office equipment and personal computers. These growth markets require electroless copper which means that the waste solutions will contain significant levels of an organic chelator such as EDTA or Quadrol. One consequence of these developments is that it is becoming increasingly difficult for many manufacturers to meet existing and proposed requirements for the amount of copper discharged to publicly owned treatment works (POTW) or to receiving surface waters.

The EPA regulations for the Metal Finishing Industry which were proposed August 31, 1982, set the copper pretreatment standards for new and existing metal finishing sources at a maximum for any one day of less than 3.72 milligrams per liter (mg/l) copper and an average of daily values for 30 days, which shall not exceed 1.09 mg/l copper.

For existing job shop electroplaters and printed circuit job shops, the pretreatment standard is 4.5 mg/l maximum for any one day and 2.7 mg/l for the average of 4 consecutive monitoring days. However, many POTW's and receiving streams have required limits for copper much more stringent than EPA Guidelines, and values of <0.1 mg/l copper occasionally must be met.

Treatment methods for electroless copper rinse waters depend greatly on the particular chelate/copper complex used in the electroless copper process. Treatment methods to be discussed include (a) recovery of the chelate/copper complex and recycle to the plating bath, (b) destruction of the chelator and removal of copper by conventional techniques, and (c) removal of copper by proprietary techniques.

C-6

Environmental I
Session C

Copper Removal from Metal Finishing Waste Solutions

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(8) Federal Register, 46, No. 241, p.61283 (December 16, 1981).

Table 2

OPERATING COST

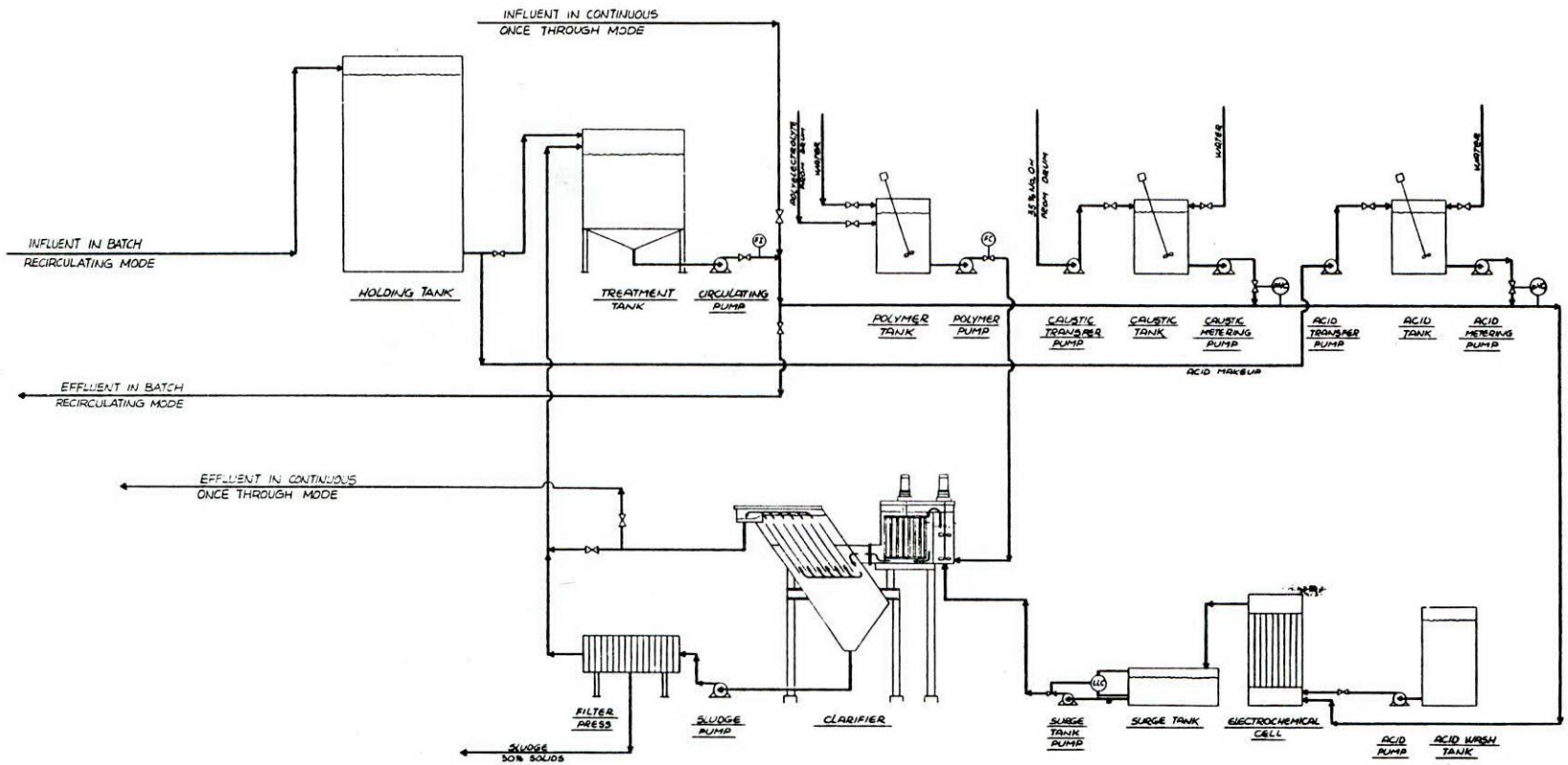
Basis: Multiple heavy metal removal with average electrode consumption of 3 lbs/lb heavy metal.

	Quantity/lb Heavy Metal	Cost/Unit	Cost/lb Heavy Metal
Electrodes	3 lbs.	$0.30/lb	$0.90
Power	5 kwh	$0.04/kwh	$0.20
			$1.10

Table 1

TYPICAL PLANT DATA

Plant	Influent/Effluent, mg/l				
	Hex Chrome	Zinc	Copper	Nickel	Lead
A	9/0.04	2.3/0.1	--	--	--
B	--	--	11/0.7	--	--
C	178/0.01	--	--	189/0.8	--
D	6.7/0.05	10.4/0.23	0.2/0.05	9.4/0.4	1.51/0.01



PROCESS FLOW DIAGRAM
ELECTROCHEMICAL HEAVY METAL REMOVAL PROCESS
FIGURE 2

or continuous mixing tanks and dry, curbed areas for raw chemical storage for sodium metabisulfite, lime, sulfur dioxide, etc. makes floor space with chemical precipitation much greater.

3. In the chemical precipitation process, raw chemical unloading, storage, make-up, and testing for proper dosage are labor intensive. Unplugging chemical lines, cleaning valves, pumps, and mixer blades involves man-hours above and beyond what most plants are willing, or even prepared, to accept. Maintenance costs of plants handling dry chemicals with mechanical devices are invariably high. Suitable ventilation must be provided for chemical storage and make-up areas, particularly with powder-type chemicals. Operation and maintenance costs for the electrochemical process are about one-half that for chemical precipitation.

4. At chemical precipitation plants, laboratory equipment is necessary to monitor raw chemical dosages. Where constant monitoring is not performed, there is a tendency to overdose to assure completion of the chemical reaction. This results in higher costs of raw chemicals and additional sludge generation. Surges from the plating plant will occur and chemical dosages must vary to reflect these changes, buffered somewhat by holding tanks.

5. The overall annualized cost of the electrochemical process is approximately half of the chemical precipitation cost.

Summary

Field operating experience over many years with a large number of electrochemical heavy metal removal units has proven the cost-effectiveness of the technology. In addition, the sludge resulting from the process has been found to be non-toxic and non-hazardous by Environmental Protection Agency criteria. Treated water using this process can be recycled back to the electroplating plant for water conservation.

Toxicity Test for leachability. The sludge sample is acidified to a pH of 5 with acetic acid and allowed to stir for 24 hours, and then the resulting liquid is analyzed for heavy metal content. In the case of chrome, the test permits 5.0 mg/l in the leachate and the electrochemical process regularly shows a chrome content in the order of 0.02 to 0.05 mg/l, which means it is safe by a factor of 100. Other heavy metals produce similar results.

If a sludge meets the Extraction Procedure Toxicity Test, an application is made to the Environmental Protection Agency for delisting of the sludge from the hazardous to the non-hazardous status. Sludge from the electrochemical process easily meets the Extraction Procedure Toxicity Test and has been formally delisted in the Federal Register (8) so that the sludge is considered non-toxic and non-hazardous by the EPA. This facilitates easy and economical disposal of the sludge even though chrome as chromic hydroxide is present. Any non-hazardous landfill can be used as far as the Federal EPA is concerned, but some localities may impose additional testing requirements prior to granting a disposal permit.

Operating Costs

Table 2 shows the operating cost for the electrochemical process. This is based on a plant removing several heavy metals simultaneously with an average electrode consumption of three pounds per pound of heavy metal as the elements, i.e. Cu, Ni, Cr, Zn, Pb, etc., not as the hydroxides. The cost will increase or decrease slightly as the chrome concentration varies since chrome is the only metal undergoing chemical reduction and this element consumes iron electrodes as shown in equation (1).

Capital Cost

The capital cost of an electrochemical heavy metal removal plant is completely dependent on the quantity of wastewater to be treated and the concentration of heavy metals present. An analysis of capital cost of electrochemical versus traditional chemical precipitation plants designed with equivalent equipment standards and similar degrees of automation indicate the following:

1. Basic equipment cost of the electrochemical process is competitive with, or slightly higher than, chemical precipitation.

2. Since the electrochemical process is a compact "packaged" plant, the building space requirements are significantly less than chemical precipitation. Batch

solids which were formed in the reaction.

These suspended solids must be removed in a clarifier. Prior to entering the clarifier, about one mg/l of anionic polyelectrolyte is added as a flocculant which aids in the separation of solids in the clarifier. Lamella-type clarifiers are frequently used since they require less floor space than the traditional circular clarifiers. The effluent from the clarifier will have less than 20 mg/l suspended solids, and of course, the effluent water will meet EPA discharge requirements.

Underflow from the clarifier will be about one percent solids and will contain the heavy metals as metal hydroxides. Most plants run the clarifier underflow through a sludge pump into a filter press where it is dewatered to about thirty percent solids. The filtrate is recycled back to the clarifier and the filter cake is dumped, usually once per shift.

2. Batch Recirculation Mode

When platers have heavy metal concentrations above 50 mg/l, it is frequently more cost-effective to operate the electrochemical process on a batch recirculation basis. Wastewater is collected in a holding tank or sump, and at convenient intervals a predetermined quantity is transferred to a treatment tank. As usual, the water to be treated is brought up to a pH of 6 to 9 to satisfy EPA discharge requirements and is pumped through the electrochemical cell and clarifier. Since all of the heavy metals will not have been removed in one pass due to the high initial concentration, the water from the clarifier is recycled back to the treatment tank for additional recirculation through the system. The recirculation continues until the material in the treatment tank meets specifications for discharge or recycling back to the plating line.

It was mentioned earlier that the electrochemical process generates excess hydroxyl ions thereby increasing the pH slightly as the water passes through the cell. When operating in the recirculation mode, some acid must be added through a pH controller to keep the pH in the optimum 6 to 9 range. This acid can be raw, untreated wastewater from the holding tank, assuming it is low pH.

Non-Hazardous Sludge

The Environmental Protection Agency has established criteria whereby sludges are determined to be toxic or non-toxic (7). A sample of the sludge is tested using the Extraction Procedure

watts are required per pound of heavy metal removed. The amperage can be calculated from Faraday's Law and a typical cell would operate at about 25 amps DC. The voltage on the cell is a function of the electrical conductivity of the wastewater and can vary from 50 to 400 volts DC. The plants are supplied with 220 or 440 volt AC power and rectification equipment within the unit makes available the necessary direct current.

The amperage required is a function of the flow of wastewater and the heavy metal concentration. As the flows or concentrations change, the amperage is modified so that the effluent heavy metal concentration is within specification.

Normal operation on a once-through basis requires that the wastewater be delivered to the cells at about 25 psig, and after setting the proper amperage on the cells, no further attention is needed by the operator. In order to keep the electrodes clean and operating at proper efficiency, the flow to a given cell is turned off once a day for a period of about twenty minutes so that the cell can go through an acid wash procedure. Wastewater is drained from the cell and then a dilute sulfuric acid or hydrochloric acid solution is recycled from the acid tank through the cell and back into the acid tank for about five minutes. This cleans any residual material off of the electrodes. The acid solution is then drained into the acid tank and the cell is put back on the line. About once a month, the dilute acid solution is changed.

Chelating agents represent a serious problem for traditional chemical precipitation methods of heavy metal removal since the metals are kept in solution by the chelating compound. It is well-known that iron breaks chelates, and in the electrochemical process this takes place in the cell, making removal of chelated metals quite simple.

Methods of Operation

The Electrochemical Heavy Metal Removal Process can be operated in two distinct modes, depending upon the wastewater treatment requirements. Figure 2 illustrates the process flow diagram.

1. Continuous Once-Through Mode

Many electroplaters have rinsewater streams containing a fairly constant heavy metal concentration in the range of about 10 to 50 mg/l. Under these conditions the wastewater in a pH range of 6 to 9 is pumped through the electrochemical cell with the proper amps being applied. Residence time in the cell is only about 10 seconds. Treated water leaving the cell contains the metal hydroxides as suspended

$$Na_2Cr_2O_7 + 6Fe(OH)_2 + 7H_2O \longrightarrow$$

$$2Cr(OH)_3 + 6Fe(OH)_3 + 2NaOH \qquad (1)$$

While this reaction indicates the chemical reduction taking place if hexavalent chrome is present, it is not at all necessary that chrome be present for the removal of all other heavy metals. It will be noted that no sulfates are formed as in chemical precipitation thereby making the treated water suitable for recycling to the plating operation.

Other heavy metals such as copper, nickel, zinc, lead, tin, vanadium, etc. are coprecipitated with the ferric hydroxide, resulting in a mixture of insoluble metal hydroxides. The reaction proceeds quite favorably in the pH range of 6 to 9, which is the pH level prescribed by the EPA for wastewater discharge. Since some excess hydroxyl ion is present, the pH will increase 0.5 to 1.0 units in passing through the cell. No other chemicals are added. Table 1 shows typical plant operating data.

Figure 1 illustrates the configuration of an electrochemical cell. A bipolar arrangement is used wherein one side of each electrode is the anode and the other side is the cathode. The ferrous ion produced at the anode and the hydroxide ion produced at the cathode diffuse into solution and react forming ferrous hydroxide. A small amount of hydrogen gas formed is vented from the cell. In the process of the reaction, the carbon steel electrodes are consumed and theoretically 3.22 pounds of iron would be required to react one pound of hexavalent chrome to the trivalent state. Actual sludge analysis shows about 3.5 pounds of iron per pound of chrome, and generally, the electrodes are changed after about 75 percent of the metal has been consumed, which is around once a month. To assure even wearing on the plates, the polarity is reversed once a day, converting the anode to the cathode, and visa versa. Since metals other than chrome do not require reduction and are simply coprecipitated with the iron, lesser amounts of electrode are needed, usually in the order of 1 to 2 pounds of iron per pound of heavy metal.

Sludge generated by the electrochemical process is slightly greater, on a stoichiometric or theoretical basis, than the chemical process. However, in actual operation, the chemical precipitation method uses substantially greater than theoretical chemicals, whereas the electrochemical process is very nearly theoretical in electrode usage. Therefore, the electrochemical process generally produces less sludge than the chemical method.

Only a small amount of electric current is needed, as very high Faraday efficiencies are achieved. Only about five kilo-

ELECTROCHEMICAL REMOVAL OF HEAVY METALS FROM WASTEWATER

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Environmental regulations are quite specific in limiting the amount of dissolved heavy metals in electroplating and printed circuit board wastewater discharged to municipal sewers or streams. Generally, two or more heavy metals are present, and since each metal hydroxide has its own pH point for minimum solubility, it is quite difficult to meet the EPA regulations consistently with traditional chemical precipitation methods. Chelating agents further complicate the problem.

About ten years ago, the electrochemical process for removing heavy metals was developed and today nearly 100 plants are in operation with flow rates from 5 to 1400 gallons per minute. This technology overcomes the basic theoretical problems of multiple metal chemical precipitation and results in a more cost-effective wastewater treatment system.

A number of articles on the process have been presented (1,2,3,4,5) and three U.S. patents (6) describe the technology.

Electrochemical Heavy Metal Removal Process

The process may be thought of as being the reverse of electroplating. In the case of electroplating, a plate is lowered into a tank and attracts the chrome solution, thus attaching or coating the plate and simultaneously weakening the remaining tank solution.

In wastewater treatment, the tank solution is the waste chrome, and the iron plate is once again lowered into the solution. However, this time the iron migrates from the plate to the solution, and after the attachment takes place, the properties of the chrome change, making it denser, and subsequently settles to the bottom of the tank and simultaneously weakens or uses up the plate.

In the electrochemical process, a direct current is conducted through a cell containing carbon steel electrodes. This generates the ferrous ion, which in the case of hexavalent chrome, reduces it to trivalent chrome. The overall reaction is as follows:

C-5

Environmental I
Session C

Electrochemical Removal of Heavy Metals from Wastewater

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The optimum approach for the recovery and treatment of electroless processing wastes is when the first rinse following the electroless processing step is considered as a dragout solution which is allowed to increase in metal content and made up with fresh water each time the electroless solution is dumped. In this manner of processing, the metal would be recovered electrolytically by adding the dragout rinse to the dumped process solution and electrolyzing the whole, somewhat diluted solution mix. The advantage is a more complete metal recovery with very minimal additional equipment or operating cost and at the same time a significantly reduced volume of filter sludge generation.

The deposit obtained on the cathode was bright and metallic, with good adhesion. The aluminum content of the solution after 7 hours of electrolysis was 1,800 ppm, during which time 2.9 g/l of copper were removed.

As can be seen from the extremely high current efficiencies in these two examples, the aluminum cathode was protected from excess dissolution, while the bulk of the metal deposition was due to the electrolytic and autocatalytic processes. The result is a practical electrolytic recovery technique for metal values contained in spent electrolysis processing solution.

Since the quantity of electroless processing solutions being used is relatively small, the metal value recovered from these spent baths in itself cannot easily amortize the cost of the equipment at a fast rate. It must be remembered that if we do not make a good-quality metal deposit from the spent electroless processing solution, that metal content must be turned into sludge. There is, of course, disposal cost associated with the generation of this sludge. This cost must also be considered in our evaluation of the economics of the electrolytic recovery equipment.

The second stage of this new system approach deals with the treatment of the rinsewaters following the electroless process solutions. The technique used combines the advantages of sulfide precipitation with adsorption and filtration. The rinsewaters are diverted to a reaction tank in which sodium sulfide is added. The additions of sodium sulfide are closely controlled and monitored by a newly developed sulfide control instrument. From here the rinsewaters are passed through a specially designed filter onto which an adsorbing media has been coated. As the solution passes through the media, metal sulfides are filtered out and any residual soluble metals are adsorbed. The spent batch dumps following electrolytic recovery are also diverted through this system where residual metals, including any dissolved aluminum, are removed. Approximately 4 lbs. of media is used for each pound of metal removed. The effluent discharge from this system is able to meet total metal and free sulfide concentrations of less than 1 ppm. The following table shows the approximate capital and operating costs for this recover/treatment system. The complete package occupies a total floor space of approximately 50 sq. ft.

Table III

Typical Operating Costs

	EL/EMR/Sorption Filter system	Sorption Filter Unit Only	No Treatment
Equipment Costs	$ 65,600	$ 61,200	--
Operating Costs (media usage, energy, chemicals, labor)	7,000/yr.	16,400/yr.	--
Hauling Costs	38/yr.	150/yr.	37,500/yr.
Total	$ 72,638	$ 77,750	$ 37,500

Example 1

A spent electroless nickel plating solution was placed in a laboratory plating cell consisting of an aluminum cathode centered between two mild steel anodes. The solution pH was adjusted to 8.0-8.5. This pH was maintained by periodic additions of sodium hydroxide during the electrolysis. The solution volume electrolyzed was 2.5 liters, and the temperature maintained at 140° F. The cathode current density used was 4 Amperes/sq. ft. The results of this test are contained in Table I below.

Table I

Time hour	Soluble Ni (g/l)	Cathode Efficiency	Cumulative Cathode Efficiency
0	5.23	--	--
1	4.11	1534%	1534%
2	2.85	1726%	1630%
3	2.25	812%	1358%
4	1.29	1324%	1349%
6	0.70	399%	1033%
7	0.40	416%	944%
8	0.35	73%	836%
9	0.29		

After nine hours of electrolysis, the cathode deposit was inspected and found to be adherent, bright, and metallic. Analysis of the resulting solution showed 27.4 ppm aluminum and 14.0 ppm iron.

Example II

In a second example, a 500 ml sample of spent electroless copper plating solution was treated. During electrolysis, the pH is maintained at 11.0-11.5. The plating cell was the same as that used in the previous example with a current density of .2 to .4 Amps/sq. ft. on the cathode being maintained. The results of this test are contained in Table II below.

Table II

Time hour	Soluble Ni (g/l)	Cathode Efficiency	Cumulative Cathode Efficiency
0	2.99		
1	1.63	819%	819%
2	1.21	252%	536%
5	0.175	208%	339%
6	0.064	67%	294%
7	0.0059	35%	256%

Another Way

A more practical solution to the problem would seem to be the development of a system which minimizes sludge generation by producing directly a usable metallic deposit with minimal operator attention. In order to accomplish this, it would seem reasonable to divide the problem into two areas. First is the concentrated batch dumps of electroless processing solutions which contain relatively high concentrations of metal. The approach here would be to remove the metal electrolytically. The relatively high metal concentration lends itself well to this technique without resorting to high-surface-area-type equipment from which the deposited metal cannot be directly removed. Since the majority of metal waste is produced by these batch dumps, the direct recovery of these metal values seems most reasonable as well as most efficient. The second area involves the treatment of dilute rinsewaters. While electrolytic techniques have been developed for this purpose, the problems encountered that were mentioned earlier often make this approach questionable.

A system has recently been developed which incorporates electrolytic recovery with state-of-the art waste treatment technology for chelated metals. The electrolytic recovery step is performed only on the concentrated batch dumps. Conventional electroplating approaches strip out the metal content of an electroless solution, yielding a coarse, powdery deposit and very low efficiencies, even if the solution has been modified by the addition of various chemicals, pH changes, etc. Recent laboratory investigations, however, revealed that by placing aluminum shapes such as sheet, rods, or wire into spent electroless plating baths, fast recovery and good-quality metal can be deposited. Initially, an electrochemical reaction occurs which deposits a thin metallic layer on the aluminum surface as represented by the following reaction:

$$2\ Al + 3\ NiCl_2 \rightarrow 3\ Ni + 2\ AlCl_3$$

This "strike" layer then provides the base for further metal build-up by the autocatalytic mechanism.

In an attempt to control the dissolution of aluminum, an external cathodic potential was applied to the aluminum sheet. The laboratory cell in this experiment took the form of a conventional electroplating cell in which an aluminum cathode was placed between two steel anodes. This modification proved to be highly successful. The electrodeposition was very rapid. The cathode plate was fine-grained and was built to a sufficient thickness so that the deposit could be periodically removed and reused. The dissolution of the aluminum was also significantly inhibited by the cathodic potential. The process can be illustrated by the following examples.

metal compounds are not responsive to the conventional waste treatment technology of neutralization or high-pH treatment precipitation and settling. For many years now, intensive research on a widespread international scale has been conducted to overcome these difficulties in metal finishing waste treatment. A practical solution should not propose to exchange one problem for another. For example, the treatment of electroless and immersion plating wastes should not generate sufficient quantities of sludge so that this sludge presents its own disposal problem.

Some Typical Solutions

One common method for treating electroless wastes is the addition of reducing agents such as sodium borohydride,[1] sodium hypophosphite or sodium hydrosulfite[2] at elevated temperatures to reduce the soluble metals to their metallic or oxide forms. The sludges produced in these processes contain relatively impure metal powders which are extremely susceptible to air oxidation and require further treatment due to the presence of interstitial waters containing relatively large amounts of free chelating agents. These chelates will over a relatively short period of time cause redissolution of some of the metal oxide in the sludge. This sludge must therefore be considered a hazardous waste and treated accordingly.

The use of conventional ion exchange systems, as well as newly developed resin technology, has been proposed for the treatment of electroless wastes. Conventional cation exchange resins are extremely inefficient due to their affinity for the alkaline earth metals over the heavy metals. Systems involving these resins, therefore, require large columns and frequent regeneration. Most chelating resin systems available today are not effective on all chelate materials. One system, for example, will not remove metals that are complexed with EDTA.[3] In addition, the regenerant from most ion exchange or chelate resin systems will require further treatment in order to reclaim or otherwise remove the metal content.

Electrolytic techniques which utilize high surface area cathodes and/or non-conductive fluidized beds[4, 5] have also been used for the treatment of electroless wastes. These systems fall into the same category as electrodialysis, ultrafiltration, reverse osmosis, or evaporation in that the end result is the generation of a concentrated metal-containing solution. The metallic deposit generated on the high surface area cathodes must be stripped, and the resulting solution treated chemically or by conventional electrolytic means to remove the metal content unless this concentrate can be added back to the processing solution. Each system requires additional equipment before ultimate disposal of the waste can be achieved.

THE RECOVERY AND TREATMENT OF METALS FROM SPENT ELECTROLESS PROCESSING SOLUTIONS

Kevin E. Warheit
Lancy International, Inc.
Zelienople, Pennsylvania 16063

Introduction

Electroless plating is a growing segment of metal finishing, finding particular application in the electroplating and electronics industry. The electroless plating process employs a solution in which salts of the metal to be plated are dissolved and held in solution by the use of certain chelating and/or complexing agents. The metal deposition from these baths is an autocatalytic process which proceeds on previously sensitized metal, plastic, or glass surfaces. The rate of metal deposition is controlled by the type and amount of reducing agent present as well as the type of chelating agents used, rather than from an external electric power source. Electroless plating results in a fine-grained metal deposit very similar in appearance and function to that of an electroplated deposit. It is most often used as a starting deposit for subsequent electroplating in the process of plating on plastics, printed circuit boards, electroformed dies, and other metallic objects, with hard-to-reach intricate metal surfaces.

Some electroless plating processes are also known as "immersion plating" systems. These systems are not based on the electron donor being a reducing compound, but depend on an electrochemical exchange reaction. The metal to be deposited is reduced on the surface of the workpiece and a proportional amount of base metal from the workpiece is dissolved. Since the base metal of the object to be plated is replaced by chemical displacement, the electrochemical potential of the metal to be deposited has to be more negative than that of the metal on which the deposit occurs.

The Treatment Problem

As metal is deposited from either electroless or immersion plating solutions, the metal content of the solution is partially depleted. Metal salts and their appropriate chelating agents must then be added to replenish this metal loss. In time, after several chemical replenishment additions, the inorganic salts from the metal additions and the decomposed reducing agents accumulate. This slow accumulation of chemical content of the solution reduces the deposition rate and may affect the crystal structure of the deposit. At this point, a portion must be replaced with fresh solution or all of the electroless plating solution must be discarded.

Discarded plating solutions and waste rinsewaters, because of their metal content, require waste treatment so that the residual metals discharged in the effluent will be at a minimum concentration. Chelated

C-4

Environmental I
Session C

The Recovery and Treatment of Metals from Spent Electroless Processing Solutions

Kevin Warheit
Lancy International, Inc.
Zelienople, PA

Table 1
(Continued)

13. Mabbett, A.N., OSHA-An Overview for Printed Circuit Manufacturers, Printed Circuit Fabrication, Vol. 6, No. 1, January, 1983.

14. Colson, P.M., The Evolution of OSHA, Industry, Vol. 48, No. 1, January, 1983.

Table 2

REGIONAL OFFICES FOR OCCUPATIONAL SAFETY AND HEALTH

U.S. DEPARTMENT OF LABOR

REGION I:	(CT, ME, MA, NH, RI, VT)
	16-18 North Street 1 Dock Square, 4th Floor Boston, MA 02109 Tel. No.: (617) 223-6710
REGION II:	(NY, NJ, PR)
	Room 3445, 1 Astor Place 1515 Broadway New York, NY 10036 Tel. No.: (212) 944-3426
REGION III:	(DE, DC, MD, PA, VA, WV)
	Gateway Building, Suite 2100 3535 Market Street Philadelphia, PA 19104 Tel. No.: (215) 596-1201
REGION IV:	(AL, FL, GA, KY, MS, NC, SC, TN)
	1375 Peachtree Street, N.E. Suite 587 Atlanta, GA 30309 Tel. No.: (404) 881-3573
REGION V:	(IL, IN, MI, MN, OH, WI)
	230 South Dearborn Street 32nd Floor, Room 3244 Chicago, IL 60604 Tel. No.: (312) 353-2220
REGION VI:	(AR, LA, NM, OK, TX)
	555 Griffin Square, Room 602 Dallas, TX 75202 Tel. No.: (214) 767-4731

Educated and informed employers and employees will together help ensure that safe and healthful working conditions are maintained in the electroplating-metal finishing facility.

ACKNOWLEDGEMENT

Minor portions of this manuscript are reproduced in part or in modified form with permission of PMS Industries, Inc. publishers of Printed Circuit Fabrication, from an article entitled "OSHA - An Overview for Printed Circuit Manufacturers" by the author, Vol. 6, No. 1, January, 1983.

sible, is given suggestions on how to reduce or eliminate the hazard.

Because employers, not employees, are subject to legal sanctions of the OSHA standards, the employer controls the extent of participation by employees or their representatives in the visit. OSHA encourages full employee participation however, and the consultant must be allowed to confer with individual employees as necessary during the walk-through survey in order to recognize and evaluate the nature and extent of hazards.

KEEPING UP-TO-DATE

Clearly, OSHA cannot succeed in its mission without fully informed employers and employees. Questions about OSHA should be referred to the nearest OSHA Regional Office (Refer to Table 2).

Employers are also encouraged to establish and maintain a reference library of publications which can be used for education, training, hazard recognition, evaluation, and control purposes. A list of recommended publications is found in Table 2. Many of the publications listed in Table 2 are available free of charge from OSHA and were used in preparing this article. The nearest OSHA Regional or Area Office can provide a complete listing of current materials.

The National Institute for Occupational Safety and Health (NIOSH) publishes a catalog, DHHS (NIOSH) Publication No. 82-116 which lists all numbered publications, health hazard evaluations (HHE), and technical assistance (TA) reports, contract reports, and other educational and training materials. A copy of the revised and just released 5th Edition of the catalog is available from the NIOSH, Cincinnati, OH office listed in Table 5. NIOSH material provides additional technical data which is usually not found in OSHA publications.

In addition, a significant amount of reference material is available from state and local governments; nationally-recognized standards-producing scientific and service organizations e.g., National Fire Protection Association, Factory Mutual System, National Safety Council; trade and education associations e.g., American Electroplaters' Society, The Institute for Interconnecting and Packaging of Electronic Circuits. Individuals are encouraged to contact the organizations listed in Table 4 for specific occupational health and safety reference material.

STANDARDS

The general duty clause of the Act states that each employer "must furnish...a place of employment which is free from the recognized hazards that cause or are likely to cause death or serious physical harm to employees."

In carrying out its duties, OSHA is responsible for promulgating legally enforceable standards. It is the employer's responsibility to become familiar with standards applicable to his establishment, and to recognize, evaluate, and control potential hazards via administrative or engineering controls. Even where OSHA has not promulgated specific standards, employers are responsible for following the intent of the Act's general duty clause as noted above.

OSHA's regulations are collected in Title 29 Code of Federal Regulations, (CFR), Part 1900-1999. Part 1910, General Industry Standards regulates industrial operations including electroplating and metal finishing.

An OSHA Subscription Service publication exists in order to keep the public current with OSHA standards. This service provides all standards, interpretations, regulations and procedures in easy-to-use loose-leaf form, with changes and additions automatically issued to the subscriber for an indefinite period of time. The service is available only from the Superintendent of Documents, Washington, D.C. It is not available from OSHA or from the Department of labor. Volume I includes the General Industry Standards. For current prices, contact the nearest OSHA Regional Office (Refer to Table 2).

EMPLOYER RESPONSIBILITIES

Employers have certain responsibilities under the Occupational Safety and Health Act of 1970. Employers must:

- Meet general duty clause responsibility to provide a workplace free from recognized hazards that are causing or are likely to cause death or serious physical harm to employees, and comply with standards, rules and regulations issued under the Act.
- Be familiar with mandatory OSHA standards, and make copies available to employees for review upon request.
- Inform all employees about OSHA.

- Examine workplace conditions to make sure they conform to applicable standards.

- Minimize or reduce hazards via administrative or engineering controls.

- Make sure employees have and use safe tools and equipment (including personal protective equipment), and that such equipment is properly maintained.

- Use color codes, posters, labels or signs to warn employees of potential hazards.

- Establish or update operating procedures and communicate them so that employees follow safety and health requirements.

- Provide medical examinations when required by OSHA standards.

- Report to the nearest OSHA office any fatal accident or one which results in the hospitalization of five or more employees.

- Keep OSHA-required records of work-related injuries and illnesses, and post a copy of the totals from the last page of OSHA No. 200 during the entire month of February each year. (This applies to employers with 11 or more employees.)

- Post, at a prominent location within the workplace, the OSHA Poster (OSHA 2203) or equivalent for state approved programs informing employees of their rights and responsibilities.

- Provide employees, former employees, and their representatives access to the Log and Summary of Occupational Injuries and Illnesses (OSHA No. 200) at a reasonable time and in a reasonable manner.

- Cooperate with the OSHA compliance officer by furnishing names of authorized employee representatives who may be asked to accompany the compliance officer during an inspection. If none, the compliance officer will consult with a reasonable number of employees concerning health and safety in the workplace.

- Not discriminate against employees who properly exercise their rights under the Act.

- Post OSHA citations at or near the worksite involved. Each citation or copy thereof, must remain posted until the violation has been abated, or for three working days, whichever is longer.

- Abate cited violations within the prescribed period.

EMPLOYEE RESPONSIBILITIES

Although OSHA does not cite employees for violations of their responsibilities, each employee "shall comply with all occupational safety and health standards and all rules, regulations, and orders issued under the Act" that are applicable. Employees should:

- Read the OSHA poster at the jobsite.

- Comply with all applicable OSHA standards.

- Follow all employer safety and health rules and regulations, and wear or use prescribed protective equipment while engaged in work. Employers can enforce health and safety policies and take disciplinary action against employees for violation of established rules of procedure.

- Report hazardous conditions to the supervisor or management.

- Report any job-related injury or illnesses to the employer, and seek treatment promptly.

- Cooperate with the OSHA compliance officer conducting an inspection if he or she inquires about safety and health conditions in the workplace.

- Exercise their rights under the Act in a responsible manner.

CURRENT DEVELOPMENTS AND TRENDS

Since election of the Reagan Administration, the federal government, including the Occupational Safety and Health Administration has been more practical in dealing with industry regarding environmental, safety, and health issues.

Program emphasis has been redirected to those areas where the greatest return on expenditures can be realized. In most cases, standards have not been relaxed but compliance schedules have been more flexible. Local Area Directors of the

Occupational Safety and Health Administration have been given greater authority to deal with local companies who are under a compliance schedule or who may disagree with a citation or penalty. Employers can now request an informal review of their case with the local OSHA Area Office and hopefully resolve the issue rather than pursue a formal contesting procedure.

OSHA's priorities have also been redirected to include a greater emphasis on occupational health areas of concern (i.e., toxic and hazardous substances, noise, ergonomic impacts). A greater number of industrial hygienists have been added to OSHA's staff and new standards have been adopted or proposed to deal with these serious issues. OSHA's activities are expected to continue to focus on the control of chemicals/hazardous substances in the workplace for the immediate future.

Since its establishment in 1970, OSHA has experienced severe growing pains. A more mature administration currently exists under the direction of Mr. Thorne Auchter, Assistant Secretary of Labor for Occupational Safety and Health. During his first two years, Mr. Auchter has stressed overall management improvement for the Agency, the need for states to assume a greater role in the implementation and enforcement of health and safety programs, and the necessity of developing a new standards promulgation system.

Emphasis will be placed on the development of "performance" rather than specification standards. Needless standards will continue to be eliminated; those that have not or do not have a significant impact on employee health and safety.

The Agency has also developed and is currently implementing a "Voluntary Compliance" program for employers. Under the program, employers will be exempted from general scheduled inspections, yet will be required to internally monitor employee health and safety and coordinate closely with the OSHA Area Office. Specific reporting requirements for employers however, are an integral part of the program.

On a periodic basis, OSHA publishes a list of regulations which are scheduled for review or development. This list provides general information and an insight concerning areas of emphasis. Table 3 is a partial list of current regulations pending internal review or proposed rulemaking that have been scheduled for action by OSHA during the period October, 1982 through October, 1983. Many of these actions will impact on electroplaters and metal finishers.

A statement recently made by Mr. Auchter at the 70th National Safety Congress helps put the current attitude of OSHA in perspective. He stated "now is not the time for employers to slack off on safety and health" and noted that workers' compensation costs are rising and new toxic substances are entering the workplace. Because of this, Auchter said, "we would encourage management when making difficult personnel decisions not to back off from safety and health. It can pay off today more than ever before." (Reference: National Safety Council, OSHA Up-to-Date, Vol. XII, No. 1, December, 1982)

OCCUPATIONAL HEALTH AND SAFETY PROGRAM ELEMENTS

The OSHA General Industry Standards require that certain specific programs be established and implemented in order to help ensure the creation of a safe and healthful work environment.

The Occupational Safety and Health Review Commission which decides employee citation contests has made it clear on a number of occasions that when a company cannot show that it has an effective health and safety program it is "on a collision course with the Review Commission". The Commission insists upon a "well planned and administered safety program that gets its support and direction from the very top officials of the company".

Every company should develop a written occupational health and safety program. The extent of the program will vary depending on the actual or potential hazards present due to the type(s) and number of manufacturing process operation(s). A topical outline of such a program is focused in Table 4.

The purpose of the program is to document established policies, responsibilities, and procedures and to define services and major program elements. The scope of the program, its objectives, and a statement of policy, usually a general statement of the company's support for employee health and safety, should be included in the program document. Definitions should be included as appropriate to help ensure a common understanding among program participants of certain terminology contained in the document.

Most importantly, a section concerning individual responsibilities regarding implementation of the program should be prepared. Department supervisors, and employee responsibilities should be carefully defined to include their relationship and roles. Once these basic administrative related

areas have been developed, attention should focus on the various health and safety program elements. These elements are usually categorized under the broad headings of either industrial hygiene and safety or occupational health.

INDUSTRIAL HYGIENE AND SAFETY

The primary purpose of these various programs is to recognize, evaluate, and control actual or potential hazards. An Occupational Safety and Health Hazards Inventory Program should be developed to include the completion of a preliminary walk-through survey and comprehensive follow-up special studies, as required. The survey and studies should include the identification of:

1. General sanitary and comfort conditions;
2. Raw materials utilized;
3. Products or by-products produced;
4. Sources and types of air contaminants;
5. Nature of the contaminants;
6. Physical agents or conditions present;
7. Intensity of exposure relative to operating time and personnel exposed;
8. Duration of exposure;
9. Control measures observed at the time of the survey or study; and
10. A complete evaluation of all parameters associated with the exposure.

The inventory should be updated on a periodic basis as new process operations are added or existing processes modified. Via the inventory, the employer is able to correlate employee positions with the hazards inherent to the job function. Placement and periodic job-position related examinations-screening programs can thus be scheduled as required. The inventory of health and safety hazards is both a key and critical element of the total program.

Based on the results of the inventory, Material Safety Data Sheets (OSHA Form 20) should be obtained or developed for all toxic/hazardous-chemical substances utilized in the manufac-

turing process operations. The Data Sheet should include information regarding health effects and safe work practices. Specific information provided should include:

1. Symptoms of toxic exposure, acute and chronic;

2. Diagnostic determinance of overexposure;

3. First aid;

4. Administrative measures to be taken in an emergency situation;

5. Personnel protective and emergency/first aid equipment; and

6. Recommended environmental-engineering controls.

In order to implement an effective Occupational Health and Safety Program, an Occupational Safety and Health Committee should be established. The committee's responsibilities should include:

1. Promoting safety and health consciousness among company personnel; and ensuring compliance by the company with the provisions of applicable laws and regulations including the Occupational Safety and Health Act of 1970.

2. Developing and recommending the establishment of specific safety, industrial hygiene and occupational (employee) health policies, programs and implementing instructions; the promulgation of occupational safety and health program objectives and goals; and health education (preventive medicine) and training programs.

3. Reviewing implementation of the occupational health and safety programs with operating departments; disseminating guidelines and technical information; resolving questions and employee concerns in the most direct manner.

A separate policy document should be developed to define the organization, membership and responsibilities of the Occupational Safety and Health Committee.

OCCUPATIONAL HEALTH

Health examinations constitute another primary element of an Occupational Health and Safety Program. Such examinations

include pre-employment/pre-placement, periodic job-related, and administrative. Certain voluntary health maintenance examinations may also be provided as personnel and other resources permit.

Administrative procedures should be developed to provide for the treatment of employee illness and injury emergencies during all shifts. Emergency medical equipment and supplies should be installed in designated locations throughout the facility. At least one regular full-time employee per workshift should be adequately trained in the use of emergency equipment and supplies.

All illness and injury emergencies should be reported to the Personnel Department for inclusion in the employees records.

SPECIFIC PROGRAMS

Depending on the nature of the process operations, legal requirements, and the desires of the company, numerous specific additional health and safety programs may be developed. The programs may concern an employee's exposure to a particular hazard i.e., eye, noise-hearing, etc. or may relate to health surveillance, chronic disease, illness-absence monitoring, education and training, and medical records-directives.

The development of an occupational health and safety program which contains the basic elements listed in Table 4 will not only allow electroplaters and metal finishers to meet legal requirements, but should also reduce the evidence of on-the-job disease, illness and injury.

FREE ON-SITE CONSULTATION

Congress has authorized, and OSHA now funds, a free on-site consultation service for employers in every state. Consultants from the state government or a private contractor help employers identify hazardous conditions and determine corrective measures. The free service is available upon employer request. Priority is given to smaller businesses, and emphasis is placed on highly hazardous job sites.

A typical consultative visit consists of an opening conference, a walk-through survey of the company's facility, a closing conference, and a written summary of findings. During the walk-through, the employer is told which OSHA standards are applicable and what they mean. The employer is informed of any violations of those standards and where pos-

Table 1
(Continued)

2. Sax, N.I., Dangerous Properties of Industrial Materials, 5th Edition; Van Nostrand Reinhold, 1979.

3. National Fire Protection Association, Fire Protection Guide on Hazardous Materials, NFPA 470 Atlantic Avenue, Boston, MA 02210.

4. National Safety Council, 444 North Michigan Avenue, Chicago, IL, 60611 Fundamentals of Industrial Hygiene, 2nd Edition.

5. American Conference of Governmental Industrial Hygienists, Committee on Industrial Ventilation, P.O. Box 16153, Lansing, MI 48901, Industrial Ventilation, A Manual of Recommended Practice, 17th Edition, 1982.

6. Merck & Company, Inc., Rahway, NJ, The Merck Index, An Encyclopedia of Chemicals and Drugs, 9th Edition.

7. Burgess, William, Recognition of Health Hazards in Industry, John Wiley and Sons, Inc., 1981.

8. American Conference of Governmental Industrial Hygienists, 6500 Glenway Avenue, Building D-5, Cincinnati, OH 45211, Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment.

9. Felton, J.S., Organization and Operation of an Occupational Health Program, J. Occupational Medicine, 6:25, 93, 132 (3 parts) 1964.

10. American Medical Assocation, Council on Occupational Health: Scope, Objectives and Functions of Occupational Health Programs, J. American Medical Association, 174:533, 1960.

11. Cohen, S.R., Another Look at the In-Plant Occupational Health Program, J. Occupational Medicine, 15(11):869-873, 1973.

12. American Medical Association, Company Medical Policies for Occupational Health Programs, Revised 1973, Chicago, Illinois.

Table 1

OCCUPATIONAL HEALTH AND SAFETY REFERENCE PUBLICATIONS

GOVERNMENT

1. All About OSHA. (OSHA #2056)

2. Closing Conference Guide. (OSHA #3030)

3. Department of Transportation, Hazardous Materials 1980 Emergency Response Guidebook, DOT-P 5800.2.

4. Employer Rights and Responsibilities following an OSHA Inspection. (OSHA #3000)

5. Investigating Accidents in the Workplace. (OSHA #2288)

6. NIOSH, Health and Safety Guide for Electroplating Shops, DHEW (NIOSH) Publication No. 75-145.

7. NIOSH, Good Work Practices for Electroplaters, DHEW (NIOSH) Publication No. 77-201.

8. NIOSH, Hazardous Waste Sites and Hazardous Substance Emergencies, DHHS (NIOSH) Publication No. 83-100.

9. NIOSH/OSHA, Occupational Health Guidelines for Chemical Hazards, Publication No. 81-123.

10. NIOSH/OSHA, Pocket Guide to Chemical Hazards, DHEW (NIOSH) Publication No. 78-210.

11. OSHA Handbook for Small Business. (OSHA #2209)

12. OSHA Publications & Training Materials. (OSHA #2019)

13. Occupational Safety and Health Administration, General Industry Standards, 29 CFR 1910. (Subscription Service Available)

14. Worker Rights Under II(c). (OSHA #3032)

PRIVATE

1. National Safety Council, 444 North Michigan Avenue, Chicago, IL, 60611 Accident Prevention Manual for Industrial Operations, Seventh Ed.

Table 2
(Continued)

REGION VII:	(IA, KS, MO, NE) 911 Walnut Street, Room 406 Kansas City, MO 64106 Tel. No.: (816) 374-5861
REGION VIII:	(CO, MT, ND, SD, UT, WY) Federal Building, Room 1554 1961 Stout Street Denver, CO 80294 Tel. No.: (303) 837-3883
REGION IX:	(CA, AZ, NV, HI, Guam, American Samoa, Trust Territory of the Pacific Islands) 450 Golden Gate Avenue, Box 36017 San Francisco, CA 94102 Tel. No.: (415) 556-0584
REGION X:	(AK, ID, OR, WA) Federal Office Building, Room 6003 909 First Avenue Seattle, WA 98174 Tel. No.: (206) 442-5930

Table 3

PROPOSED RULEMAKINGS OR REGULATIONS PENDING REVIEW BY OSHA

Proposed Rulemakings

Carcinogen Policy
Part 1990

Labeling: Hazard Communication
Part 1910.1200

Lead-Reconsideration of Whole Standard
Part 1910.1025

Noise-Hearing Conservation Amendment
Part 1910.95 (e)-(s)

Respiratory Protection
Part 1910.134

Walking/Working Surfaces
Part 1910, Subpart D

Regulations Pending Review

Electrical Safety-Related Work Practices
Part 1910, Subpart S (new section)

Electrical Standards-Construction
Part 1926, Subpart K

Engineering Controls vs. Respirators: Generic Question
Part 1910

Hazardous Materials
Part 1910, Subpart H

Noise-Review of the Standard as a Whole
Part 1910.95

Table 4

OCCUPATIONAL HEALTH & SAFETY PROGRAM ELEMENTS
TOPICAL OUTLINE

1. PURPOSE

2. SCOPE

3. OBJECTIVES

4. POLICY

5. DEFINITIONS

6. RESPONSIBILITIES

   a. Employee Relations Department

   b. Department Managers and Supervisors

   c. Department Occupational Health and Safety Officer

   d. Employees

   e. Occupational Medicine Consultant

   f. Occupational Health Nurse

   g. Plant Engineer

   h. Occupational Health and Safety Consultant

Table 4
(Continued)

7. SERVICES AND PROGRAMS

a. INDUSTRIAL HYGIENE AND SAFETY

(1) Occupational Safety and Health Hazards Inventory Program

(2) Safety, Industrial Hygiene Surveys/Special Studies, and Monitoring

(3) Toxic/Hazardous Substance Control Program

(4) Occupational Safety and Health Committee

b. OCCUPATIONAL HEALTH

(1) EXAMINATIONS

(a) Pre-placement Employment Questionnaire and Pre-placement Examination

(b) Periodic Job-Related Examinations

(c) Voluntary Health Maintenance Examinations

(2) TREATMENT OF ILLNESS AND INJURY

(a) Occupational Illness or Injury

(b) Non-Occupational Illness or Injury

Table 4
(Continued)

(c) Emergency Care After Normal Working Hours

(d) First-Aid

(3) SPECIFIC PROGRAMS

(a) Occupational Vision Program

(b) Hearing Conservation Program

(c) Illness - Absence Monitoring

(d) Chronic Disease and Disability Surveillance

(e) Immunization Program

(f) Pregnancy Surveillance Program

(g) Epidemiological Investigations

(h) Employee Health and Safety Education Program

(i) Medical Records

(j) Medical Directives

(k) Transportation

8. REFERENCES

Table 5

SOURCES OF OCCUPATIONAL HEALTH AND SAFETY MATERIAL

I. FEDERAL AGENCIES:

Superintendent of Documents
U.S. Government Printing Office
Washington, D.C. 20402

National Technical Information Service
Department of Commerce
5285 Port Royal Road
Springfield, VA 22151
(Order Desk (703) 487-4650)

National Institute for Occupational Safety and Health (NIOSH)
Publications Dissemination, DTS
4676 Colubmia Parkway
Cincinnati, OH 45226

Occupational Safety and Health Administration
U.S. Department of Labor
200 Constitution Ave., N.W.
Washington, D.C. 20210

Occupational Safety and Health Review Commission
1825 K Street, N.W.
Washington, D.C. 20006

National Center of Toxicological Research
Food and Drug Administration
5600 Fishers Lane
Rockville, MD 20857

II. PROFESSIONAL ASSOCIATIONS AND ORGANIZATIONS:

American Association of Occupational Health Nurses
575 Lexington Avenue
New York, NY 10022

American Industrial Hygiene Association
475 Wolf Ledges Parkway
Akron, OH 44311

American Society for Testing and Materials
1916 Race Street
Philadelphia, PA 19103

American Society of Safety Engineers
850 Busse Highway
Park Ridge, IL 60068

American Conference of Governmental Industrial Hygienists
P.O. Box 1937
Cincinnati, OH 45201

American Medical Association
535 North Dearborn Street
Chicago, IL 60610

Air Pollution Control Association
4400 Fifth Avenue
Pittsburgh, PA 15213

Board of Certified Safety Professionals
501 South Sixth Street
Suite 101
Champaign, IL 61820

Table 5
(Continued)

III. TRADE ASSOCIATIONS:

American Insurance Association
85 John Street
New York, NY 10038

American Mutual Insurance Alliance
20 North Wacker Drive
Chicago, IL 60606

American Electroplaters' Society
1201 Louisiana Avenue
Winter Park, FL 32789

The Institute for Interconnecting and Packaging Electronic Circuits
3451 Church Street
Evanston, IL 60203

IV. TECHNICAL SERVICE ORGANIZATIONS:

American National Standards Institute
1430 Broadway
New York, NY 10018

Factory Mutual System
1151 Boston-Providence Turnpike
Norwood, MA 02062

Underwriters Laboratories, Inc.
207 East Ohio Street
Chicago, IL 60611

National Fire Protection Association
470 Atlantic Avenue
Boston, MA 02210

National Safety Council
444 North Michigan Avenue
Chicago, IL 60611

V. EMERGENCY INFORMATION SERVICES:

Poison Control Centers*

*Consult local white pages telephone directory for center serving your area.

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American National Red Cross
National Headquarters
Safety Programs
17th and D Streets, N.W.
Washington, D.C. 20006

E-4

Environmental II
Session E

Recovery Methods Which Will Meet Future Hazardous Waste Regulations

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RECOVERY METHODS WHICH WILL MEET FUTURE HAZARDOUS WASTE REGULATIONS

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The process wastewater from the electroplating industry contain cyanides and heavy metals. Because of effects on the environment, discharges are regulated by the federal, state, county, or city ordinances requiring installation of treatment technology. Treatment technologies most likely to be installed are neutralization and precipitation technology to destroy the cyanide and remove the heavy metals as hydroxides.

The sludge is commonly disposed of in landfills. This practice is regulated primarily due to the presence of the heavy metal hydroxides. The heavy metals may leach due to changes in their environment. The leached metal may contaminate surface runoff, groundwater or both. To prevent any leaching of the metals, secure and chemically maintained land disposal sites are required. The cost of disposal has become greater because of the heavy metal presence and also because the secure landfill sites are expensive to create and maintain. Finally, new sites may not become available because of resistence on the part of the host community itself.

Since a landfill site has a finite capacity, sludges, in the form generated at the electroplating plant, may not be acceptable to the operator of the site. Such sludges usually contain about three percent solids requiring volume reduction by dewatering to conserve this capacity. Dewatering requirements necessitate installation of a filter press or a centrifuge.

Improper land disposal causes certain problems:

1. Contamination of the surface and the ground waters by heavy metal migration.

2. Permanent loss of metals if the site undergoes a physical change of use.

3. Dilution in metal contents if the sludges are mixed with other types of waste material.

Wet and dry processes can be used for metal recovery. In wet processes, separation reactions are carried out at atmospheric temperatures and pressures. In dry processes, separation reactions take place at elevated temperatures. The former processes are generally classified as hydrometallurgy and the latter as pyrometallurgy.

Pyrometallurgical treatments for segregated and selected sludges are:

1. Direct recycle to a smelter after dewatering.

2. Direct recycle to metal alloy industry on a small basis.

For economic feasibility, the pyrometallurgical operation would require a very large scale and concentrated feed material. The hydroxide sludges fail to meet these two requirements.

Hydrometallurgical processes for mixed and segregated sludges require:

1. Aqueous dissolution of metals by leaching.

2. Recovery of individual metals or metal compounds from this solution.

There are certain advantages for using hydrometallurgical processes. Metals may be won directly from the solution by concentration, electrolysis, or hydrogen reduction. Fuel requirements are low as the processes are carried out at low temperatures. However, solution purification and concentration upgrading may be absolutely necessary before metal recoveries are possible.

The following reagents are solvents for many minerals and metallic constituents: sulfuric acid, ferric sulfate, ammonia and ammonium carbonate, sulfur dioxide, ferric chloride, hydrochloric acid, and nitric acid. The order given is about that of their importance. Metal winning from solutions by such operations as cementation or electrolysis is commonly practiced from the metal sulfate solution.

Sulfuric acid is the most important leaching reagent due to cost, minor corrosion problems, and solubility for many metal forms. Ferric sulfate may be obtained cheaply from spent pickle liquors. Its primary function is to provide a sulfate solution. Ammonia and ammonium carbonate may be the most suitable reagents for hydroxide sludges because they possess better selectivity for solubilizing metal constituents in a hydroxide sludge. The reagent cost is very high and their recovery in the process would be mandatory from an economical point of view.

The purpose of a solvent is to bring the metal or metals into solution from which individual separations are made. This operation provides pure solutions and removal of major impurities.

Leaching of hydroxides by either sulfuric acid or ammonia will provide lean solutions. Copper may be recovered from lean sulfate solutions by cementation. Iron will displace copper quantitatively from a solution. The product, although rich in copper, may be highly contaminated with iron so that only a smelter may be able to handle it. A technique which is becoming widely accepted for concentrating solutions is the one of ion exchange. The ion exchange medium may be solid or liquid. Generally speaking, concentrating by solid organic resins is known as ion exchange (IX) and by liquid organic resin is known as solvent extraction (SX).

Liquid ion exchange is a relatively new technique which combines the concept of ion exchange and liquid-liquid extraction for the removal and recovery of metal ions from aqueous streams.

Liquid ion exchange is similar to conventional ion exchange using solid resins. Aqueous feed solution is contacted (mixed) with an active reagent in a mixing chamber or column. Ions are extracted from the feed in exchange for hydrogen ions or other transferable ions carried by the

liquid ion exchange reagent. The liquid ion exchange reagent is a long chain organic, and is generally used as an "extractant" solution in a hydrocarbon solvent such as kerosene. The exchange process occurs via a three-step mechanism.

First, the hydrated or complexed metal ion diffuses to the aqueous/liquid resin interface.

Second, the ion is stripped of its hydration layer and complexes with the liquid ion exchange reagent at the interface, making the interfacial transition.

Third, the organic/metal complex diffuses into the bulk organic phase.

Extraction of the metal ion into the organic phase is followed by re-extracting the metal ions with an aqueous stripping solution. In the case of acid extractants, stripping is done with a dilute mineral acid. Often, as in two of the examples, the extractant phase picks up ionic or molecular species in addition to the desired ones, and these are extracted in a "scrubbing" step using a weak reagent before the stripping step.

The final step is to recover the metal itself and regenerate or dispose of the stripping solution. This step is just as important as extraction and stripping, but is frequently given inadequate attention. The easy, but expensive route, is to neutralize the stripping solution and generate a neutral waste stream or sludge. The best approach is one which regenerates the stripping solution and recovers the metal directly, electrolytically or by direct reduction, or as an insoluble salt.

The benefits derived from liquid ion exchange are:

1. Increased metal concentration in the stripping solution relative to the feed, up to one hundred fold or more, can be the key to metal recovery by electrowinning, crystallization, or precipitation.

2. Recovery of one metal in the presence of others present with a high background level of other unwanted metals.

The process must achieve these desired results within the allowable conditions of time, temperature, concentrations, pH, equipment and cost.

Second, all feed streams extractants, stripping solutions, and recovered metal values must be accounted for completely. A "cradle-to-grave" approach for all streams is essential.

Third, the extractant system should have good long-term operating characteristics. These include chemical stability, good metal-complex solubility, very low solubility in feed and stripping solutions, and good phase separation characteristics.

Fourth, interferences must be identified and treated in advance.

Electrolytic metal recovery is one of a growing number of tools available to the materials extracted from metal wastes.

Electrolytic metal recovery is selective, removing only one metal. Electrolytic metal recovery does recover the most valuable constituent of the dragout--the metal. The metal is also the component of the dragout that is responsible for the formation of the sludge.

The choice between electrolytic metal recovery and one of the concentrative methods of recovery is basically an economic one. Capital expenditures for the recovery equipment, and the operation costs, must be considered along with the recovery value of the metal. The complexity of the equipment and the skill required of the operator, as well as the amount of operator time necessary are also important factors in the decision.

Electrolytic metal recovery is not a new technology. The mining industry has used electrolytic means of refining ores for many years, and copper has been recovered from pickling solutions for a significant period of time. There is considerable use of electrolysis for the recovery of metals from the concentrate from the final solvent extraction phase.

Cathode polarization poses an acute problem for recovery from a very dilute solution. In general, as deposition proceeds, the area of solution next to the cathode becomes depleted in metal ions, forming a polarized layer. The ions must diffuse into and across this layer before they can be plated out. There are fewer ions present in dilute solutions, so the rate of diffusion into and across the polarized layer is much slower, and the layer becomes thicker and more depleted. Severe cathode polarization can lead to poor quality deposits: the formation of dark, powdery, burned areas and trees that can grow across to the anodes and short out the cell. The efficiency at the cathode can be greatly reduced, as the electricity is used to decompose water and form hydrogen gas, instead of plating out the metal. There are a number of ways that the problems associated with cathode polarization can be reduced: by running at a lower current density, adjusting the chemistry and temperature of the solution, and agitating the solution.

When deposition is carried out at a low current density, the polarized layer is narrower and metal ions can diffuse into and across it more easily. For a given amount of metal, the larger the cathode surface area, the lower the current density necessary to plate out the metal. One way of increasing the cathode surface area is through the use of a large tank with many rows of cathodes and anodes. This approach is cumbersome, at best, and to recover from low concentration rinse waters, hundreds of pairs would be needed as in an electrolytic tank house.

Electrolytic recovery requires, for economic reasons, a concentration of metal ions in the 3-6 g/l range. Furthermore, when an electrolytic metal recovery cell is used for the recovery of metal from a solvent extraction cell, the initial metal concentration is high enough that it is often economically feasible to reduce the concentration significantly.

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F-1

Electronics II
Session F

A New Process for Recovering Gold as Potassium Gold Cyanide

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A New Process for Recovering Gold as Potassium Gold Cyanide

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Introduction

Potassium gold cyanide is the common gold compound used in the electroplating industry. Thus, in the spent gold plating bath, the plating dragout solution, and the parts rinse water, gold exists as $Au(CN)_2^-$ ion. The present approach to recovering gold, as illustrated in Fig. 1, is to convert the $Au(CN)_2^-$ ion to metallic gold and then change the reclaimed gold back to potassium gold cyanide. With the more concentrated solutions, most of the gold is separated first either by electroplating or by precipitation with zinc. The more dilute solutions are passed through an ion exchange column for complete recovery (<1 ppm). The resins are then incinerated and the gold is recovered from the ashes. Although in principle all the gold is recovered, there are too many steps involved and it is time consuming. With the high price of gold, the longer the turn-around time, the higher is the inventory cost. A process that would directly recover gold as potassium gold cyanide would have significant cost advantages and is desirable.

One approach to recover gold as potassium gold cyanide is the use of anion exchange resins. Strong basic anion exchange resins are capable of absorbing $Au(CN)_2^-$ ion

quantitatively. AMBERLITE* IRA-400 resin has a capacity of 0.66 gram of Au/gram of dry resin.[1] Recently, we showed that a thiocyanate organic/water solution can elute the $Au(CN)_2^-$ from resins rapidly.[2,3] Thus, instead of removing the gold by electroplating or by precipitation, anion exchange resins could be used to collect all the $Au(CN)_2^-$ and a method of separating $Au(CN)_2^-$ from the eluent as $KAu(CN)_2$ would yield the desired process. Crystallization appears to be a simple way to obtain $KAu(CN)_2$ if the eluent can be supersaturated. Since the solubility of pure $KAu(CN)_2$ in water is temperature dependent,[4] it should be possible to have crystallization when the elution process is operated at a higher temperature. By running the elution in a packed bed column, the $KAu(CN)_2$ concentration of the effluent can reach the saturation limit under appropriate operating conditions.

The objective of this study is to demonstrate the feasibility of recovering directly the $Au(CN)_2^-$ ions from resins as potassium gold cyanide. Process implementation is also discussed.

Experimental

Large scale gold desorption columns (height 40 cm,

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* Trademark of Rohm and Haas Co.,Philadelphia, PA.

d=2.6 cm) were run with AMBERLITE IRA-400 and IRA-900 OH form resins. The gold-containing resins were prepared by mixing the resins (as received) with the appropriate amount of potassium gold cyanide solution to make 16 wt% gold in the dry resins. The eluent was 4.88 M KSCN in 50 vol% dimethylformamide. For each experiment the column was kept at 50°C with an external water jacket.

The AMBERLITE IRA-900 resin was filtered from the gold solution and placed immediately into the column. To pack the resin, the column was filled with distilled water, which was then pumped out. The resulting height of the resin bed was 40 cm. The column was pumped at 3.5 ml/min with fresh eluent entering the top of the column. Eluent samples were taken every minute with an automatic sampler. Approximately 400 ml of eluent passed through the column. The gold content of the eluted resin (107 grams dry) was determined gravimetrically to be <0.01%.

With AMBERLITE IRA-400 resin, two columns were run (~90 g dry resin) at two flow rates, 3 ml/min and 18 ml/min. The column was packed by pouring the resin in its original gold solution into the column, and this solution was displaced as fresh eluent was added. In both runs, potassium gold cyanide crystallized out rapidly.

The eluent samples were analyzed for gold using atomic

absorption spectroscopy and for SCN^- using the Volhard method. Samples containing potassium gold cyanide crystals were collected and cooled to 0^oC before filtering. Some samples were washed with 10 ml of 0^oC distilled water. The crystals were dried in a 50^oC vacuum oven and then analyzed for their Au and SCN^- content.

Results

Figure 2 depicts the gold concentration of the effluent versus the amount of eluent passed through the ion exchange column containing AMBERLITE IRA-900 resin. The breakthrough curve is sharp as expected because the exchange between $Au(CN)_2^-$ and SCN^- at 50^oC reaches equilibrium in about 10 minutes.[3] To determine the extent the gold was eluted, the gold content of the resin was analyzed. Because the dried resin contains less than 0.01% gold, the elution is complete. Another observation from this experiment was that potassium gold cyanide did crystallize out as white crystals. Without washing, one sample of the dried crystals contained 60.8% gold or 89% $KAu(CN)_2$. The difference is attributed to KSCN contamination. This is reasonable because the sample filtrate has a relatively high SCN^- concentration. Figure 3 shows the SCN^- concentration of the effluent.

Experiments with AMBERLITE IRA-400 resin showed similar

behavior--the potassium gold cyanide crystallized out quantitatively. Without washing, the crystals also had a 90% content of potassium gold cyanide. With washing, the crystals had a gold content of 68.3%, i.e., they were 100% pure $KAu(CN)_2$.

Discussion

Pure potassium gold cyanide is recovered quantitatively and better than 99.99% of the gold is eluted from AMBERLITE resins in the column operation. It takes less than 4 ml of eluent/gram of dried resin to accomplish such a separation. This ratio of eluent volume/gram of dried resin is much smaller than that of the work of Burstall et al.[1] With the laboratory set-up, the complete elution of gold takes less than two hours. When the process is optimized, a shorter time may be expected. Scale-up of this arrangement should not pose any difficulty.

These promising results suggest a new approach to recovering gold based on the gold plating facility. Major sources of gold to be reclaimed are the spent plating bath, dragout solution, and parts rinse solution. A set-up involving anion exchange resin columns can perform most of the recovery work. First consider recovering gold from solutions. The spent plating bath and dragout solution have a high concentration of gold. A typical bath (75 liters) in

a high speed strip plater has five pounds of gold in $Au(CN)_2^-$ form. Instead of reducing the $Au(CN)_2^-$ ions to metallic gold either by plating or by adding zinc, only about 7.6 pounds of dried resin are needed to absorb that amount of gold. A column containing Ø.5 cubic foot of AMBERLITE IRA-4ØØ wet resin would have 45% extra capacity.

Figure 4 depicts one process scheme. Two columns are used in the absorption step. The first column removes most of the gold and the second column provides the back-up. Column #2 becomes the first column when gold is eluted from Column #1. The effluent from the crystallizer may be recycled if the KOH is removed either by electrodialysis or Donnan dialysis.[5] Once any start-up problems are solved, it should take at most three days to recover the potassium gold cyanide from the plating bath: one day for absorption, one day for elution and crystallization, and one day for drying of the potassium gold cyanide. At other times, the columns can be used to absorb gold from the rinse solutions.

This proposed scheme of using resin columns to recover gold as potassium gold cyanide is more cost effective than other processes. It is also simple enough that each plating facility could have its own recovering system. The reduction of inventory cost and the savings from shipping the scrap to the refiner would be substantial.

ACKNOWLEDGMENT

Rohm and Haas Co., Philadelphia, PA, kindly supplied the resins used in this study.

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TABLE 1

CAPACITY OF AMBERLITE IRA-400 RESIN FOR SEVERAL METALLIC CYANIDE COMPLEXES[1,7]

METAL	COMPLEX	Capacity, Metal Adsorbed per g Dried Resin	
		GRAM	MILLIMOLE
Gold	$Au(CN)_2^-$	0.66	3.3
Silver	$Ag(CN)_2^-$	0.34	3.2
Nickel	$Ni(CN)_2^-$	0.11	1.8
Copper	$Cu(CN)_4^{-3}$	0.08	1.3
Cobalt	$Co(CN)_6^{-3}$	0.08	1.3
Zinc	$Zn(CN)_5^{-3}$	0.08	1.3
Iron	$Fe(CN)_6^{-4}$	0.05	0.9

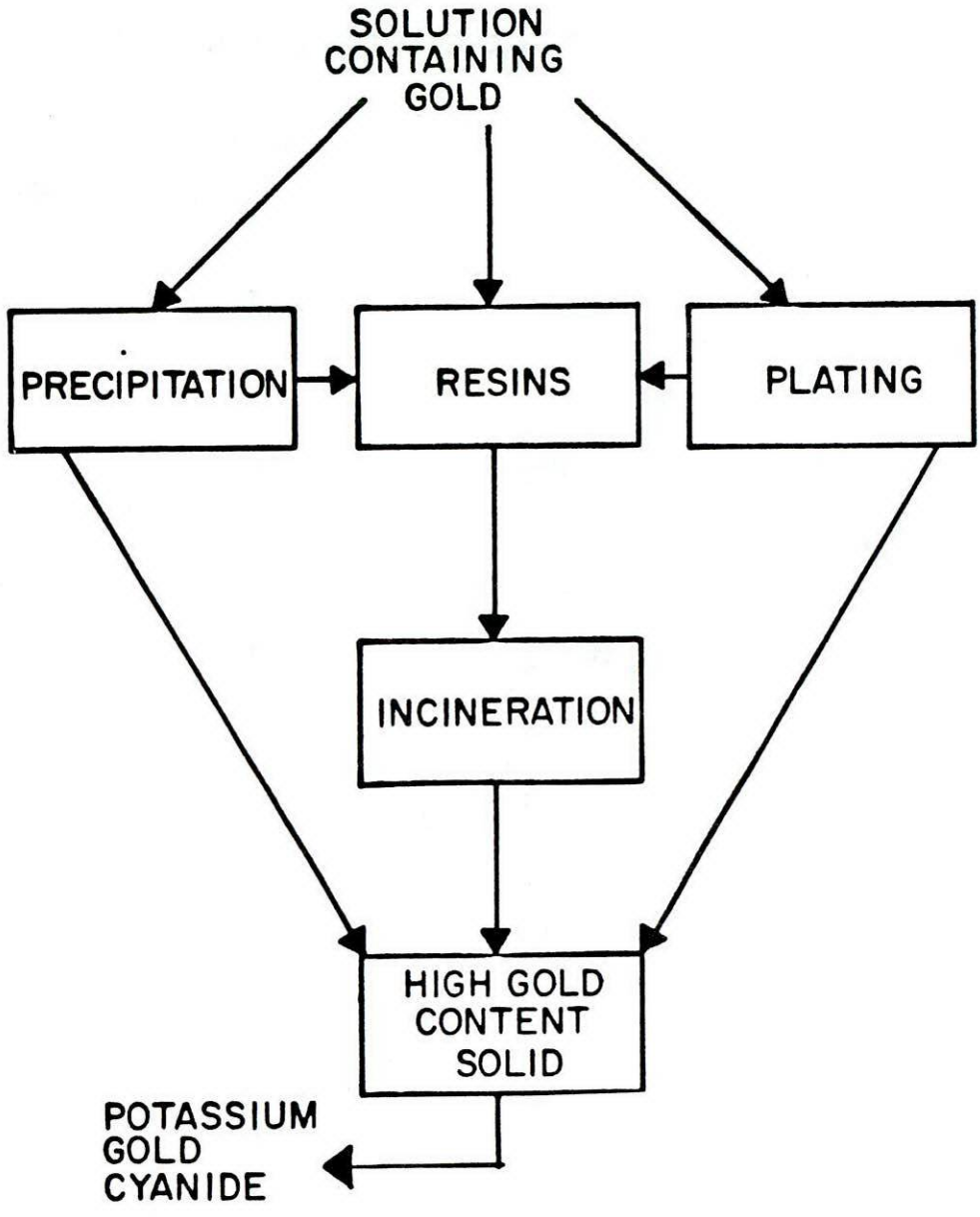

Figure 1 Present process scheme of recovering gold.

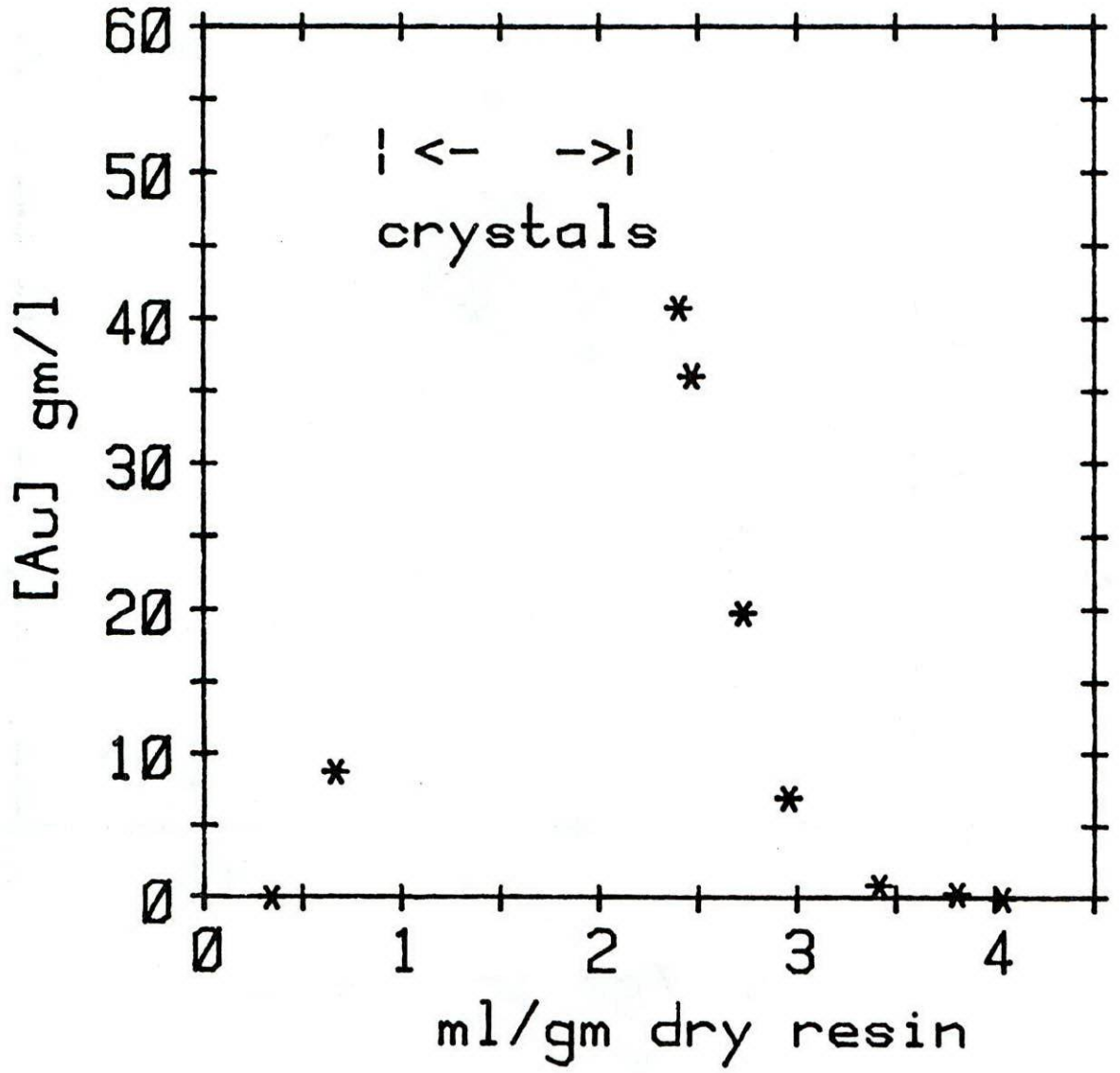

Figure 2 Gold concentration of the effluent versus eluent volume/gram dried resin, 50°C, 3.5 ml/min, 107 grams of dried resin (AMBERLITE IRA-900 OH).

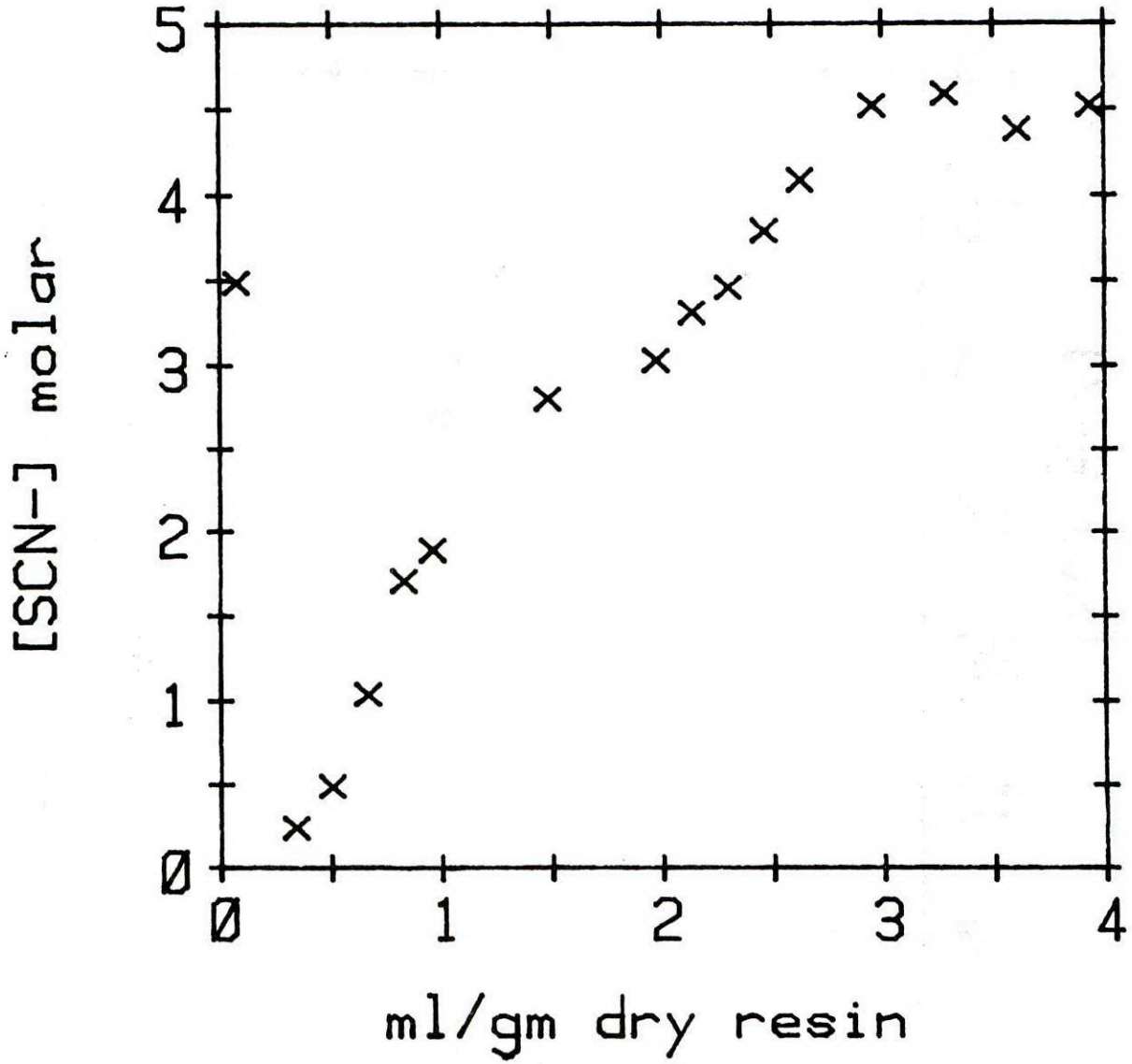

Figure 3 Thiocyanate concentration of the effluent versus eluent volume/gram dried resin, same column as Fig. 2.

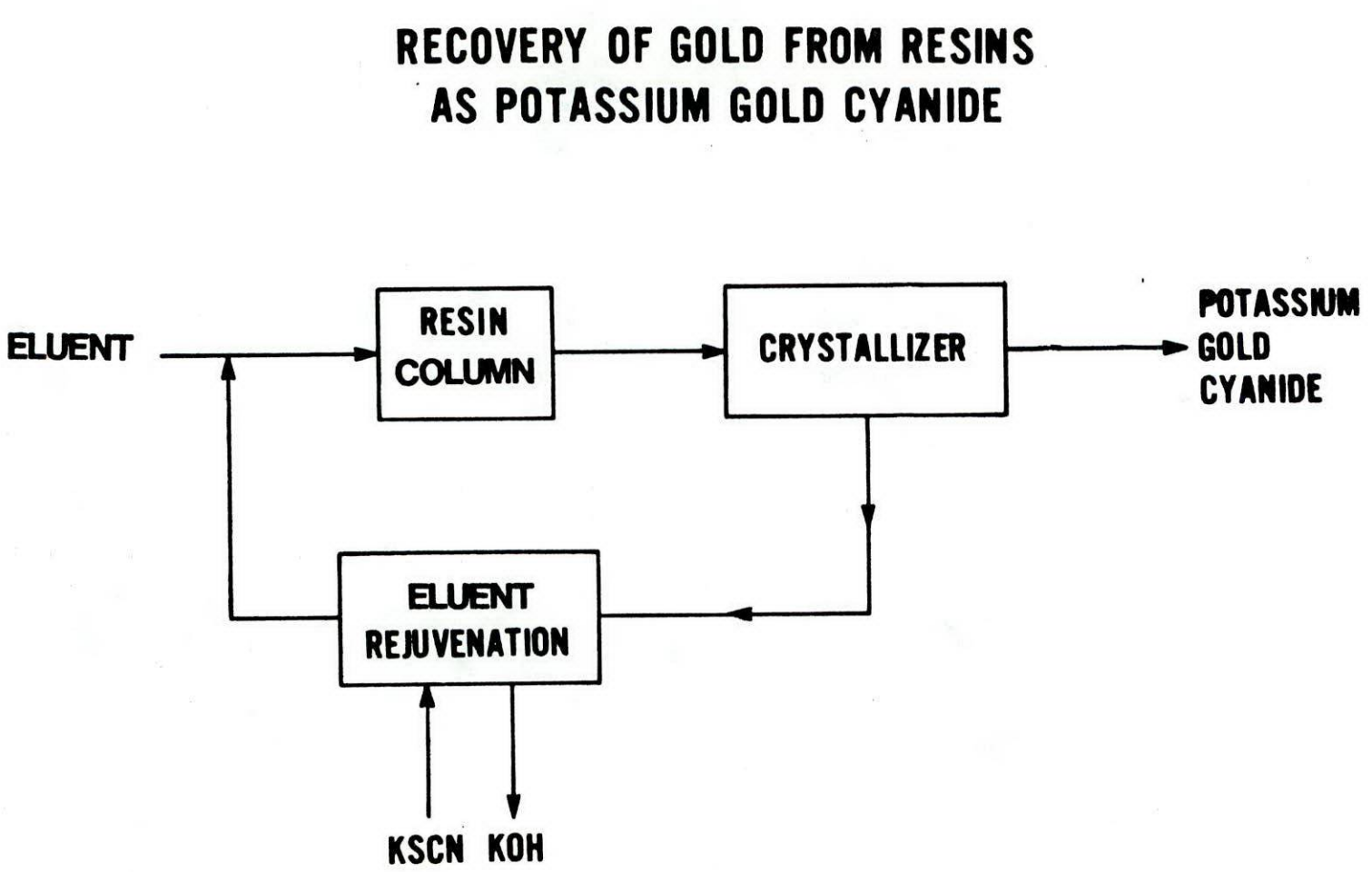

Figure 4 Proposed process scheme for recovering gold from solution as potassium gold cyanide.

F-2

Electronics II
Session F

Analysis of Organic Components in Copper Plating Baths by Liquid Chromatography

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Analysis Of Organic Components In Copper Plating Baths By Liquid Chromatography

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INTRODUCTION

While the copper plating of printed circuit boards is a straight-forward chemical operation in many installations, present and future computer boards require finer lines, higher aspect ratio of thru-holes and ever larger number of layers. A single load of multilayer substrates may be worth several tens of thousands of dollars at the stage when the thru-holes are plated, and loads lost through plating defects cannot be tolerated.

Improving the quality of acid copper plating evolves into a task of monitoring the chemical state of the plating bath. This is trivial with respect to the basic ingredients: $CuSO_4$ and H_2SO_4. The particularly difficult part is monitoring the low concentration level of organics that are added as plating modifiers and the extra contaminants that arrive by leaching or accident. Generally, the problem is further compounded by the proprietary nature of the additives and the fact that the actual active organics may be 1) decomposition products of the orignial additives, 2) impurities accompanying the additives, and 3) combinations of normally inactive constituents. In the past, even the additive manufacturers have had only a rough quality control over their productions.

Typically the Hull cell test is used to judge the state of a bath and its future performance. However, bath analysis must be considered at all steps: during plating, during clean-up, during conditioning and during storage. This paper shows how high performance liquid chromatography (HPLC) can be used to obtain information about the organic constituents in a acid copper bath.

HPLC TECHNIQUE

In its simplest form the HPLC technique involves pushing a small liquid aliquot of the sample through a fine particle material chosen to selectively retard components relative to the sample liquid front. The retarded components can then be detected by various means and even collected separately if desired.

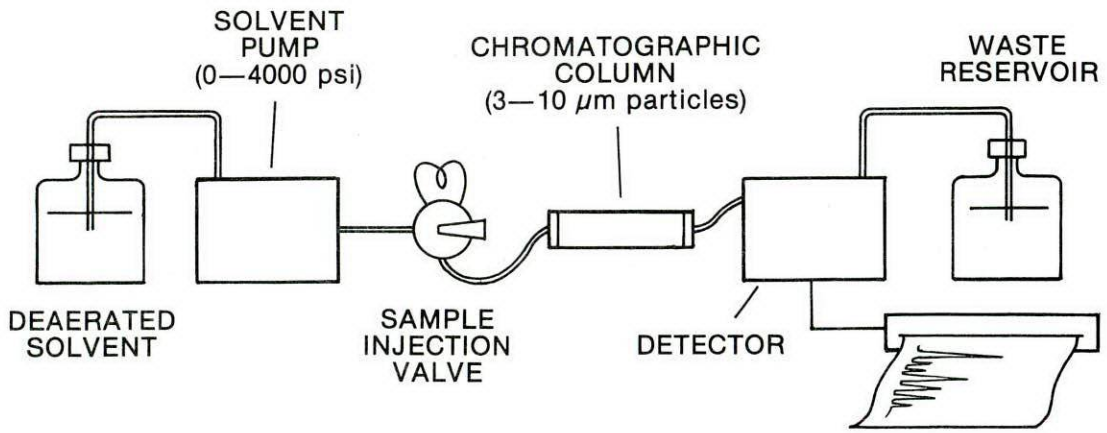

Figure 1. Components of a Typical High Performance Liquid Chromatograph

Development of an HPLC method for a particular analysis requires finding the best choice of solvent, column packing and detector based upon the starting material being analyzed. Since the starting additives are proprietary secrets and the decomposition products are undocumented, the preliminary HPLC investigation must be wide ranging in scope; several columns, solvents and detectors must be tried. HPLC cannot identify the molecular composition of a component without ancillary information from a standard or from other characterization techniques. This identification can be a very time-consuming and difficult task.

HPLC can provide an easy way of monitoring a component if conditions can be found to separate that component from the rest of the sample. Of all the components found in a bath, presumably only a few are critical to the quality of the deposit. Therefore once components have been detected by HPLC, they should be tested by an electrochemical technique to determine their effect on the plating. It would be best if only the important components could be monitored.

INSTRUMENTATION

The HPLC system used consisted of a high pressure pump*, an injector valve** with 200 μl filling loop, Z Module column holder***, a U.V. detector**** equiped with a 254 nm filter and a 10 mV strip chart recorder. The columns were #RPC18 bonded phase on 10 μm silica. Solvents were filtered and deaerated using a 0.2 μm filter. Samples of additives were filtered before injection into the HPLC system. Since the plating bath contains 10% H_2SO_4 which may be detrimental to the silica packing, the column was checked by frequently running a standard solution of an additive. The column was not seen to degrade significantly over the time of 100 injections.

PROCEDURES

Samples were run in the isocratic mode. Water was used to elute water-soluble components; then the system was flushed with acetonitrile to remove the more non-polar components. It was found that the acetonitrile had to be flushed out with at least 100 ml of H_2O in order to obtain reproducible retention times in subsequent sample runs.

Isocratic runs were made on pure additive formulations with 30% acetonitrile/ 70% H_2O to resolve components and obtain a total distribution of components. Addition of a paired-ion reagent was used to obtain better separation of peaks. Tetrabutylammonium tetrafluroborate was preferred; tetrabutylammonium phosphate could not be used because it forms insoluble copper phosphate species in the column.

RESULTS

This study was confined to using ultraviolet detection of components in the samples. The U.V. detector is selective for those compounds having significantly strong chromaphores at 254 nm. Peak height is dependent on both concentration and U.V. molar absorptivity and the latter is unknown for any of the single components in the samples used here. Consequently the chromatographic peaks should not be taken as a direct indication of sample concentration.

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**Waters Associates, Milford, MA
***Rheodyne Inc., Cotati, CA
****ISCO, Lincoln, NE

Figure 2 shows the effect of the paired ion reagent on the resolution of PCM-T***** components using the C18 column and 30% acetonitrile. The intense U.V. peak at 2.2 minutes is moved to around 5.3 minutes by the reagent. Thus this component is probably an anionic system that interacts strongly with the $(Bu)_4N^+$ ion. The other components show only small shifts and therefore are probably not anionic.

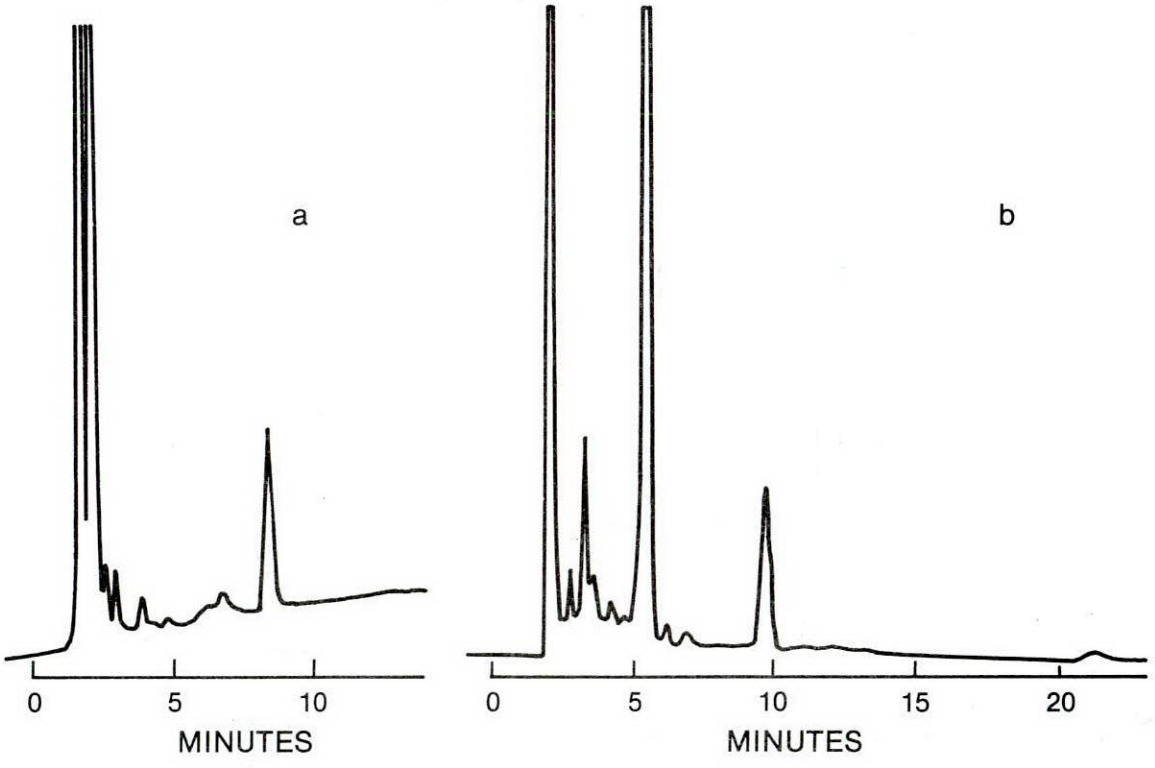

Figure 2. Chromatograms of Pure PCM-T, U.V. Detection:

a) 30% acetonitrite/70% H_2O, 0.2A full scale, 254 nm, C18 column

b) Same as A but with 0.1F paired ion reagent in eluent

Several components are particularly sensitive to detector wavelength. Figure 3 shows typical chromatograms taken at 254 and 280 nm. The components at 3.2 and 9.7 minutes are obviously strongly dependent upon the wavelength. Preliminary data from another U.V. detector system has indicated that additional peaks will appear if detection is done at 210—220 nm.

Several columns were tried in order to obtain as large a separation of components as possible. Figure 4 shows the results with an SCX column which has a bonded cation exchange functional group on silica. Water elution gives high resolution but the peaks are asymmetric indicating a particularly strong component interaction with the stationary phase. Increasing the acetonitrile content of the mobile phase decreases the retention time and resolution of all the components. The general conclusion was that the SCX column offered no distinct advantage over the C18 column.

*****LeaRonal, Freeport, NY

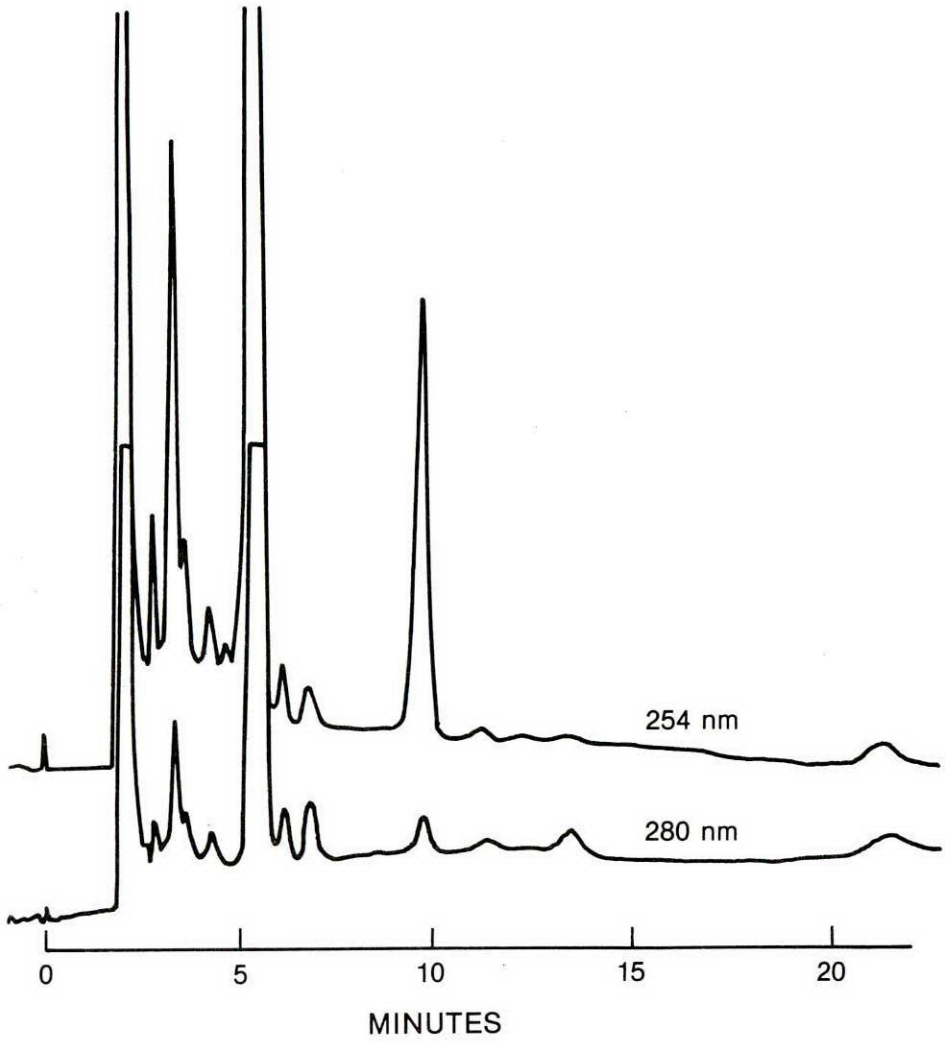

Figure 3. Chromatograms of Pure PCM-T at Two Wavelengths:
a) 254 nm
b) 280 nm

One of the operations in the management of production baths is carbon treatment to remove impurities and reestablish a "clean" bath. Figure 5 shows the effect of carbon treatment done on a laboratory scale on a diluted pure additive sample to determine which components are sensitive to absorption. Only 10 minutes was allowed for the treatment before the sample was filtered and injected into the HPLC system.

As can be seen the peaks above 5 minutes showed considerable changes, whereas the presumably polar components (below 5 minutes) showed little or no reduction in intensity on carbon treatment. It is not surprising that the less polar compounds would be more sensitive to carbon treatment. It indicates that carbon treatment may not remove all the components. Apparently additional chemical treatments often used prior to carbon treatment are needed to affect the more polar components. It is apparent from Figure 5 that the completeness of carbon treatment can easily be monitored by HPLC measurements.

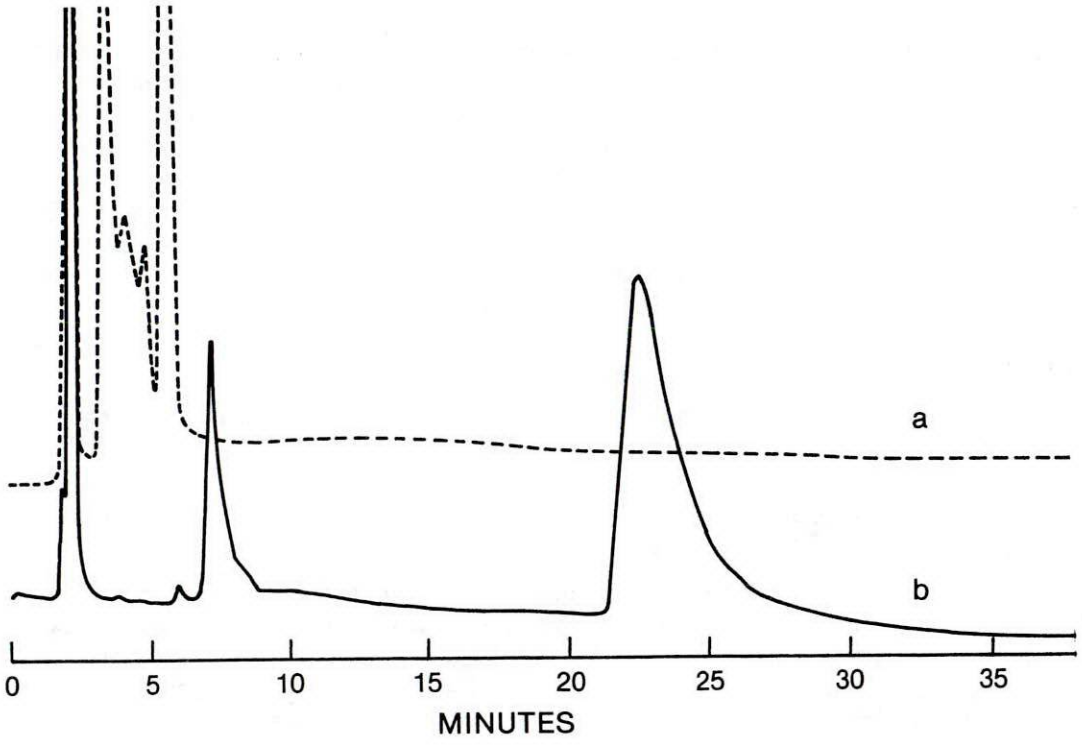

Figure 4. Chromatograms of pure PCM-T on a Cation Exchange Column:
a) 50% acetonitrile/50% H_2O, 254 nm, 0.2A full scale
b) 100% H_2O, 254 nm

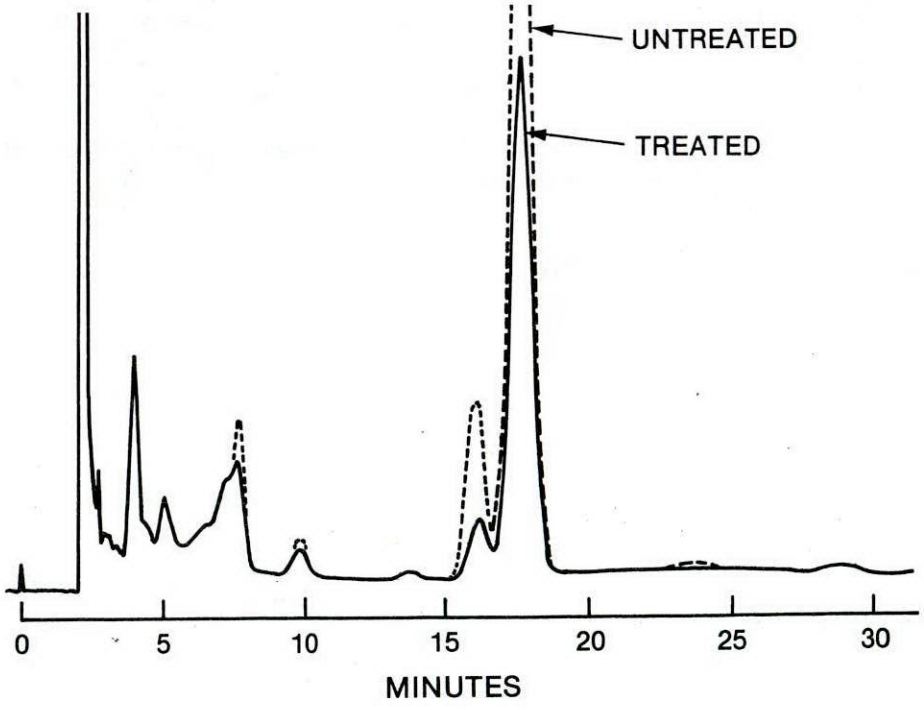

Figure 5. Chromatograms of Carbon Treated and Untreated 50% PCM-T, 254 nm, 0.05A full scale

Analysis of samples from actual production baths has centered upon the water elution fractions. Figure 6 shows several typical chromatograms. Samples contained $CuSO_4$ and H_2SO_4 in the usual concentrations and PCM-T nominally at a level of 4 ml per liter of bath solution, but actually much higher based on cyclic voltammetic methods [1]. The peak at 5 minutes in these solutions comes from the original PCM-T. This PCM-T peak changes in intensity with use and processing of the bath. Significantly the peaks between 2 and 5 minutes in the production bath are absent in pure PCM-T. These may be indicators of the amount of additive decomposition that has occurred in using the bath. Just before carbon treatment these peaks are very intense. They are reduced significantly by chemical and carbon treatments and then build up again upon adding brightener and using the bath.

Figure 7 shows samples from a bath which was not behaving correctly, following a carbon treatment. Surprisingly, no additive peaks showed up in this bath when brightener was added or after plating resumed. These HPLC results clearly show that the additives had not been brought up to the levels existing prior to the carbon treatment cycle.

Separation of the sample components into fractions make it possible to study the electrochemical behavior of each component or group of components. A preliminary study of the cyclic voltammetry of the HPLC water-eluted components has been done. When $CuSO_4$ and H_2SO_4 was added to the water-eluted fraction and subjected to cyclic voltammetry, no copper deposition suppression was found. This indicates that the HPLC water fraction components and the CV suppressors are different species in the plating baths.

CONCLUSIONS

The water eluted, U.V. detected, HPLC technique measures one of the components in the original PCM-T (the 5 minute peak, Figure 6) and a group of polar compounds (below 5 minutes) which are absent in PCM-T but present in production tanks. A third group, the copper-deposition suppressors, are monitored independently by CV.

(1) W. O. Freitag and M. Manning, "Analysis of Additives in Acid Copper Baths by Cyclic Voltammetry" in these preceedings.

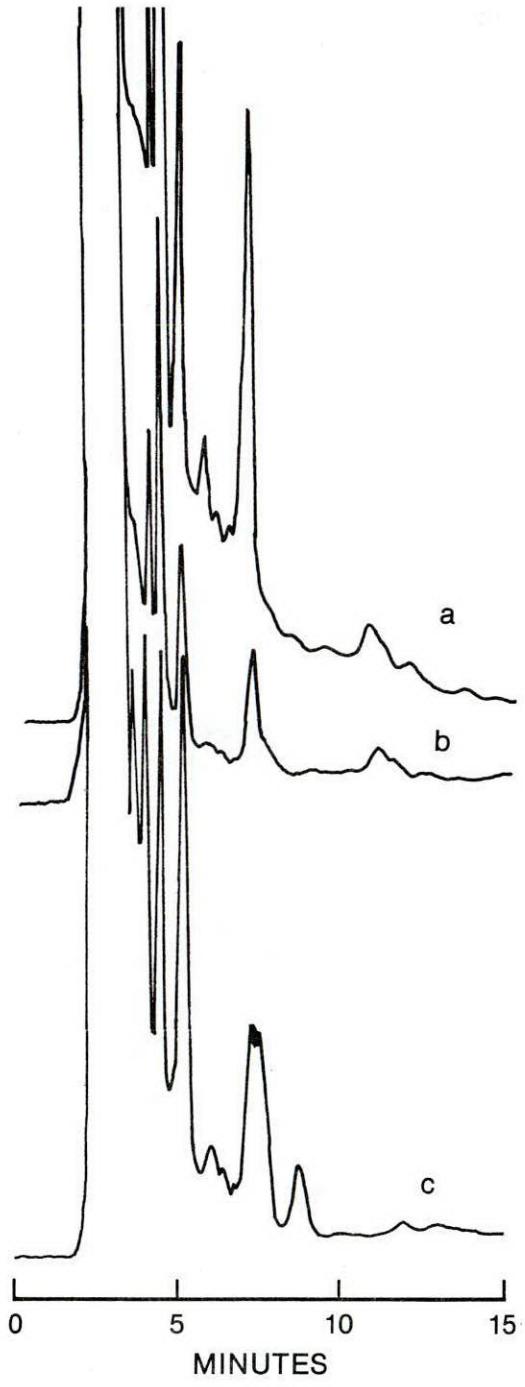

Figure 6. Chromatograms of H_2O Elution Fraction of Production Bath Samples:

a) Bath after long period of use

b) Bath after typical clean-up treatment

c) Bath after put back in use

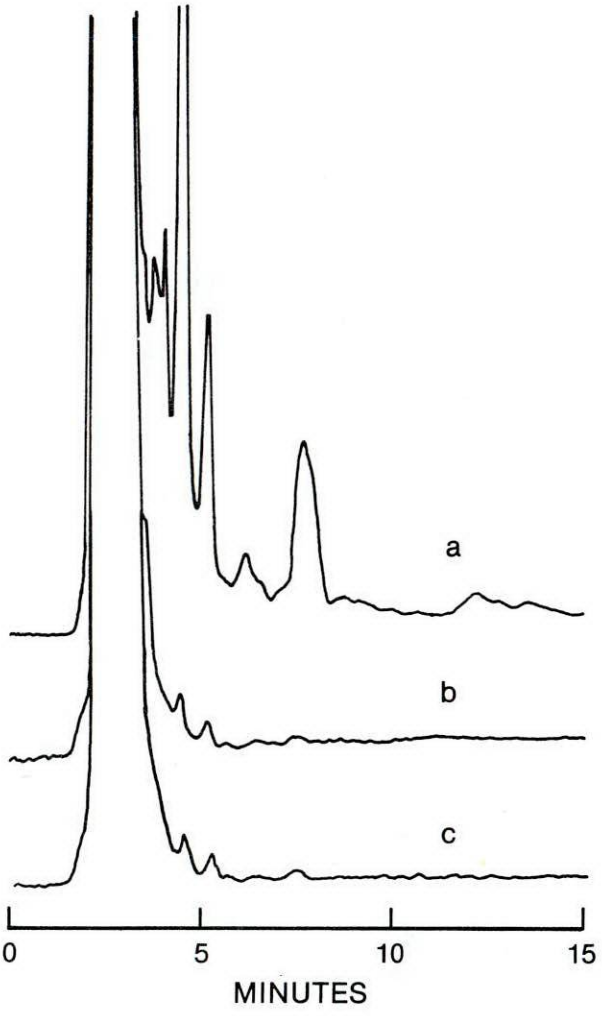

Figure 7. Chromatograms of H_2O Elution Fraction of Production Bath Sample:

a) Bath after long period of use

b) Bath after cleanup

c) Bath put back into use but malfunctioning

F-3

Electronics II
Session F

Multi-Test Capability of Plating Parameters Using a Continuous Flow Analyzer

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MULTI-TEST CAPABILITY OF PLATING PARAMETERS USING A CONTINUOUS FLOW ANALYZER

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Tarrytown, NY 10591

Introduction

Analytical chemistry is a science of measurement that affects every technical discipline, whether it be for process information, quality control or to satisfy government regulations. The analytical requirements will vary with respect to need from infrequent individual analyses to continuous on-line monitoring of critical parameters.

The plating industry is no exception. Analysis of key parameters and plating contaminants continue to be of moderate concern. Depending upon the particular need, the kinds of analyses and total number, will vary considerably in scope and whose workload cannot be predicted in advance. To obtain maximum efficiency in the laboratory flexibility of procedures is most important.

Laboratory management must weigh the quality of data needed against factors influencing the cost of obtaining them. Further, other criteria must be satisfied for an approach to qualify in handling a variable, unknown workload. Qualifications are:

- high analysis rates to process samples quickly
- excellent precision and accuracy
- highly-selective methods to meet individual requirements
- wide spread use to establish validity through round-robin sample analysis and controls.

In addition, the methodology that is used, emphasis must be placed on the:

- type of analyst required
- laboratory environment.

To meet the above stated criteria, instrumental methods are always preferred because of its inherent objectivity. More specifically, continuous flow analysis provides the additional wherewithal to automate wet-chemical procedures. Flexibility of the analyzer is accomplished by changing the metering of reagents specific for a particular assay by a low-cost pump tube harness.

Experimental

The multi-test continuous flow analyzer consists of the following basic modules: sampler, pump, colorimeter, recorder, and multi-test cartridge. The physical arrangement of these modules is schematically represented in Figure 1.

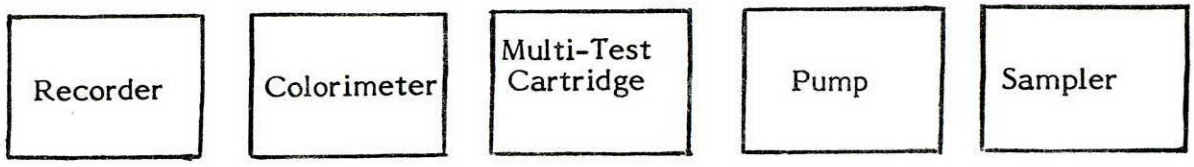

Figure 1. Schematic Representation of the Multi-Test Continuous Flow Analyzer

Samples and standards to be analyzed are placed on the turntable of the sampler which is then automatically sequenced into the analytical system. The pump via its pump tube harness continuously meters reagents into the multi-test cartridge where the wet-chemical reaction takes place. The absorbance of the chromogen that is produced is measured by the colorimeter and the results are displayed on the strip chart recorder. With appropriate calibration of the system by using standards, the results are read directly off the recorder and simultaneously provides a permanent record.

To convert the analyzer to accommodate another test only the pump tube harness located in the pump along with the optical filter in the colorimeter must be changed. Each harness is specific for each assay. The sequence of events that follow when an assay is completed is to first cleanse the system with water, remove the pump tube harness, replace it with the next harness of interest, and allow the reagents time to equilibrate in the analyzer. The system is now ready to test for the next parameter. The changeover time requires an elapsed time of approximately 25 minutes of which only 5 minutes are required to change the pump tube harness.

The pump tube harness and multi-test cartridge interface is schematically represented in Figure 2.

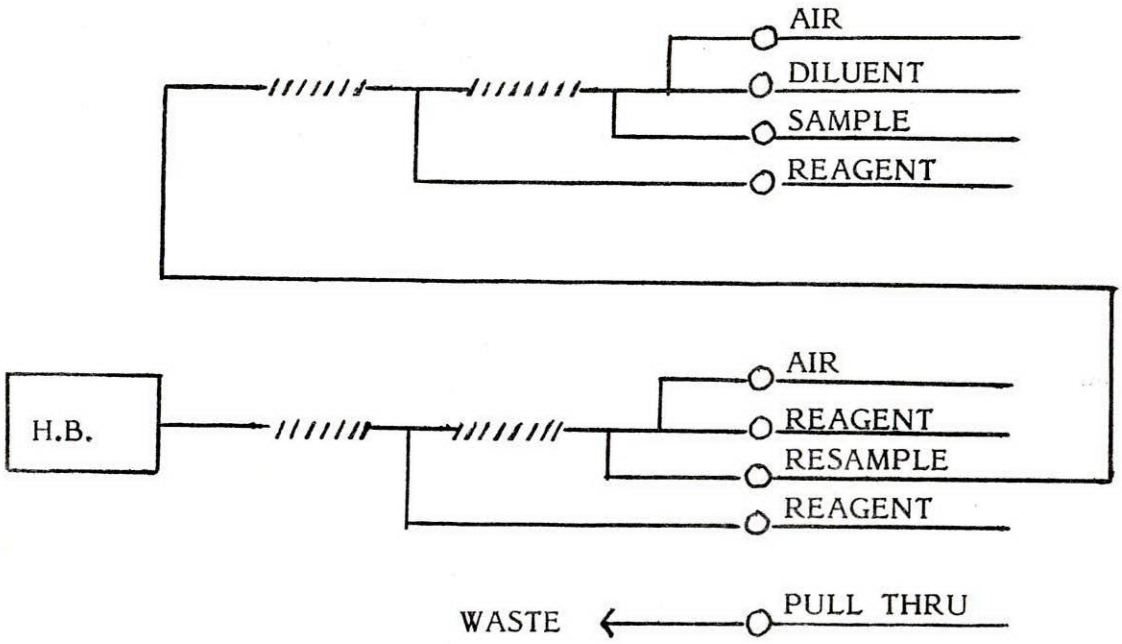

Figure 2. Interface of Pump Tube Harness and Multi-Test Cartridge

Discussion

Presently there are a total of 19 different parameters covering a wide concentration range. Table I lists these parameters in their respective baths. Several of the bath parameters require manual pretreatment. The pretreatment is necessary because of the following:

- dilution to meet the stoichiometric needs of the multi-test cartridge
- prevent precipitation
- maintain oxidation-reduction states.

Based on a workload of 50 samples and 10 standards, an analyst can perform a total of six (6) different assays in an eight (8) hour day. All the assays exhibit a coefficient of variation of $\pm$ 1% or less.

Conclusion

The multi-test continuous flow analyzer provides a highly flexible system to perform many different types of plating bath related analyses. The flexibility is accomplished by replacing pump tube harnesses that are specific for each analysis along with the optical filter. The pump tube harness is a low cost item that is treated as a disposeable item after 200 hours of use.

Change over time takes approximately 25 minutes and as many as six assays can be accomplished in one day based on a workload of 50 samples.

Table I. Parameters Applicable to the Multi-Test Continuous Flow System

PARAMETERS	RANGE	BATH	HEAT BATH / WAVE LENGTH		COMMENTS
1. Acid	.25-25% HCl	Regeneration	RT	520	
2. Acidity	.06-3.0%	Acid/Persulfate	RT	550	
3. Chloride	60-120mg/L	Copper-Dye	RT	480	10 fold dilution with reagents
4. Copper	1-10%	Cyanide Brass	RT	590	
5. Formaldehyde	.2-10 g/L	Electroless Copper	45°C	560	Dilution with reagents
6. HCl	3-10% v/v	Immersion Tin	RT	520	Manual 1:5 Dilution with water
7. Na Carbonate	1.-50 g/L	Carbonate Bath	RT	600	
8. Na Chlorite	1.6-80 g/L	OH/Chlorite	RT	480	No dilution
9. NaOH	.1-8.0 g/L	OH/Chlorite	RT	600	
10. Na Silicate	1.6-80 g/L	Silicate Bath	RT	550	
11. Palladium	1.2-2.6 g/L	Proprietary	RT	550	Manual dilution 1:20 with reagents
12. Palladium	0.02-0.2 g/L	Regeneration	RT	470	
13. Persulfate	100-140 g/L	Acid/Persulfate	37°C	450	
14. Tin II	80-150 g/L	Proprietary	RT	660	Manual dilution 1:20 with reagents
15. Tin II	0.5-55 g/L	Regeneration	RT	450	
16. Total Tin	42-80 g/L	Proprietary	37°C	520	Manual dilution 1:20 with reagents
17. Total Tin	.0-14 g/L	Immersion Tin	37°C	520	Manual dilution 1:20 with reagents
18. Total Tin	20-40 g/L	Regeneration	37°C	520	Manual 1:10 dilution with reagents
19. Zinc	.2-2.0%	Cyanide Brass	RT	620	Manual dilution 1:15 with reagents

F-4

Electronics II
Session F

Analysis of Additives in Acid Copper Baths by Cyclic Voltammetry

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Analysis of Additives in Acid Copper Baths by Cyclic Voltammetry

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INTRODUCTION

The control of additivies and contaminant concentrations in acid copper baths for multilayer printed circuit boards has been an elusive goal. The traditional means, such as Hull cell plates or "J" cell tests, are insufficiently precise and frequently yield misleading results. A major difficulty is that the additive systems consist of mixtures of proprietary materials, the individual components of which are not necessarily pure components and may themselves vary in strength or activity from lot to lot. The mechanisms by which the additives achieve their beneficial results are usually not known by the plater, and frequently not even by the vendor. The components are consumed or converted at different rates as a bath is used so that continued addition of the complete mixture may result in a gradual build-up of one of them until it is far out of proportion with respect to the others. Furthermore, some additive species are converted by oxidation or reduction at the electrodes to other species which also affect brightness, leveling, or mechanical properties of the deposits. And added to these are whatever other compounds are introduced accidentally into the plating bath such as photo-resist leachates.

The work reported here was done as part of a major effort involving research and production personnel to provide analytical methods using cyclic voltammetry (CV), HPLC, and other techniques.

A very attractive approach to this complex situation has been proposed recently by Tench and co-workers who applied CV at a rotating disk electrode (RDE) to the measurement of brightener concentration in pyrophosphate [1,2] and acid copper baths [3,4]. The assumption is made that those species responsible for brightening or leveling action are also active in a CV scan. Briefly, their method consisted of cycling a platinum RDE between a cathodic voltage just below where copper begins to deposit, to an anodic limit determined by the nature of the additive system. An anodic current peak is obtained which represents the dissolution of the copper deposited during the cathodic part of the cycle. This peak is integrated and its area, A_r, obtained while the RDE is rotating, is compared with the area obtained when the RDE is stationary, A_s, in the same sample of solution. The ratio A_r/A_s was found to correlate well with additive concentrations in freshly made-up (virgin) solutions.

Applied to production solutions, the method is more successful with pyrophospate than with acid copper solutions. With pyrophospate baths, additional information about the chloride ion concentration and the level of organic contaminants can be obtained by recording anodic currents in other parts of the voltage scan. A dedicated microprocessor-controlled instrument has been developed to carry out this analysis and is available commercially.*

This method has also been recommended for acid copper solutions using both polyether-sulfide-based additives [3] and sulfonium alkanesulfonate (SAS) additives [4]. But when applied to production solutions using these additive systems, it became apparent that contaminants and/or conversion products dominated the CV results. Correlations could not be made between data on production samples and calibration curves made on virgin baths. Modifications to this approach were necessary before information useful to plating line management could be obtained.

EXPERIMENTAL

Most of the measurements described here were made using the Qualiderm* instrument and the RDE assembly supplied with it. Additional experiments were made using an IBM** rotating disk electrode. The RDEs were fitted with platinum disks 4 mm in diameter which were pretreated by repeated cycling in additive-free copper bath (with chlorides). The "dilution-titration" experiments were done using the cell assembly shown in Figure 1. The microburette shown was often replaced by a micropipette for making additions to the Test Solution.

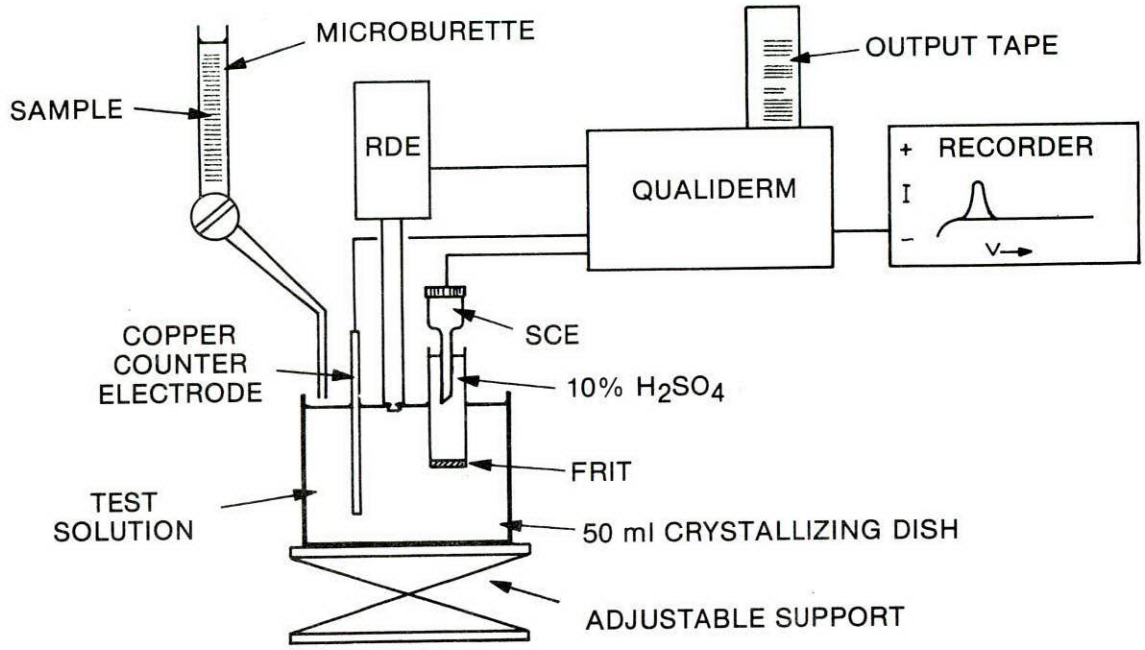

Figure 1. Test Cell for Dilution-Titration Procedure

The additive systems studied were Copper Gleam PCM*** which is an SAS-type system, and Cubath M-HY,**** a sulfide-polyether type.

The dilution-titration is carried out as follows: 25.00 ml of Test Solution is added to the test cell and the electrodes are immersed. The Test Solution was usually additive-free acid copper bath such as Cubath M make up or equivalent. The copper sulfate and sulfuric acid concentration closely matched those used in production. The chloride level was 60 ppm. The Qualiderm is set in the mode in which it continuously cycles between its voltage limits while printing out the value of A_r for each cycle. RDE speed is 2500 RPM. The anodic voltage limits are set at +1.9V SCE for M-HY and +1.6V SCE for PCM. The scan rate is 200 mV/sec. The negative voltage limit is set so that the starting Test Solutions displays an A_r value of 10 milli-Coulombs (± 10%); usually this is around −0.2V SCE. In this way, an A_r value is printed out about every 20 sec.

This initial A_r reading, before adding any Sample, is designated A_{ro}. The A_{ro} values become stable in less than 5 CV sweeps. Then increments of Sample are

* (Qualiderm™) UPA Technology, Syossett, NY
** IBM Instruments, Inc., Danbury, CT
*** LeaRonal, Freeport, NY
**** Sel-Rex, Nutley, NJ

added and a new A_r is read. Conveniently, 5 A_r values are printed for each increment (with some notation being made on the output tape at each increment) and the fifth value is taken as the data point. Additions are continued until A_r falls below 1 or 2 mC. A_r values are then normalized to A_{ro} and A_r/A_{ro} is plotted against volume of Sample added. (Linear or semi log paper can be used.) The end-point is taken as the volume where $A_r/A_{ro} = 0.50$. The entire procedure takes 15 to 20 minutes.

CALIBRATION CURVES WITH VIRGIN SOLUTIONS

The amount of copper which is deposited in the cathodic part of the cycle is sensitive to the amount of additive mixture added to the test solutions. At least one of the components of the mixture suppresses the deposition of copper, so that less copper is available for dissolution during the anodic part. This has been shown by Ogden and Tench for the polyether-sulfide system [3]. In their calibration curve, A_r/A_s decreases (after a slight initial rise) as the suppressing species is added. In this region of concentration for the M-HY system, A_s changes little because when the electrode is stationary, the amount of suppressor at the electrode surface is diffusion limited and is practically nil, so $A_s \cong A_{ro}$. Thus, curves for A_r/A_{ro} vs. volume of additive are essentially identical to plots of A_r/A_s.

In the PCM system, the suppressor is either far more active or far more concentrated in the solution supplied by the vendor. Small amounts immediately supress Cu deposition to very low values. Further additions result in a very slight increase in A_r. [4] When the initial PCM additions are on the order of microliters per liter, rather than ml/l, the suppressive effect can be shown clearly. The two additive systems produce very nearly the same shape of curve as shown in Figure 2.

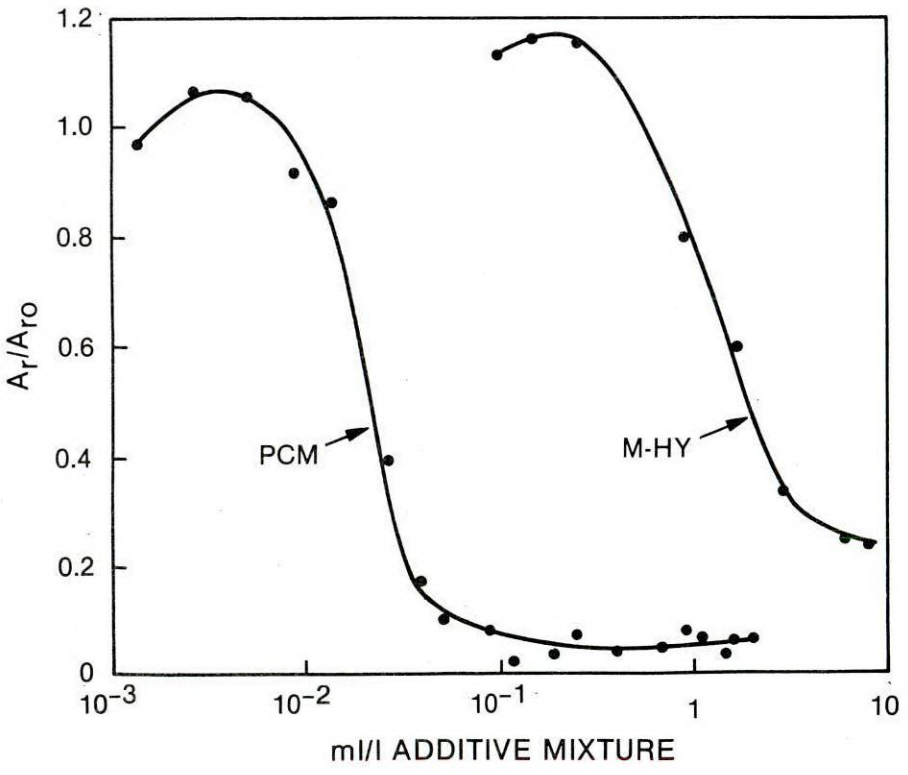

Figure 2. Calibration Curves for PCM and M-HY Additives.

Thus the copper deposition suppressors in both the PCM and M-HY additive systems apparently behave in basically the same way, but in different concentration ranges. It is not possible, of course, to distinguish a very active suppressor at low concentrations from a mild supressor at high concentration by this CV technique alone. As suppressors reach the RDE in increasing amounts, the amount of copper deposited, and hence A_r, decreases until the electrode is saturated. After this the electrode is relatively insensitive to further supressor activity until other, presently undefined, mechanisms come into play.

Therefore, the only analytically useful information is contained in that part of the curve where supression is going on, but is not yet saturated. Experience has shown that A_r/A_{ro} values are not readily reproducible in the high range (0.9 to 1.1) nor in the low range (0 to 0.2). Therefore, the end point is selected as that value for which the electrode is half-saturated, i.e., when $A_r/A_{ro} = 0.5$. The effective suppressor concentration in the samples is then proportional to the reciprocal of the amount of Sample added to the Test Solution, that is:

$$\text{Effective Concentration} = \left| \frac{V + X_{1/2}}{X_{1/2}} \right.$$

$$EC = \left| \frac{25}{X_{1/2}} \right. \quad \text{for Small X}$$

where V is the Volume of Test Solution at start and $X_{1/2}$ is the Volume of Sample added when $A_r/A_{ro} = 1/2$ as read from the plot.

Figure 3 shows EC values obtained when virgin solutions containing the indicated amounts of PCM or M-HY are used as Samples for a dilution-titration performed according to the method outlined in the Experimental Section. Straight lines are obtained which pass through the origin. The reproducibility of the EC values obtained in this way is ±10% or better. The effective concentration value can be considered as a number proportional to the product of the concentration of a suppressor and its "activity" or efficiency as a suppressor.

EFFECT OF MASS TRANSPORT

The amount of suppressive activity seen at the RDE is a function not only of the amount of suppressor present in the bulk of the Test Solution and its efficiency, but also of the rate of mass transport of that species to the electrode surface. The mass transport rate was varied in one experiment by varying the speed of rotation of the RDE. For this purpose, an IBM electrode was substituted for the UPA assembly on the instrument and its speed was varied from 0 to 5000 RPM (524 rad/sec). Additive-free Test Solution was titrated with PCM and the family of curves shown in Figure 4 was obtained.

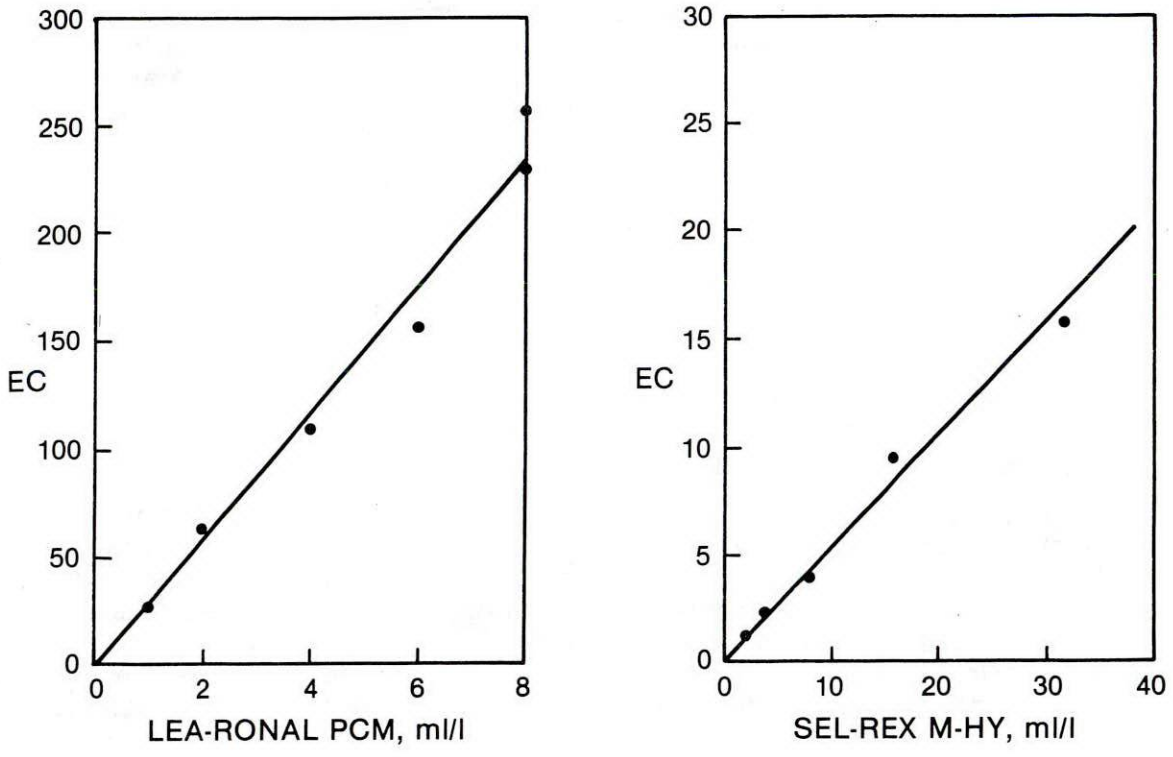

Figure 3. Effective Concentrations (EC) as Determined by Dilution-Titrations for Virgin Solutions at Various Additive Levels.

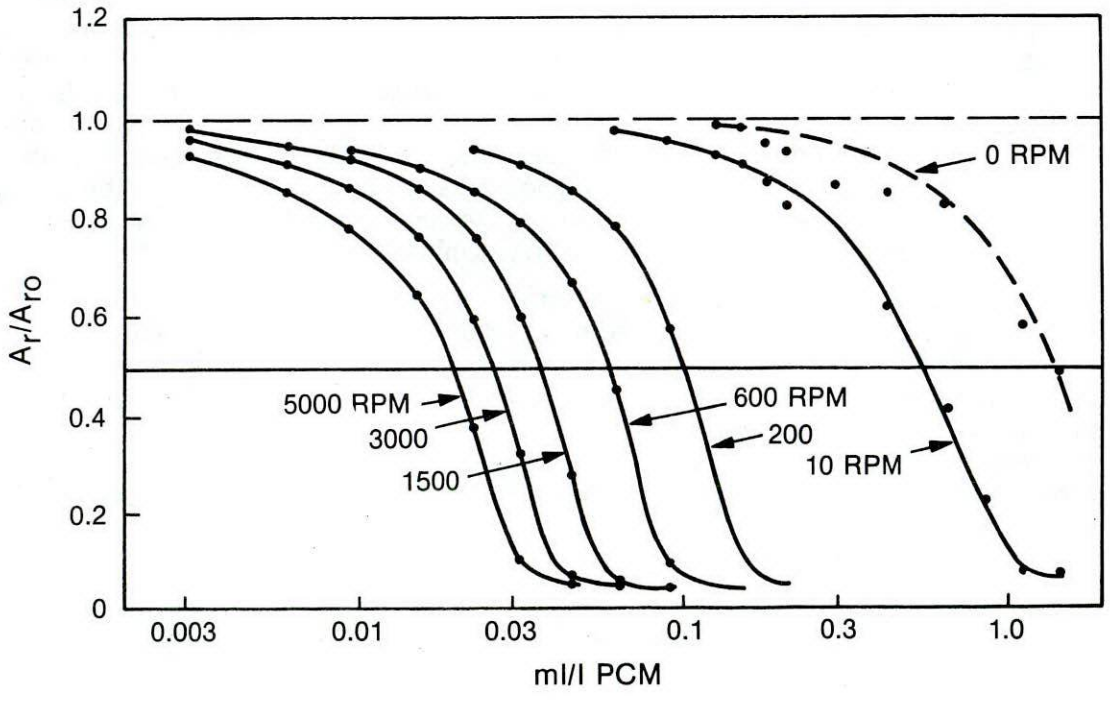

Figure 4. Effect of Electrode Speed on Calibration Curves for PCM Additive Mixture

According to the Levich equation, the rate of mass transport of a species to a RDE surface is proportional to the product $c_o \omega^{1/2}$ where c_o is the concentration of the species in the bulk of the solution and ω is the angular velocity. Therefore, for equal mass transport rates, $c_o \omega^{1/2}$, or $c_o(RPM)^{1/2}$, is a constant. For each curve in Figure 4, the value of c_o was read at $A_r/A_{ro} = 1/2$:

RPM	c_o for $A_r/A_{ro} = 1/2$ from Figure 4 - ml/l	Relative Mass Transport Rate - c_o (RPM) $^{1/2}$
0	1.4	—
10	0.56	1.77
200	0.103	1.46
600	0.060	1.47
1500	0.037	1.43
3000	0.026	1.42
5000	0.0196	1.39

Their product is seen to be reasonably constant across the RPM range. This shows that the concentration at which $A_r/A_{ro} = 1/2$ is a good measure of the concentration of the major suppressive species present, when measurements are made at constant RPM. At 10 and 0 RPM, there is a transition from rotating disk diffusion kinetics to planar diffusion: here mass transport no longer drops off as predicted by the Levich equation, and the $c\omega^{1/2}$ product rises. Planar diffusion is strongly affected by residual currents around the electrode. Their effects predominate at these low speeds and are also reflected in the increased scatter of the data points in Figure 4.

APPLICATION TO PRODUCTION SOLUTIONS

Samples were taken from active production line tanks at three plant locations over a period of several months and the EC values were determined by the above procedure. In two cases the monitoring period straddled a carbon treatment cycle. The two tanks represented in Figure 5 were operating with the PCM system, but at 2 different nominal PCM levels. (Note the difference in vertical scales). Actual levels of EC are 4 to 5 times higher in aged production baths than in a virgin solution at the same nominal PCM level. The removal of CV active species by carbon treatment is clearly evident. The first data point following the carbon treatment is the EC after bringing up the brightener level and fully dummying the tank, ready for production loads. Even in this initial "fresh solution", EC level is twice the nominal make-up level.

The situation is similar for a tank using Cubath M-HY as shown in Figure 6, the EC level rises with bath usage. EC values in this additive system are typically much lower than those for PCM. This bath had been carbon treated two weeks before the start of the monitoring period. It also experienced a period of partial shut-down late in July. Presumably the dip in EC values during that time indicates that CV-active species somehow are lost during idle periods; this is consistent with platers' experience that many tanks need an extra shot of brightener after an idle week-end.

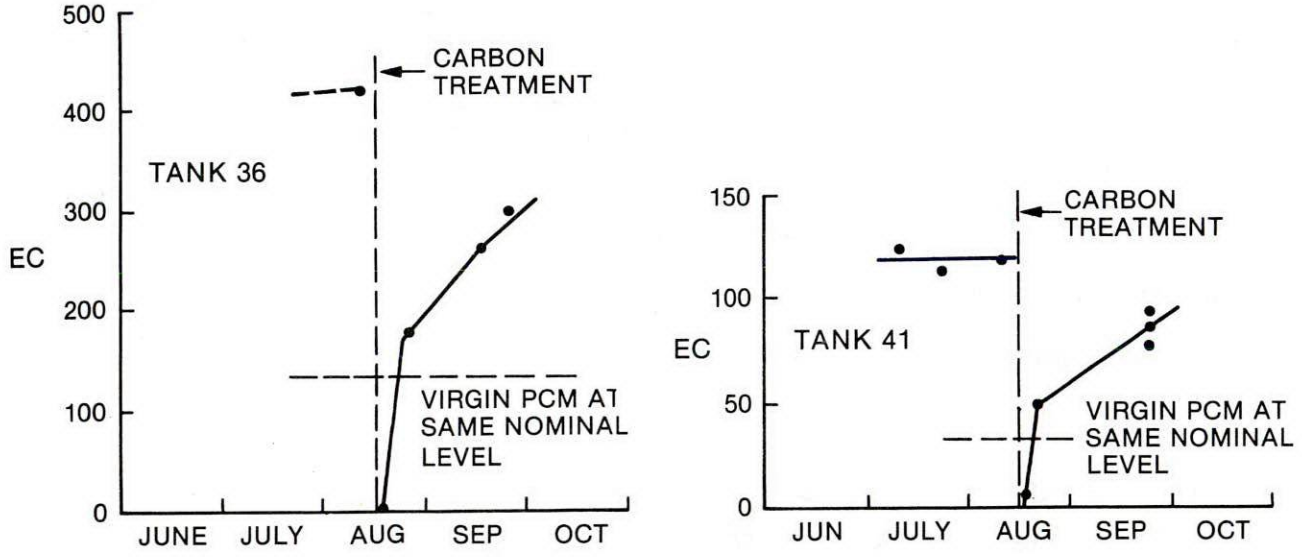

Figure 5. EC of Solutions from Production Tanks using PCM System Determined by Dilution-Titration.

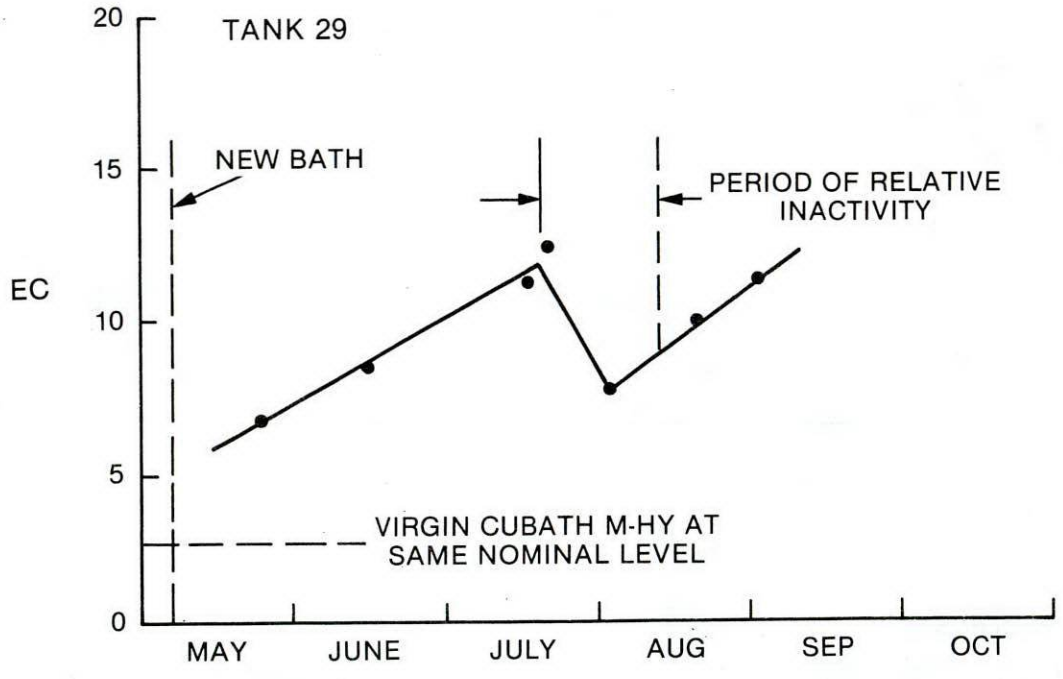

Figure 6. EC of Solutions from Production Tanks using a Cubath M-HY System Determined by Dilution-Titration.

The species which accumulate and contribute to suppressor activity in production tanks are apparently longer-lived than the original species added with the brightener mixture. The depletion of CV-active components was followed in the laboratory by prolonged plating without brightener replentishment. The CV activity of a virgin PCM solution was monitored by performing a dilution-titration every half hour while the solution was being electrolysed at 2 A in a 250 ml. Hull cell. The drop in EC with time is evident in Figure 7. When the experiment was repeated using samples from the production line, suppressive action did not diminish measurably during the three-hour test. However, the appearance of the Hull cell cathodes showed that brightening action was diminishing during this time. Thus some species responsible for the brightening of the deposits were being consumed even though the major copper deposition suppressors were not.

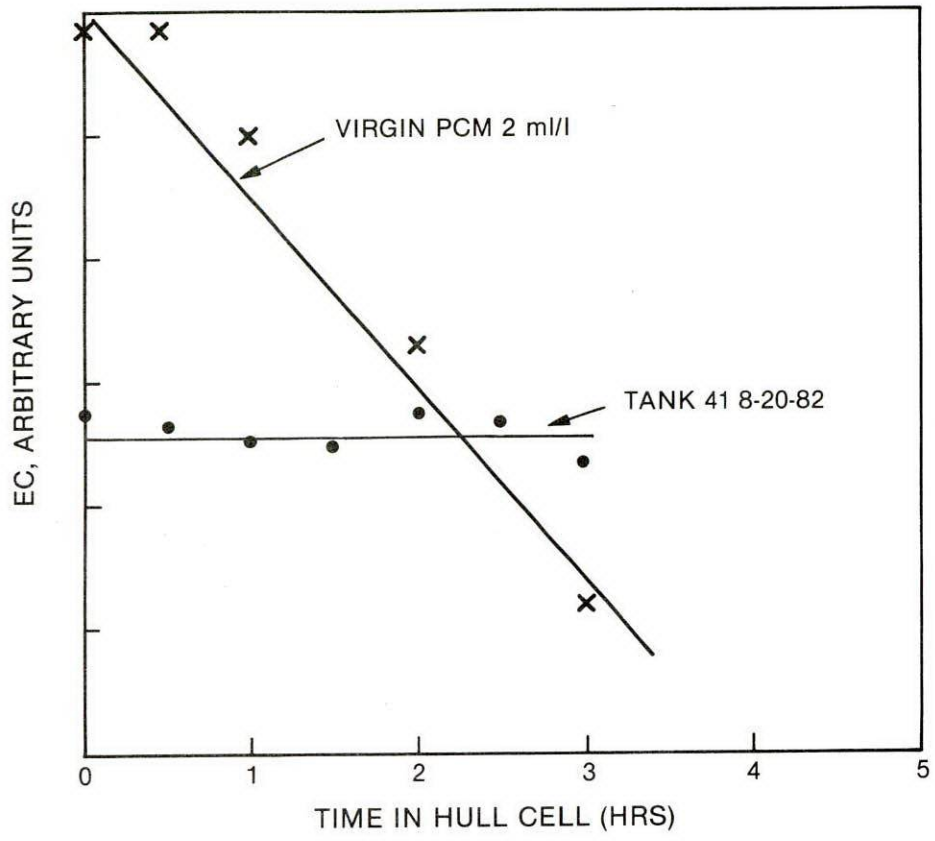

Figure 7. Depletion of Suppressors in Hull Cell Tests at 2A.

CONCLUSIONS

Cyclic voltammetry using essentially the test conditions described by Ogden and Tench can provide useful information about acid copper production baths if measurements are made at copper suppressor levels where changes in A_r are rapid with changes in concentration; i.e., on the descending part of the curve. This can be accomplished rapidly and conveniently by titrating an additive-free reference Test Solution with the unknown Sample and determining the point at which copper deposition is cut in half. The reciprocal of the volume added at this point is proportional to the effective concentration of copper deposition suppressors in the unknown.

The EC value so determined is useful in monitoring the build-up of copper suppressors which has been found to occur during use of a production bath. This should prove useful in correlating suppressor levels with board quality, in predicting the need for carbon treatment and in determining whether or not the carbon treatment is complete. The latter use is especially advantageous when more efficient carbon treatment procedures are being sought.

Production baths differ from freshly made-up baths in that they apparently contain "conversion products" from reaction of some of the original additive components at the electrodes. Some of these products are themselves copper suppressors, contribute to the EC, and are more slowly consumed than the original components.

An alternate explanation of the observed behavior is that a copper-suppressing species is not depleted with use at all, or depleted only slowly with respect to the other additive components, and simply accumulates as the bath is used and continuing brightener adds are made. This is less likely, in view of the results in Figure 7, but it is not ruled out.

The preliminary work on depletion in the Hull cell indicates that at least some component responsible for brightening is depleted under conditions where the EC remains unchanged. This places some limit on the usefulness of the EC value alone as a bath monitor and other complementary analyses are clearly needed. The assumption that activity in the CV test is a measure of brightening and leveling action in the tank is not entirely valid. However, the CV approach is providing vital new information in an otherwise chaotic area.

ACKNOWLEDGEMENTS

The authors express their appreciation to G. Garlough and W. Workman (Roseville, MN), D. Palmer (Bristol, TN) and J. C. Smith (Salt Lake City, UT) for their assistance and consultations; and to Dr. D. A. Zatko for much helpful discussion.

(1) D. Tench and C. Ogden, J. Electrochem Soc., 155 No. 2, pp 194-8, 1978

(2) C. Ogden and D. Tench, Plating & Surface Finishing, Vol. 66, No. 9, 30-4, Sept. 1979 and No. 12, 45-6, Dec. 1979

(3) R. Haak, C. Ogden and D. Tench, Plating and Surface Finishing, Vol. 68, No. 4, 52-5, April 1981

(4) R. Haak, C. Ogden and D. Tench, ilid, Vol. 69, No. 3, 62-6, March 1982

F-5

Electronics II
Session F

Differential Pulse Polarography of Organic Additives in Acid Tin and Bright Tin-Lead Plating Baths

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DIFFERENTIAL PULSE POLAROGRAPHY OF ORGANIC ADDITIVES IN ACID TIN AND BRIGHT TIN-LEAD PLATING BATHS

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Winston-Salem, N.C.

Abstract

Due to the increased use of high-speed plating, frequent and rapid plating bath analyses are needed in order to control the quality of the electrodeposited metal. Organic addition agents play important roles in plating and must be replenished more frequently in high-speed plating. Procedures have been developed using differential pulse polarography for the analysis of the grain refiner in a commercial acid tin plating bath and the brighteners in a commercially available bright tin-lead bath. This method has advantages over conventional methods by offering a simple, rapid analysis for more precise control of organic additives in the acid tin and the bright tin-lead plating baths studied and should be adaptable to other similar systems commonly used today.

Introduction

Addition agents have been used for many years in the plating industry to produce specific effects such as leveling or brightening of a deposit. The concentrations of these addition agents in the plating baths are usually quite small and exact concentrations are often quite difficult to determine. Two emerging techniques which show promise for rapid and simple analysis of organics in plating baths are High-Performance Liquid Chromatography (HPLC) and Polarography.

Since these addition agents are consumed during plating, maintenance of and sometimes balance between addition agents are required for better quality control. Due to the increased use of high-speed plating, frequent and rapid plating bath analyses are needed in order to control the quality of the electrodeposited metal.

In the past, no simple quantitative methods have existed for analysis of organic additives in plating baths. Conventional methods such as the Hull Cell or the bent cathode test, which are informative to experienced platers, do not provide simple and rapid quantitative analyses. Also, methods used for analysis of wetting agents or grain refiners by surface tension measurements are somewhat difficult and are not often used.

The addition agents in most acid tin plating baths and bright tin-lead plating baths are typically organic additives. Due to the electroactivity of most organics, polarography has been applied to the analysis of organics in plating baths. This paper deals with the determination of the concentration of the grain refiner in an acid tin plating bath and the brightener system in a tin-lead plating bath.

The grain refiner is added to provide a useful deposit. Without the grain refiner, the deposit contains loosely adherent large crystals. Too much grain refiner causes problems when a plastic is laminated to the deposit. Therefore, the concentration of the grain refiner must be maintained within a certain range to provide a quality product. With the use of polarography, this can be done quite readily.

The brightener system in this tin-lead plating bath consists of three organic additives. The first component (#1) is the main brightening agent and has been analyzed in an acetate solution using differential pulse polarography. The third component (#3) is a grain refiner and has been analyzed in the bath itself with differential pulse voltammetry with a glassy carbon electrode. The second component (#2) is a wetting agent used to emulsify the third component. Presently, the second component can not be analyzed using voltammetry. However, this component has been analyzed using UV-VIS spectroscopy, although interferences pose problems.

Background

Polarography is an analytical technique which was developed in the 1920s. Early instruments were difficult to use and thus were not utilized extensively. With the invention of improved electronics in the 1960s, better instrumentation has been made available and has gained popularity as an analytical technique, especially for environmental analysis.

Polarography is a branch of voltammetry in which the working electrode is a dropping mercury electrode (DME). Voltammetry is an electrochemical technique in which the faradaic current through the electrolytic solution is measured as a systematic varied potential is applied between a reference electrode and a working electrode. The reference electrode is almost always a saturated calomel electrode (SCE) or a silver/silver chloride (Ag/AgCl) electrode. Typical working electrodes are the dropping mercury electrode, the glassy carbon electrode (GCE), and the wax-impregnated graphite electrode. The amount of faradaic current is proportional to the concentration of the species being either reduced (gaining electrons) or oxidized (losing electrons). Therefore, the species can be quantitated.

The electrolyte solution is employed in voltammetry to provide a conductive media for electron flow during oxidation or reduction. The electrolyte is an important consideration for analysis of plating solutions, since certain species are rendered electroinactive in certain electrolytes. Organic additives are used in low concentrations in plating baths, so they often require little or no dilution with an electrolyte, since plating baths are good electrolytic solutions.

Voltammetry appears to be a good choice for analyses of plating baths, since it is an electrochemical technique. Probably the most used voltammetric technique for analysis of plating baths is the differential pulse mode. This technique offers excellent sensitivity (parts per billion in many cases) with modern equipment, and provides rapid and simple quantitative analysis for control of plating solutions.

Experimental

Acid Tin Plating Bath

This work was carried out using the PARC Model 384 Polarographic Analyzer in the DC differential pulse polarography mode (DPP) using a dropping mercury electrode (DME) with a Ag/AgCl reference electrode and a Pt wire was a counter electrode. A blank (acid tin plating bath without any grain refiner) and three standards of 0.5% (1 ml of grain refiner diluted to 200 mls with acid tin plating bath), 1.0% (1 ml of grain refiner diluted to 100 mls with acid tin plating bath), and 5.0% (5 ml of grain refiner diluted to 100 mls with acid tin plating bath) were purged with nitrogen for 4-6 minutes and then scanned from 0.200 to -0.200V. The peak of 0.020V was labelled peak 1 and used for a calibration curve. (See Appendix I).

Bright Tin Lead Bath

This work was also carried out using the PARC Model 384 Polarographic Analyzer in the DC differential pulse mode with a Ag/AgCl reference electrode and a Pt wire as a counter electrode. A dropping mercury electrode was used to analyze the additive #1. A blank solution was prepared by adding 1.5% of additives #2 and #3 to a tin-lead plating bath solution without any additives. The blank solution was then used to make three standards of 0.5% (125µl of additive #1 diluted to 25 mls with the blank solution), 1.5% (375µl of #1 diluted to 25 mls with the blank solution), and 5.0% (1.25 ml of #1 to 25 mls with the blank solution). In each case a sample of 100µl was diluted to 10 mls with an acetate buffer (0.1M, pH 4.5), purged with nitrogen for four (4) minutes, and then scanned from -0.200V to -1.20V. The peak at -0.90V was labelled peak 1 and used for calibration.

Additive #3 was analyzed with a glassy carbon electrode. A blank solution was prepared by adding 1.5% of additive #2 to a tin-lead plating bath solution without any additives. The blank solution was then used to make three standards of 0.5% (125µl of #3 diluted to 25 mls with the blank solution), 1.5% (375µl of #3 diluted to 25 mls with the blank solution), and 3.0% (750µl of #3 diluted to 25 ml with the blank solution). A sample (10 ml of each) was then purged with nitrogen for four (4) minutes and then scanned from 0.000V to 1.000V. The peak at 0.70V was labelled peak 3 and used for calibration.

Results and Discussion

Voltammetry has been successfully used in analyzing organic additives in an acid tin and a bright tin-lead plating bath. The differential pulse technique gave acceptable results for analysis of plating baths. In the case of the acid tin bath, a 3.0% standard was prepared and analyzed after the instrument had been calibrated. The results as shown in Appendix I gave an accuracy of 5-6%. Also, analysis of acid tin plating baths which had been in operation in production gave comparable results (within experimental error) as those analyzed by a HPLC method. In the case of the bright tin-lead bath, a 3.0% standard of additive #1 was analyzed and gave an accuracy of 2%. (See Appendix II). A 1.5% standard of additive #3 was analyzed and

gave an accuracy of 3%. (See Appendix II). These results are well within the requirements of accuracy needed for plating bath analyses.

The methods developed are simple to use, such that less technically oriented people can be trained to operate the polarograph. Also, these methods are fairly rapid, so that an analysis can be performed in less than ten minutes. Unlike the HPLC which requires expensive solvents for operation, the polarograph should be more cost effective to operate.

On-line control should be possible with these methods. General Dynamics has successfully designed an Automatic Monitoring and Control System (AMCS)[1] for improving printed wire board (PWB) yield and reliability. This system utilizes a Model 384 Polarographic Analyzer for doing the analyses. Such analyses are needed to maintain good quality control. For example, the concentration of organic additives has been shown to affect alloy, brightness, carbon content, and solderability of the tin-lead deposit.[2]

In conclusion, the polarographic methods developed for analysis of organic additives in acid tin and bright tin-lead baths are simple, rapid, and adaptable for on-line control for providing better quality control than conventional methods.

Acknowledgement

The author wishes to thank the Applications Staff at EG&G Princeton Applied Research for their excellent technical support, and the Winston-Salem Research Analytical Group at AMP Incorporated for their invaluable assistance and advice.

References

1 MANUFACTURING METHODS AND TECHNOLOGY FOR AUTOMATIC CONTROL OF PLATING, submitted to US. Army System Engineering, Directorate DRSMI-RST, Redstone Arsenal, Alabama, under contract No. DAAK40-78-0301.

2 TIN AND TIN-LEAD PLATING, by William E. Eckles, Rohco, Inc., Cleveland, Ohio, Printed Circuit World Expo '81 Proceedings.

MODEL 384 POLAROGRAPHIC ANALYZER

21-SEP-81
DPP
INITIAL E 0.200 V
FINAL E -0.200 V
PURGE 240 SECONDS
DROP TIME 1.0 SECONDS
SCAN INCREMENT 2 MV
PULSE HEIGHT 0.050 V
REPLICATIONS 1

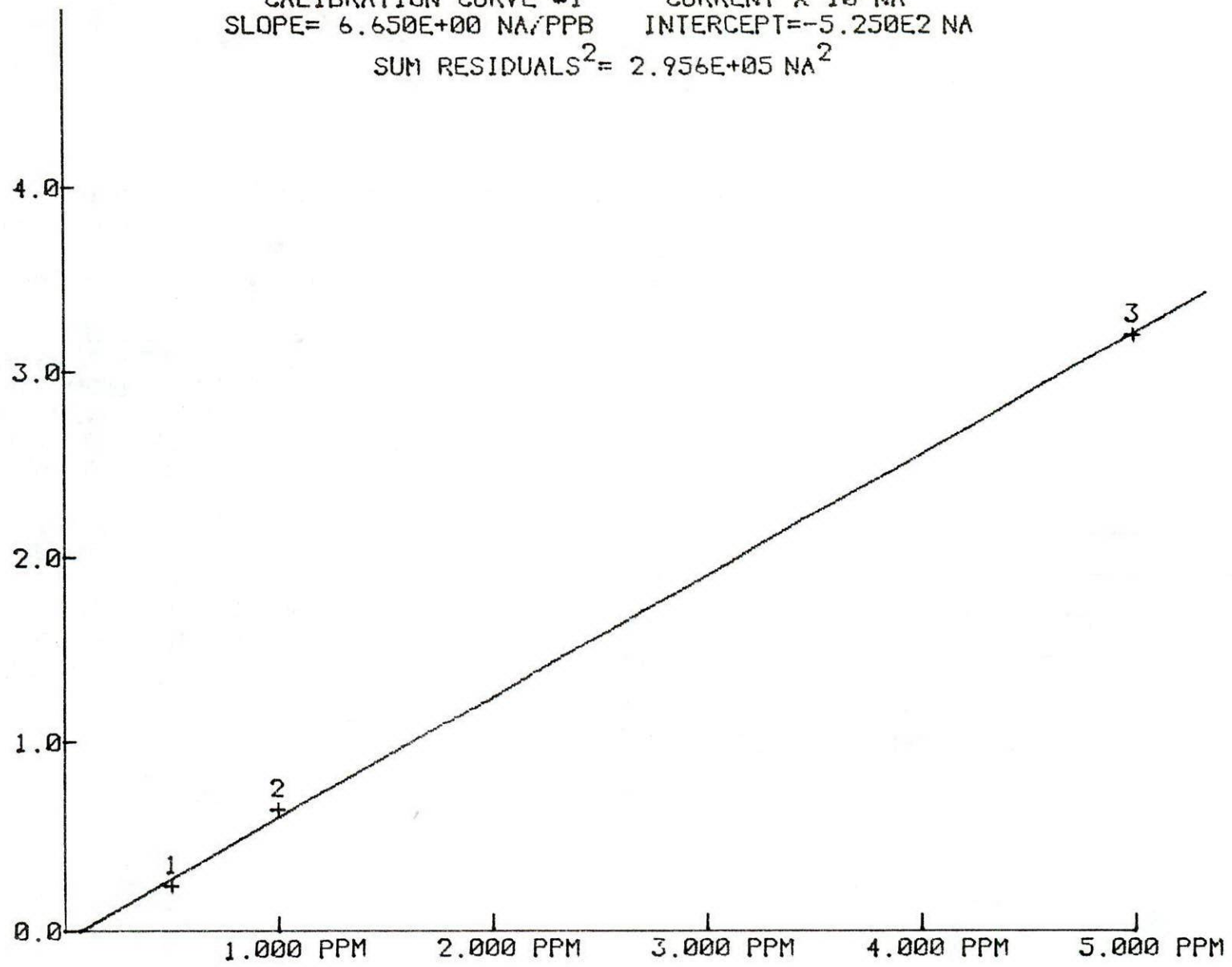
STANDARD CURVE
BLANK SUBTRACTION: YES
TANGENT FIT: NO
PEAK LOCATION: YES
DERIVATIVE: NO
FORCE LINEAR FIT: YES

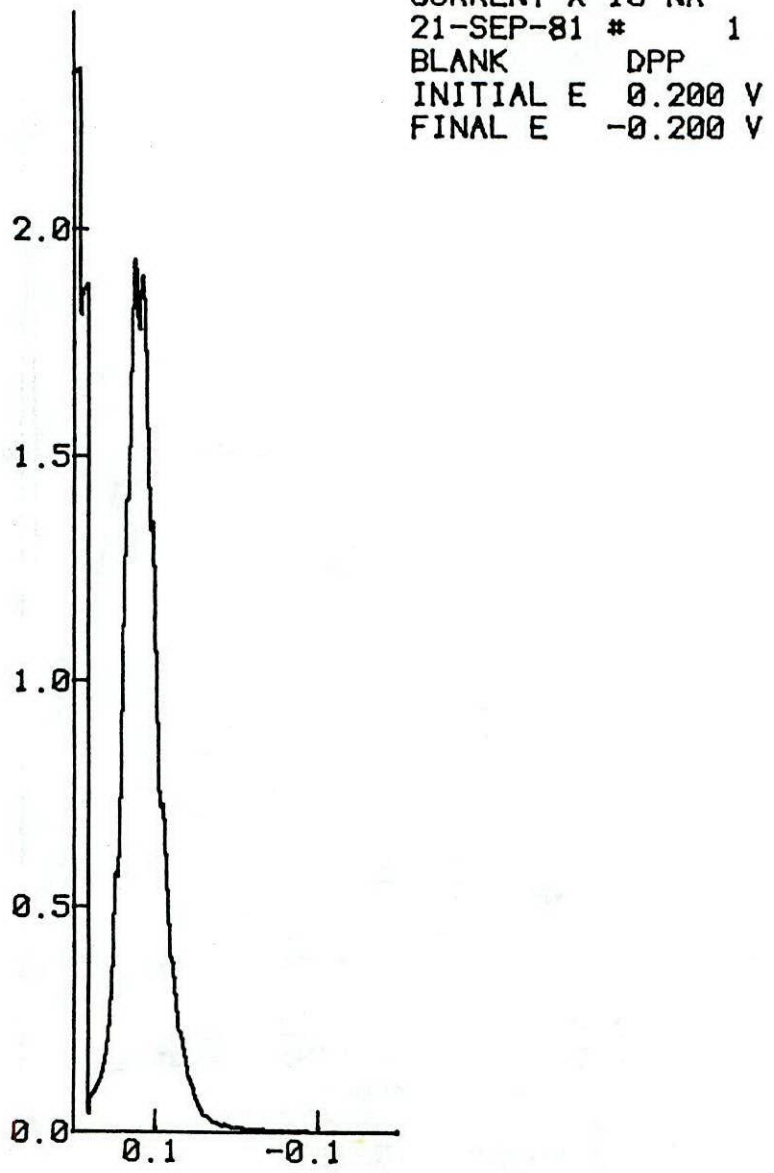
	10	11	12	13	14	15	16	17	18	19	20
OVERRIDE	Y	N	Y	Y	N	N	Y	N	N	Y	N

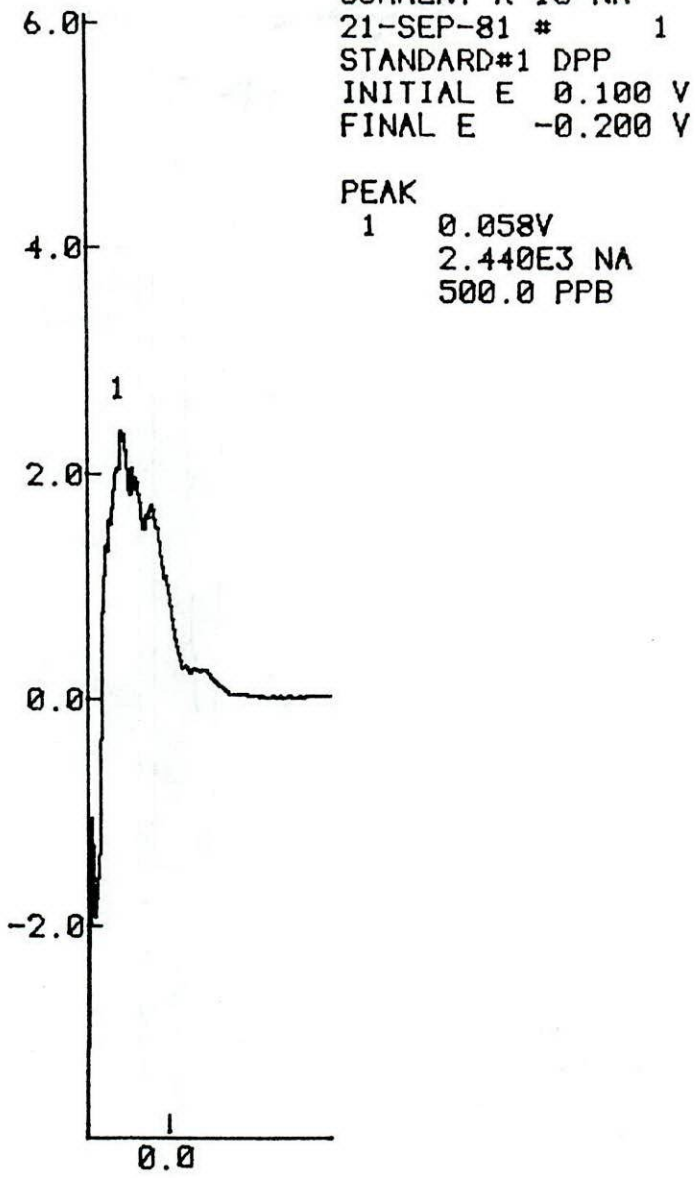
PEAK	POT	STD 1	STD 2	STD 3
1	0.020 V	500.0 PPB	1.000 PPM	5.000 PPM

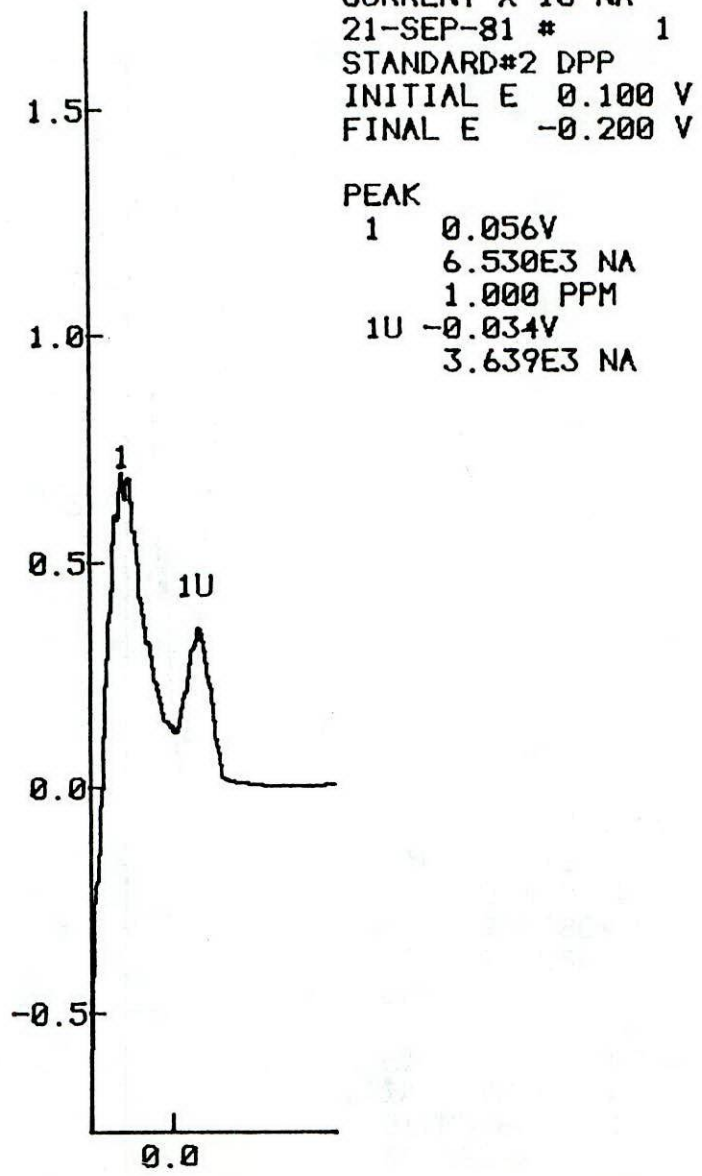
SAMPLE Acid Tin Plating Bath
ANALYTE Grain Refiner
SUPP. ELEC. Bath itself
SAMPLE PREP. No dilution of bath
Standards are recorded in %

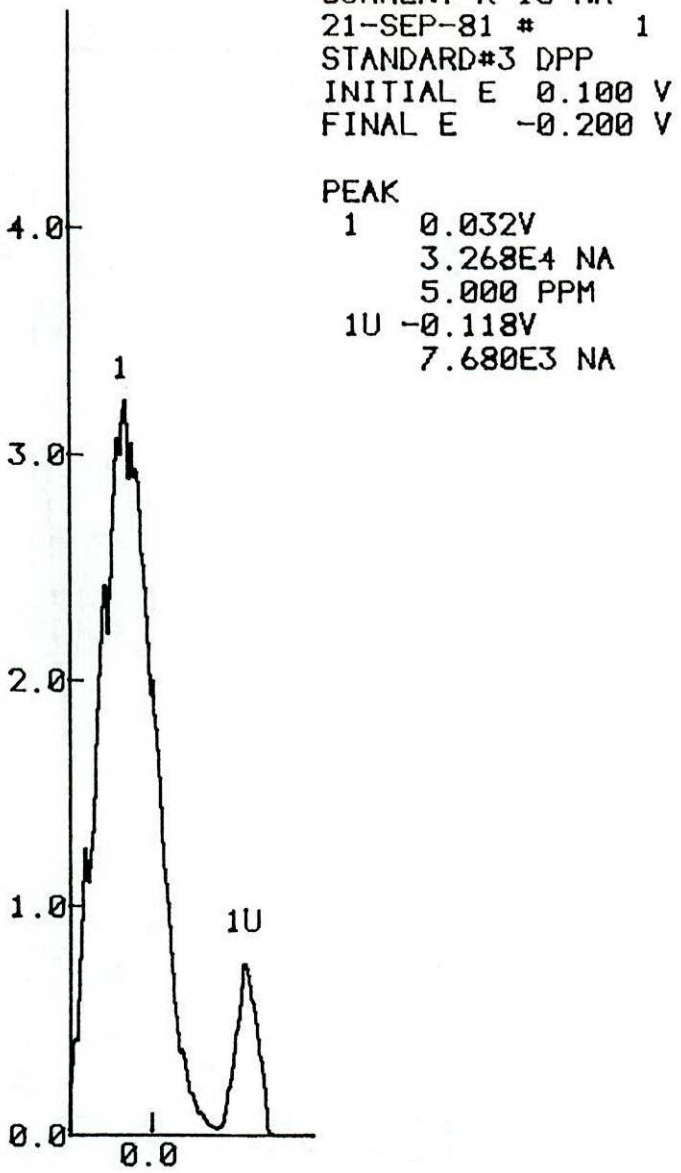
APPENDIX I

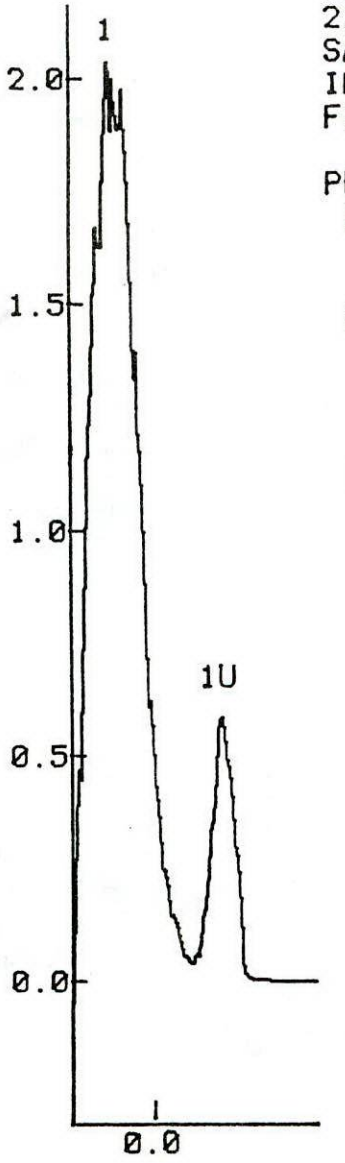

CALIBRATION CURVE #1 CURRENT X 10^4 NA
SLOPE= 6.650E+00 NA/PPB INTERCEPT=-5.250E2 NA
SUM RESIDUALS^2= 2.956E+05 NA^2
4.0
3.0
2.0
1.0
0.0
1
2
3
1.000 PPM
2.000 PPM
3.000 PPM
4.000 PPM
5.000 PPM


CURRENT X 10⁴NA
21-SEP-81 # 1
BLANK DPP
INITIAL E 0.200 V
FINAL E -0.200 V
2.0
1.5
1.0
0.5
0.0
0.1
-0.1


CURRENT X 10^3NA
21-SEP-81 # 1
STANDARD#1 DPP
INITIAL E 0.100 V
FINAL E -0.200 V
PEAK
1 0.058V
2.440E3 NA
500.0 PPB
6.0
4.0
2.0
0.0
-2.0
1
0.0


CURRENT X 10^4 NA
21-SEP-81 # 1
STANDARD#2 DPP
INITIAL E 0.100 V
FINAL E -0.200 V
PEAK
1 0.056V
6.530E3 NA
1.000 PPM
1U -0.034V
3.639E3 NA
1.5
1.0
0.5
0.0
-0.5
0.0
1
1U

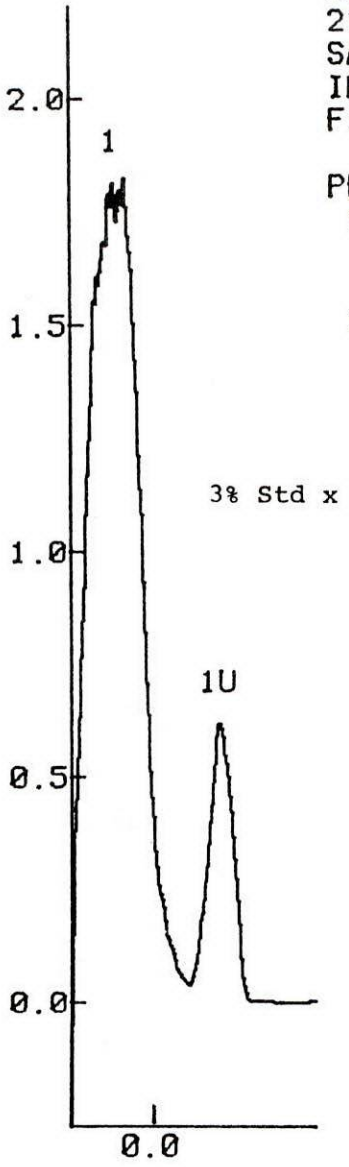

CURRENT X 10^4 NA
21-SEP-81 # 1
STANDARD#3 DPP
INITIAL E 0.100 V
FINAL E -0.200 V
PEAK
1 0.032V
3.268E4 NA
5.000 PPM
1U -0.118V
7.680E3 NA
4.0
3.0
2.0
1.0
0.0
0.0
1
1U



CURRENT X 10^4NA
21-SEP-81 # 6
SAMPLE DPP
INITIAL E 0.100 V
FINAL E -0.200 V

PEAK
1 0.050V
2.056E4 NA
3.171 PPM
1U -0.084V
5.920E3 NA

3% Standard



CURRENT X 10^4NA
21-SEP-81 # 3
SAMPLE DPP
INITIAL E 0.100 V
FINAL E -0.200 V

PEAK
1 0.046V
1.850E4 NA
2.861 PPM
1U -0.084V
6.300E3 NA

3% Std x 3 Replications

MODEL 384 POLAROGRAPHIC ANALYZER

23-DEC-82
DPP
INITIAL E -0.200 V
FINAL E -1.200 V
PURGE 240 SECONDS
DROP TIME 1.0 SECONDS
SCAN INCREMENT 2 MV
PULSE HEIGHT 0.050 V
REPLICATIONS 1

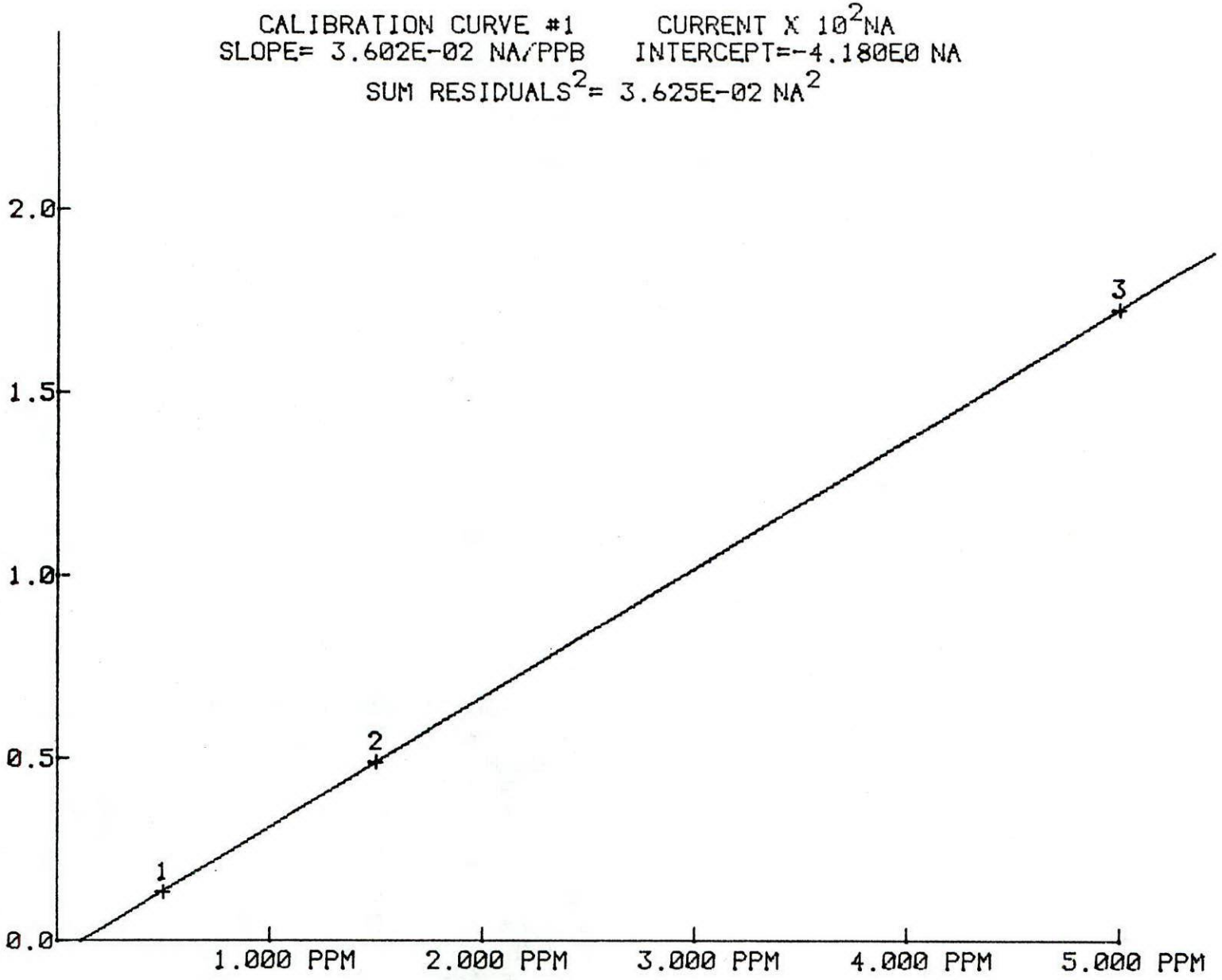
SAMPLE Bright Tin-Lead Plating Bath
ANALYTE Organic Additive #1
SUPP. ELEC. Acetate Buffer (0.1M, pH 4.5)
SAMPLE PREP. 100µℓ of sample diluted to 10 milliliters with Buffer.
Standards are recorded in %.

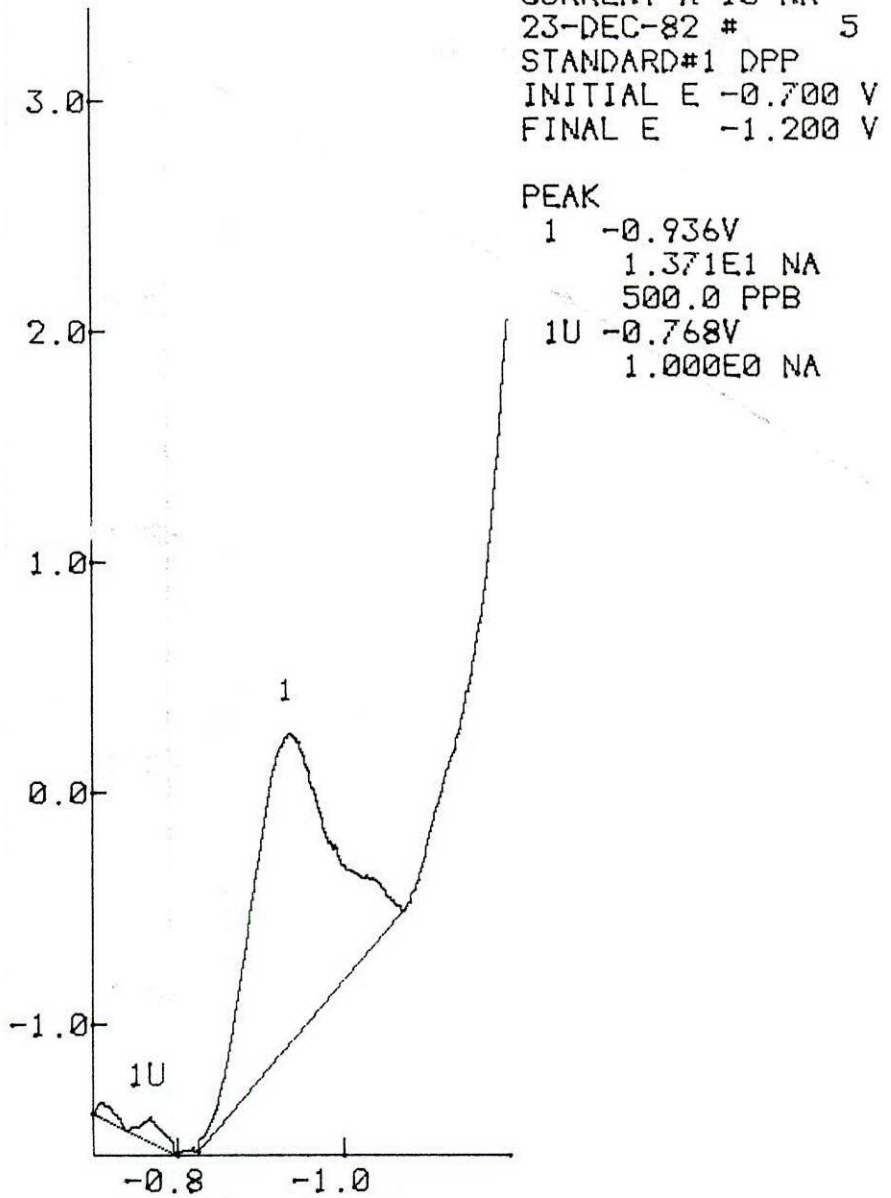
STANDARD CURVE
BLANK SUBTRACTION: YES
TANGENT FIT: YES
PEAK LOCATION: YES
DERIVATIVE: NO
FORCE LINEAR FIT: YES

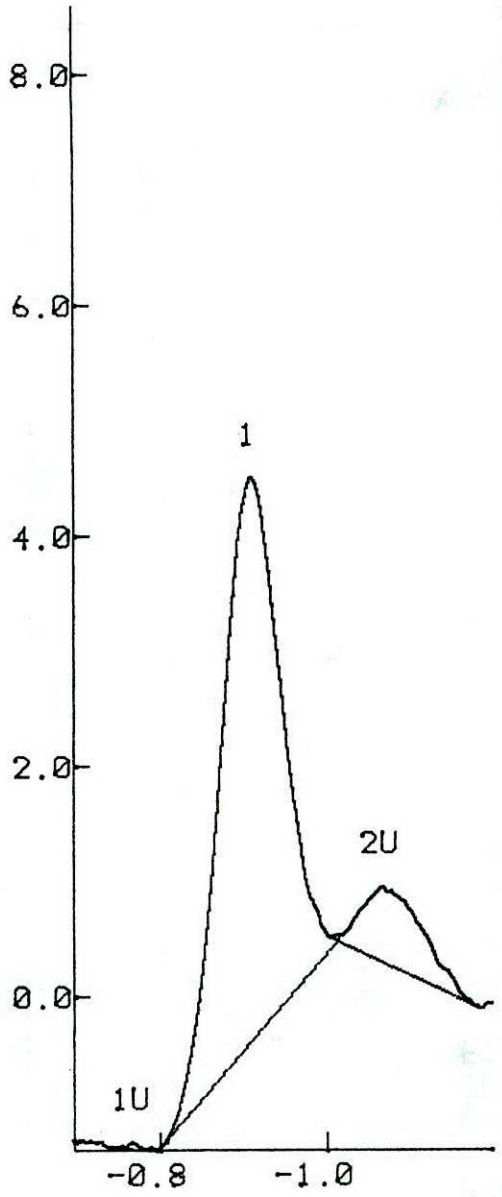
	10	11	12	13	14	15	16	17	18	19	20
OVERRIDE	Y	N	Y	Y	N	N	Y	N	N	Y	N

PEAK	POT	STD 1	STD 2	STD 3
1	-0.900 V	500.0 PPB	1.500 PPM	5.000 PPM

APPENDIX II

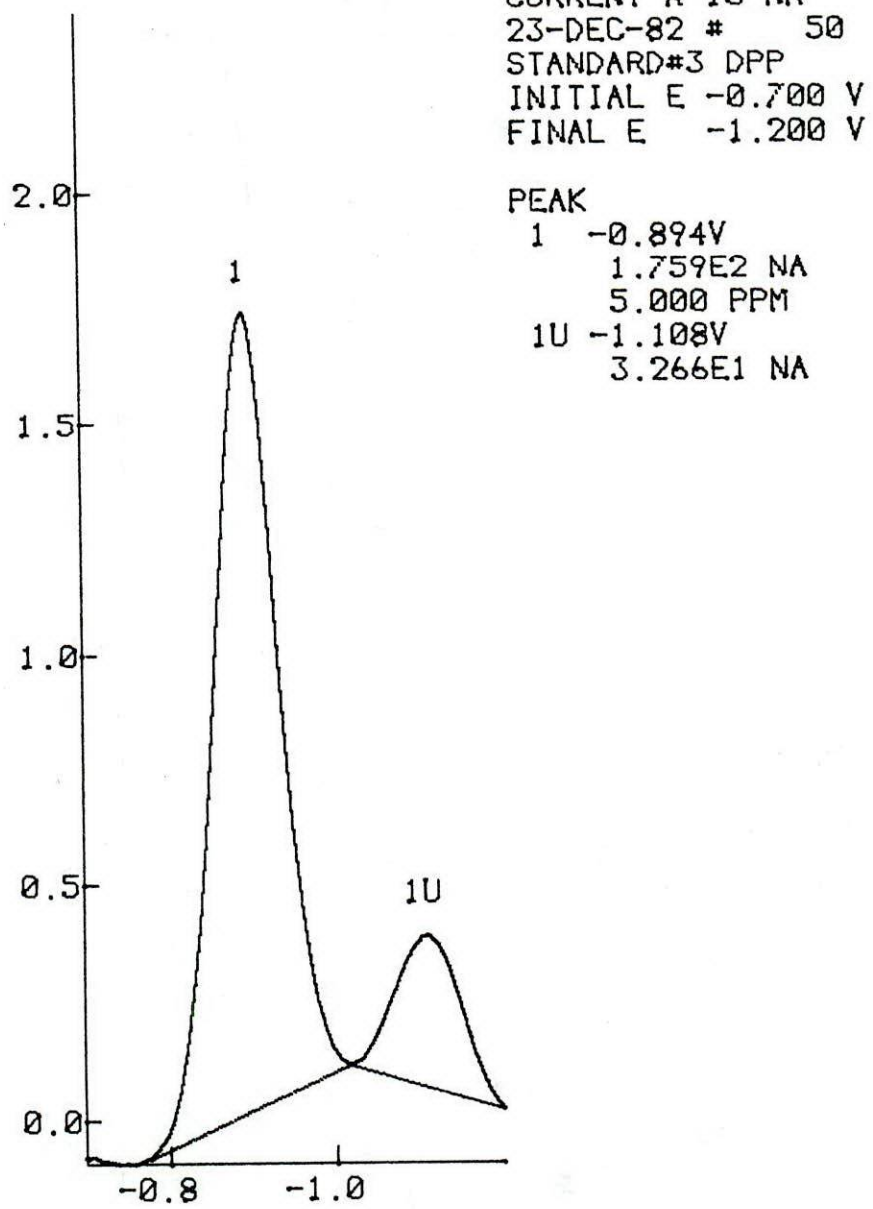

CALIBRATION CURVE #1 CURRENT X 10^2 NA
SLOPE= 3.602E-02 NA/PPB INTERCEPT=-4.180E0 NA
SUM RESIDUALS^2= 3.625E-02 NA^2
2.0
1.5
1.0
0.5
0.0
1
2
3
1.000 PPM
2.000 PPM
3.000 PPM
4.000 PPM
5.000 PPM

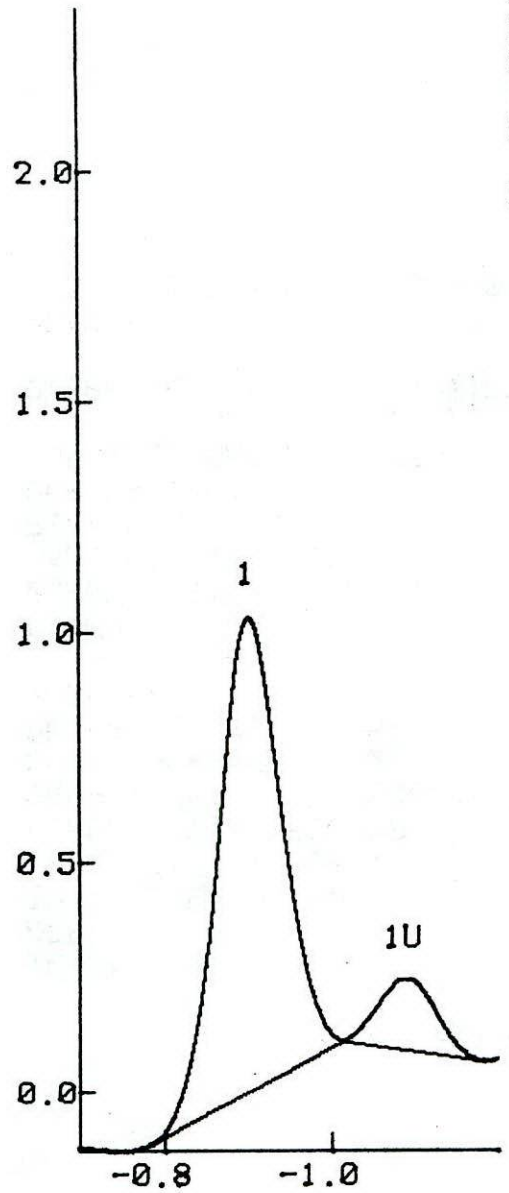

CURRENT X 10[1] NA
23-DEC-82 # 5
STANDARD#1 DPP
INITIAL E -0.700 V
FINAL E -1.200 V
PEAK
1 -0.936V
1.371E1 NA
500.0 PPB
1U -0.768V
1.000E0 NA
3.0
2.0
1.0
0.0
-1.0
1
1U
-0.8
-1.0



CURRENT X 10^{1}NA
23-DEC-82 # 15
STANDARD#2 DPP
INITIAL E -0.700 V
FINAL E -1.200 V

PEAK
1 -0.912V
5.000E1 NA
1.500 PPM
1U -0.770V
0.610E0 NA
2U -1.068V
6.670E0 NA


CURRENT X 10^2NA
23-DEC-82 # 50
STANDARD#3 DPP
INITIAL E -0.700 V
FINAL E -1.200 V
PEAK
1 -0.894V
1.759E2 NA
5.000 PPM
1U -1.108V
3.266E1 NA
2.0
1.5
1.0
0.5
0.0
1
1U
-0.8
-1.0


CURRENT X 10^2NA
23-DEC-82 # 30
SAMPLE DPP
INITIAL E -0.700 V
FINAL E -1.200 V
PEAK
1 -0.904V
1.054E2 NA
3.041 PPM
1U -1.090V
1.566E1 NA
3% Standard
2.0
1.5
1.0
0.5
0.0
1
1U
-0.8
-1.0

MODEL 384 POLAROGRAPHIC ANALYZER

10-JAN-83
DPP
INITIAL E 0.000 V
FINAL E 1.000 V
PURGE 240 SECONDS
DROP TIME 0.5 SECONDS
SCAN INCREMENT 2 MV
PULSE HEIGHT 0.050 V
REPLICATIONS 1

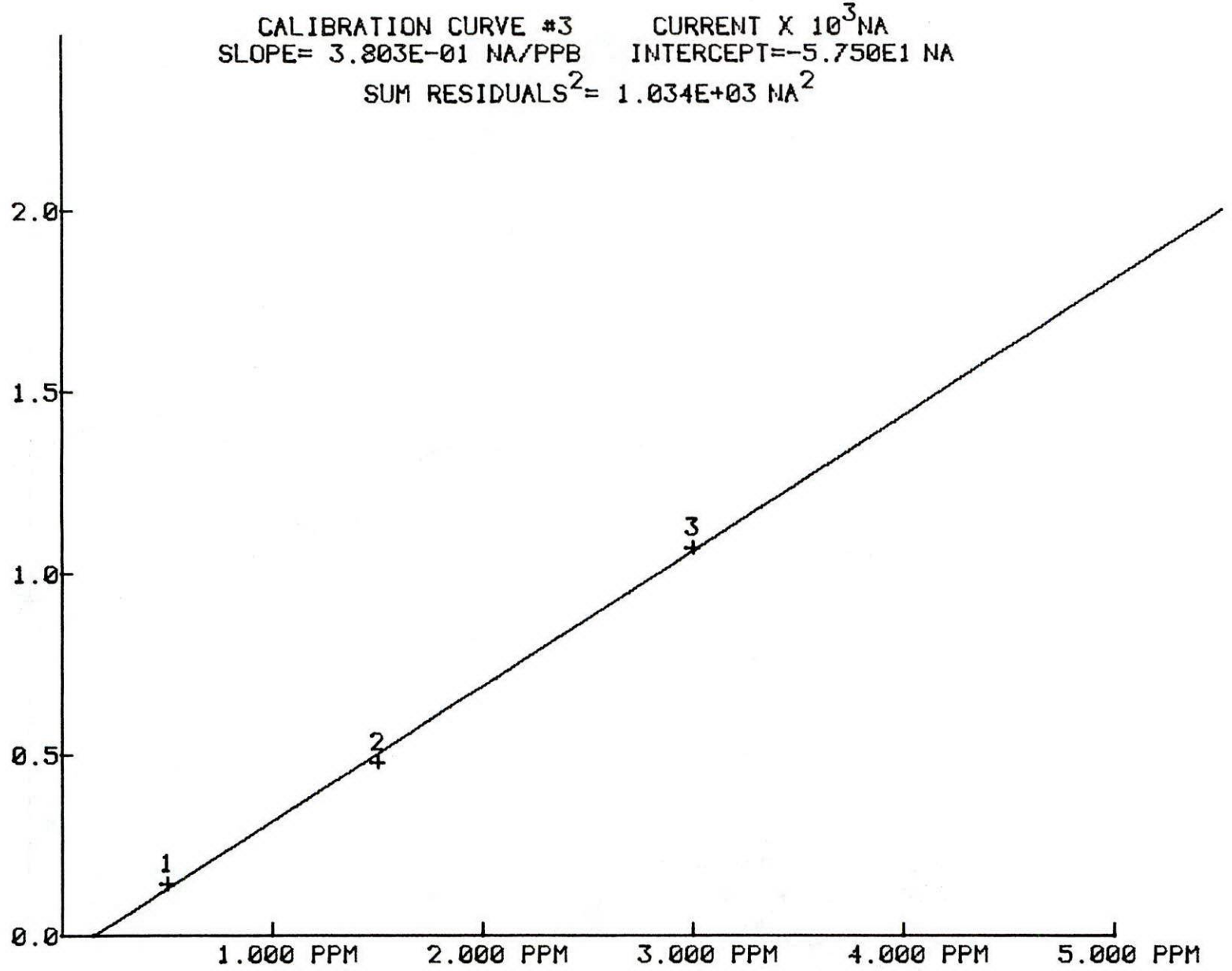
STANDARD CURVE
BLANK SUBTRACTION: YES
TANGENT FIT: YES
PEAK LOCATION: YES
DERIVATIVE: NO
FORCE LINEAR FIT: YES

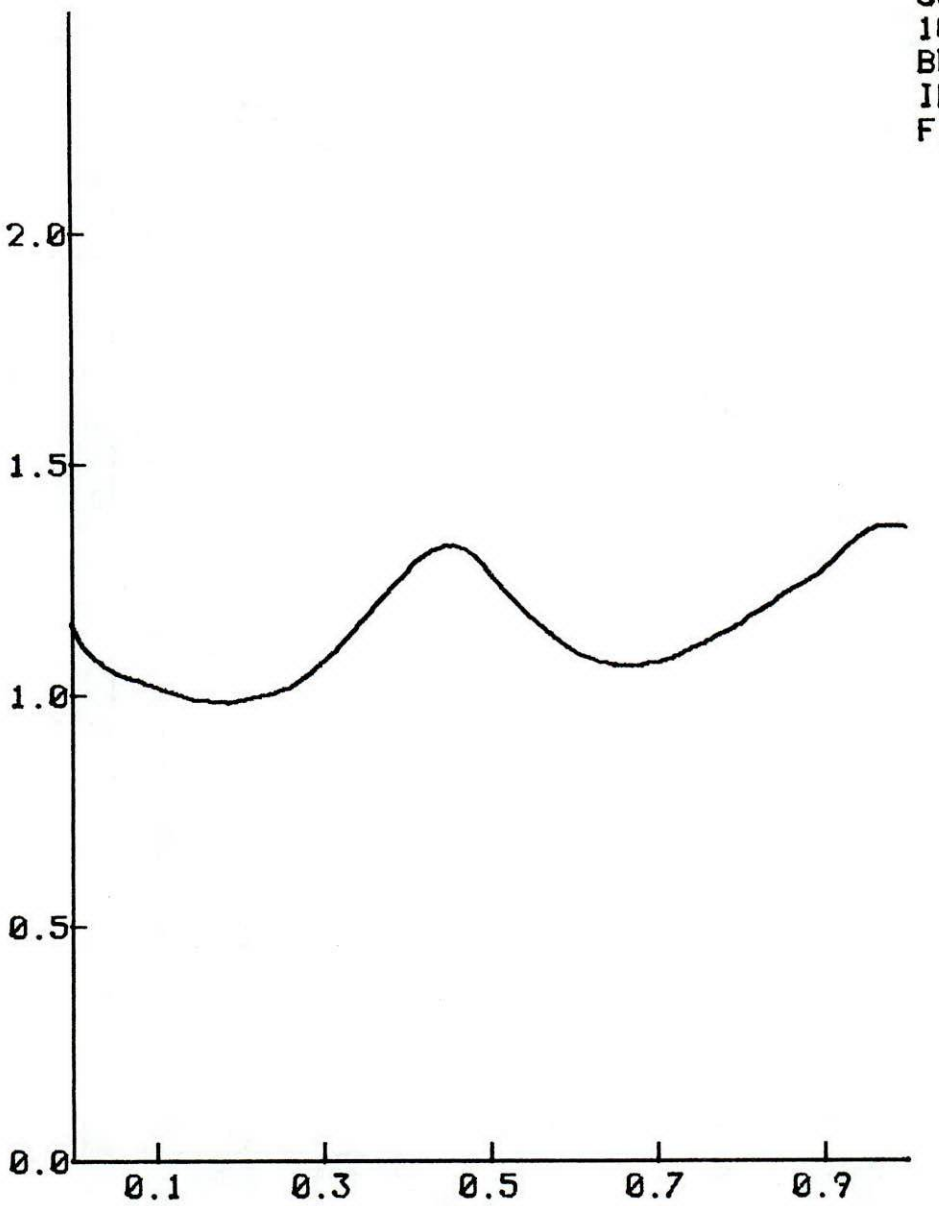
	10	11	12	13	14	15	16	17	18	19	20
OVERRIDE	Y	N	Y	Y	N	N	Y	N	N	Y	N

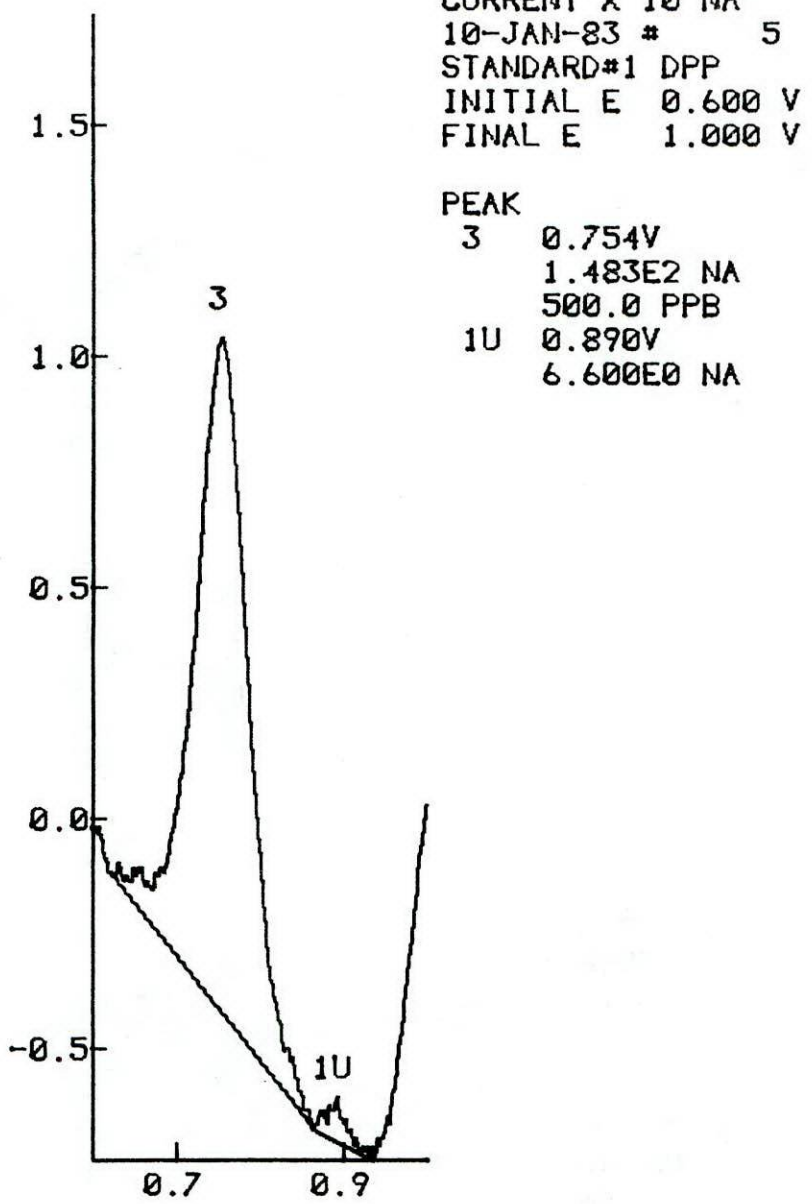
SAMPLE Bright Tin-Lead Plating Bath
ANALYTE Organic Additive #3
SUPP. ELEC. Bath itself
SAMPLE PREP. No dilution of bath
Standards are recorded in %.

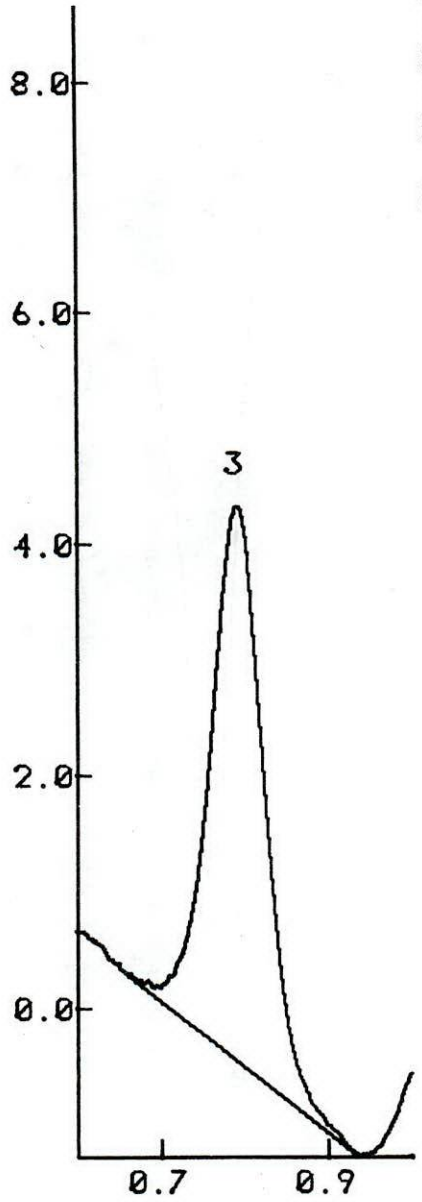
PEAK	POT	STD 1	STD 2	STD 3
3	0.775 V	500.0 PPB	1.500 PPM	3.000 PPM

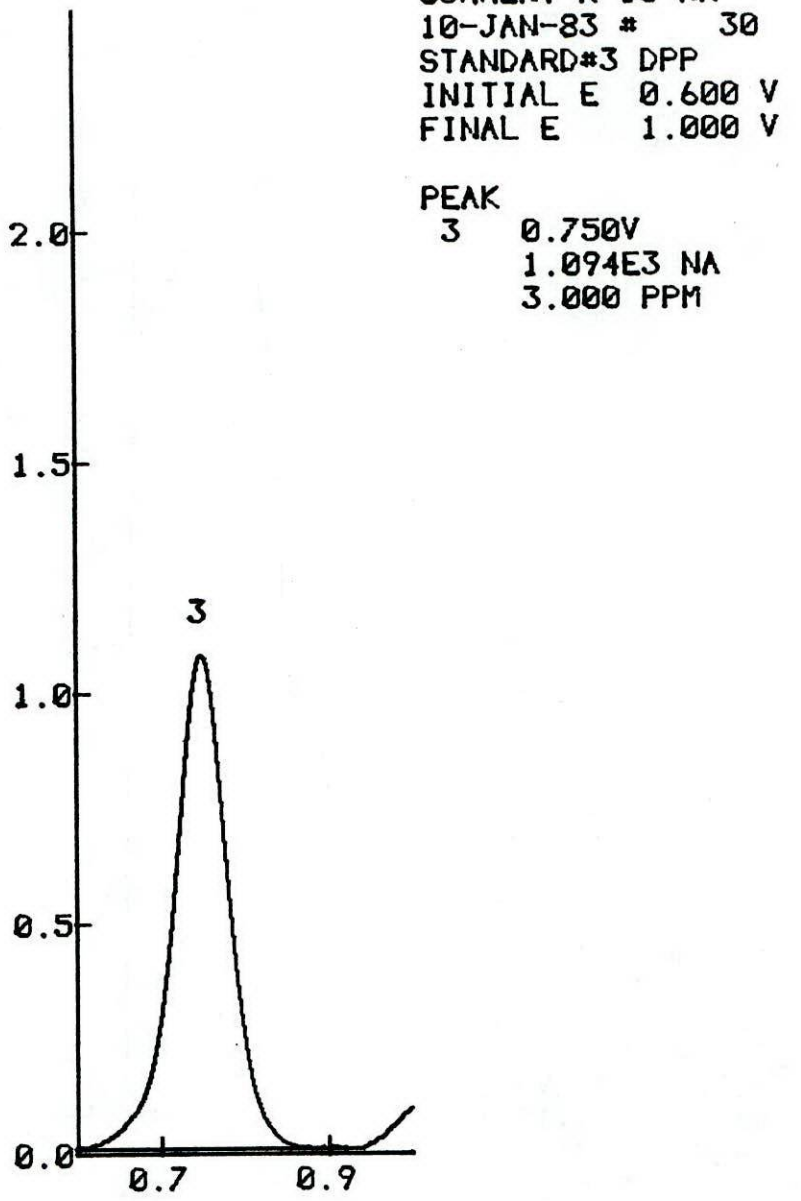
APPENDIX III

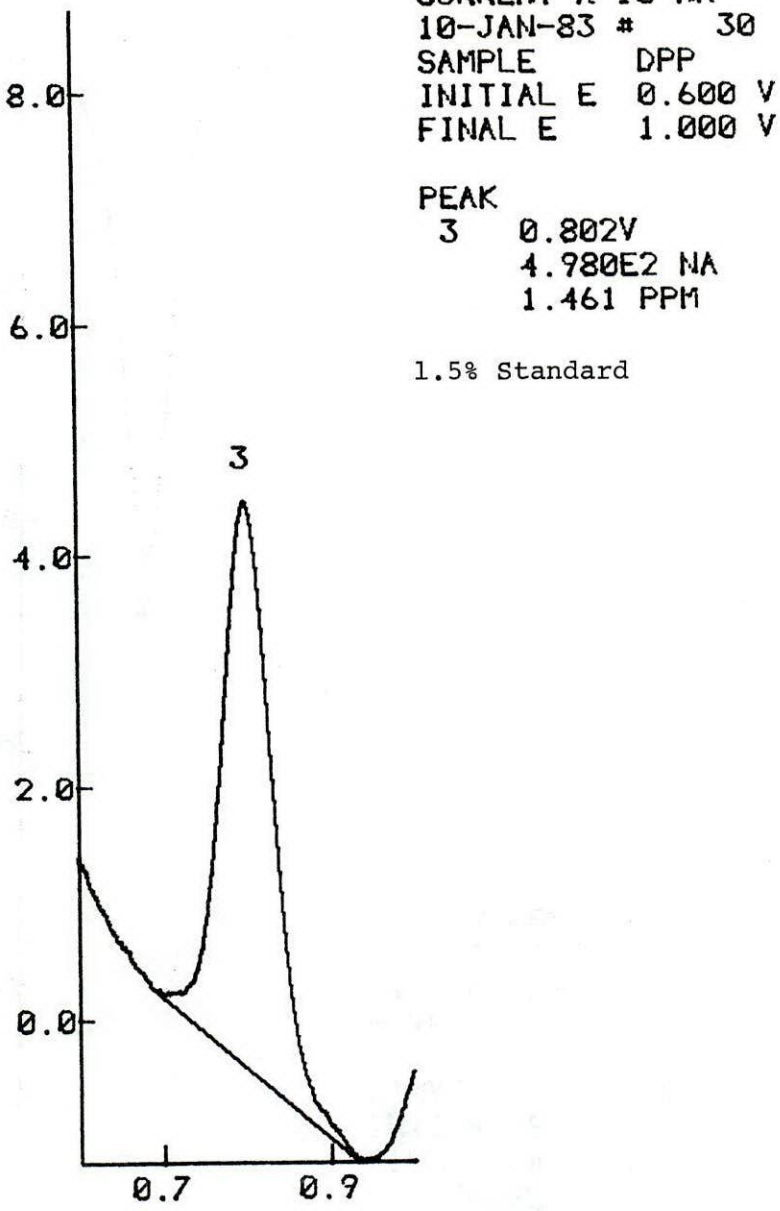

CALIBRATION CURVE #3
SLOPE= 3.803E-01 NA/PPB
CURRENT X 10^3 NA
INTERCEPT=-5.750E1 NA
SUM RESIDUALS^2= 1.034E+03 NA^2
2.0
1.5
1.0
0.5
0.0
1
2
3
4
1.000 PPM
2.000 PPM
3.000 PPM
4.000 PPM
5.000 PPM


CURRENT X 10^3NA
10-JAN-83 # 1
BLANK DPP
INITIAL E 0.000 V
FINAL E 1.000 V
2.0
1.5
1.0
0.5
0.0
0.1
0.3
0.5
0.7
0.9


CURRENT X 10^2NA
10-JAN-83 # 5
STANDARD#1 DPP
INITIAL E 0.600 V
FINAL E 1.000 V
PEAK
3 0.754V
1.483E2 NA
500.0 PPB
1U 0.890V
6.600E0 NA
1.5
1.0
0.5
0.0
-0.5
3
1U
0.7
0.9


CURRENT X 10^2NA
10-JAN-83 # 15
STANDARD#2 DPP
INITIAL E 0.600 V
FINAL E 1.000 V
PEAK
3 0.792V
4.870E2 NA
1.500 PPM
8.0
6.0
4.0
2.0
0.0
3
0.7
0.9


CURRENT X 10^3 NA
10-JAN-83 # 30
STANDARD#3 DPP
INITIAL E 0.600 V
FINAL E 1.000 V
PEAK
3 0.750V
1.094E3 NA
3.000 PPM
2.0
1.5
1.0
0.5
0.0
3
0.7
0.9


CURRENT X 10^2NA
10-JAN-83 # 30
SAMPLE DPP
INITIAL E 0.600 V
FINAL E 1.000 V
PEAK
3 0.802V
4.980E2 NA
1.461 PPM
1.5% Standard
8.0
6.0
4.0
2.0
0.0
3
0.7
0.9

F-6

Electronics II
Session F

The Use of Cyclic Voltammetric Stripping for Determination of Additive Concentration in Copper Plating Baths

Gerry Bush
UPA Technology, Inc.
Syosset, NY

The Use of Cyclic Voltammetric Stripping for Determination of Additive Concentration in Copper Plating Baths.

Gerry Bush

Director, Sales & Marketing

UPA TECHNOLOGY, INC.
SYOSSET, NY

Cracks, voids, discontinuities, thin copper plate ..... these are some of the major nemeses of the printed circuit board industry ..... until now.

A recently developed technique, Cyclic Voltammetric Stripping (CVS), has been applied to the analysis of copper plating baths, both pyrophosphate and acid copper sulfate.

The CVS method allows the manufacturer to determine the optimum conditions for circuit board plating by providing data on the additive and contaminant levels in the bath.

Research has shown that the major problems normally encountered in plating circuit board through-holes can be attributed to the brightener concentration or contaminant levels in the bath. When the brightener concentration is too low, deposits are burnt or folded-back and may not have acceptable tensile properties. Contrarily, excessive brightener in the deposit can induce brittleness or reduce solderability. Contaminants have a similar effect on the tensile and solderability properties of deposits. Only with close control via CVS can the effects of bath composition on deposit quality be accurately and precisely determined.

THE THEORY

The Cyclic Voltammetric Stripping method determines the concentration of brightening or levelling additives from the effect these additives exert on the electrodeposition rate. In this 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. Changes in the electrode surface, bath composition and other variables are compensated for by using the internal standard provided by a static electrode. The ratio (A_r/A_s) of the stripping peak (A_r) relative to that for the static

electrode in the same bath solution (A_s) is a measure of the effective additive concentration. (See Fig. 1 for typical CVS Voltammogram).

THE METHOD

A sample of the plating bath is placed in a beaker, and three electrodes (rotating, reference and auxiliary) are placed in the solution. The potential of a rotating electrode is cycled relative to a reference electrode, the current passing between the auxiliary and rotating platinum (working) electrodes. Consequently, when the working rotating electrode is sufficiently negative, copper is deposited and when the electrode becomes positive, the copper is stripped off. (Fig. 2).

Copper is being deposited all the time that the graph shows a current below the zero current line, first, when the potential is going more negative, but also when the potential is returning towards the zero potential. While copper deposition is occurring, generally some of the additive at the electrode interface is being used up, either being reduced, included in the deposit, or whatever. This parallels the experience in the regular plating bath. In fact, this beaker with its electrodes may be regarded as a miniature plating bath in its own right. When the copper is being stripped from the deposit back into the bath, the exact fate of the included additive is unknown. During the cycle, there is a net loss of additive in the region of the electrode.

Now, different additives work in different ways. Frequently they work by suppressing deposition at points of high current density. Thus allowing other regions to "catch up" and produce a smoother deposit. In this case (example, Cu-pyrophosphate with the additive in the 1 to 3 ppm region) during deposition with a rotating electrode, the additive is consumed, and on stripping, the copper is dissipated from the electrode. But the rotation brings fresh solution into contact with the rotating electrode all the time, so that the additive is always replenished and present. Thus copper deposition is influenced by the presence of the additive. On the other hand, when the electrode is stationary, no such replenishment of the additive occurs, even during copper stripping, because in fact the additive is changed (altered, destroyed) during the deposition. Consequently, during the CVS run, especially on the second and subsequent cycles, deposition occurs as if there were little or no additive present, and this is reflected in the numbers for A_r, A_s and ratio. In practise, a calibration curve is constructed using CVS and additive is replenished according to the calibration curve. One manufacturer using pyrophosphate merely adds additive to reach a ratio of 0.9 or 1.0.

In acid copper sulfate baths, a similar procedure is used. A calibration curve is prepared of "Ratio" vs. "ml of additive per liter" using fresh bath and additive. A sample of the bath in use is run and additive may be added until the correct ratio is attained.

Interestingly, when the voltammetric stripping rate parameter (A_r/A_s) is plotted as a function of the additive concentration in a fresh bath versus a contaminated production bath, the contaminants shift the curve to the right. This clearly indicates that more brightener is required in contaminated baths to produce the same effect on the electrodeposition rate. Additionally, the chloride ion level in acid copper sulfate baths can be measured with CVS. These measurements are considered to be the principal strengths of the voltammetric method.

THE INSTRUMENT

A sophisticated microprocessor based instrument has been developed to present the valuable data obtained by the CVS method. UPA TECHNOLOGY's QUALIDERM Q-100 (Fig. 3) computes and displays the A_r/A_s ratio for a given plating bath under analysis. It can also be connected to an X-Y plotter to provide a voltammogram ("fingerprint") of the bath. (Fig. 4).

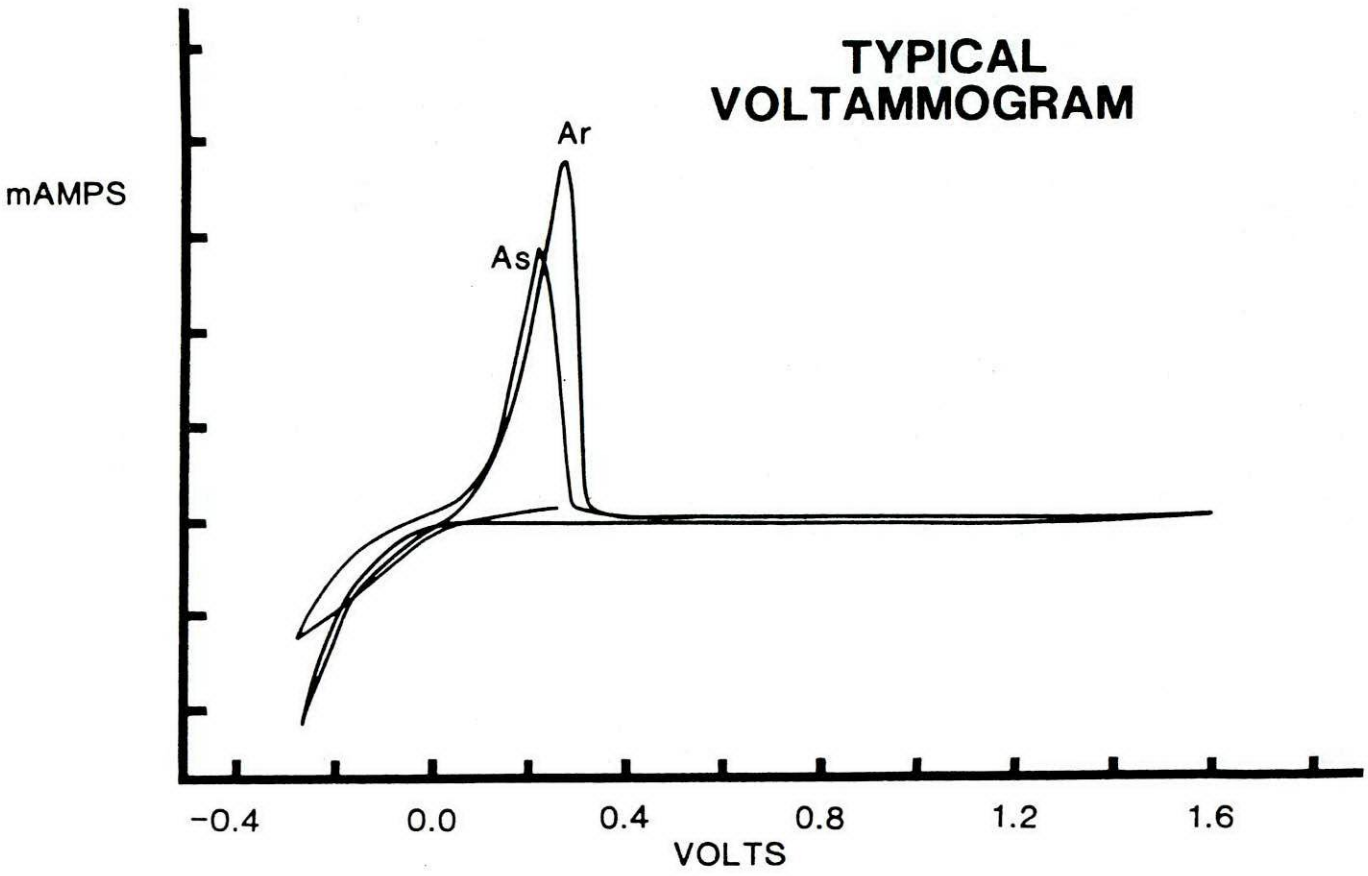
CONCLUSION

For the first time, producers of printed circuit boards can have quantitive control of their plating baths. Together, CVS and QUALIDERM yield data that allows for improved plating bath additive control and reduction of reject rates, additive waste, unnecessary carbon treatment.

References

1. C. Ogden and D. Tench, Plating & Surface Finishing, (Sept.79)
2. Haak, Ogden, Tench, Plating & Surface Finishing (April 1981)

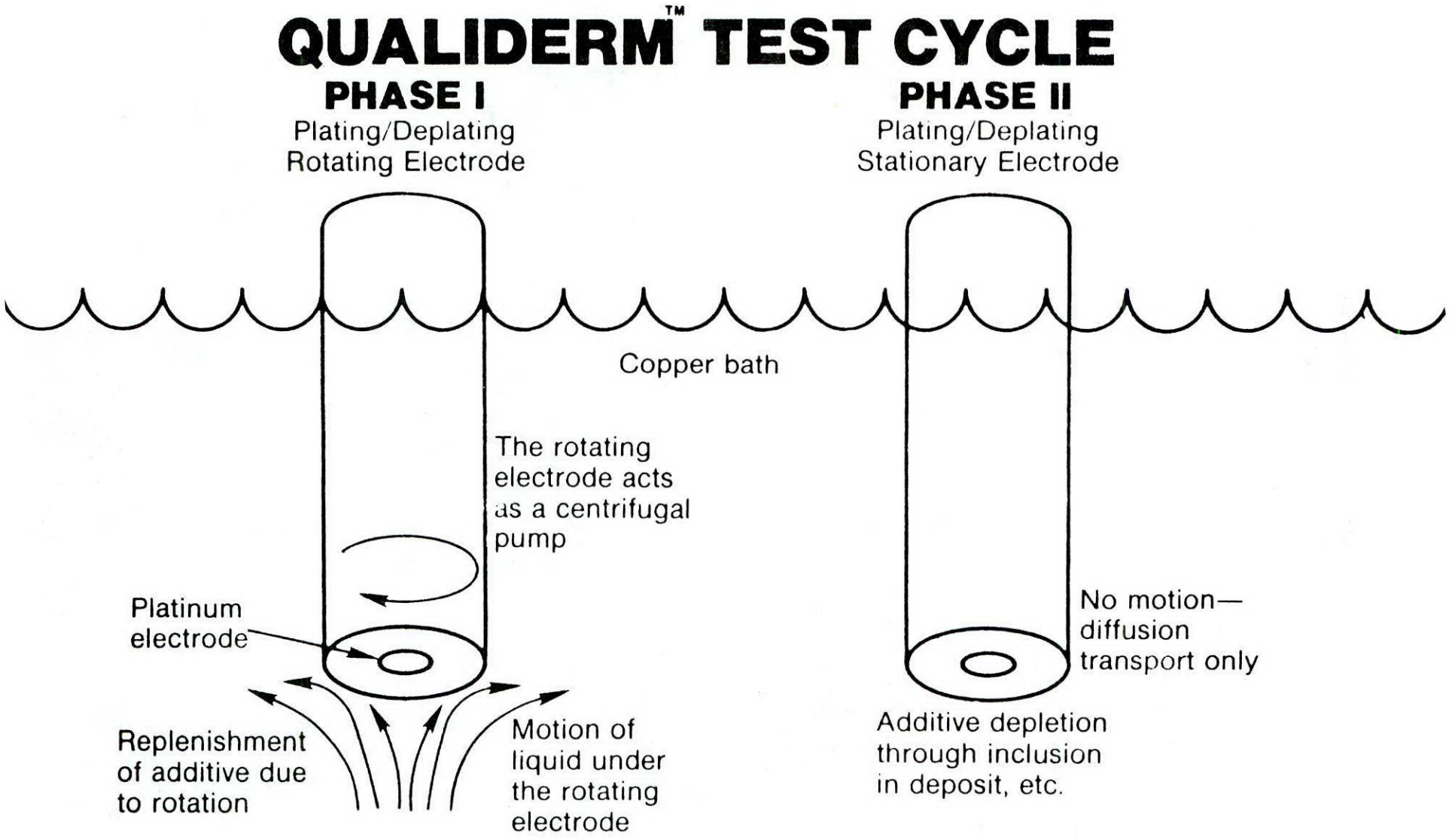
FIGURE 1



DIAG-1

Above is an example of a voltammogram, or "fingerprint" of a copper-plating bath produced by an X-Y recorder used with the QUALIDERM. The area under the peak, labeled Ar, represents the charge (coulombs) required to strip the plating from the platinum electrode while rotating. The area under the As peak represents the charge required to strip the plating from the platinum electrode while stationary. The ratio of Ar to As is an indicator of the effectivity of the plating bath and of the additive concentration.

FIGURE 2


QUALIDERM™ TEST CYCLE
PHASE I
Plating/Deplating
Rotating Electrode
PHASE II
Plating/Deplating
Stationary Electrode
Copper bath
The rotating electrode acts as a centrifugal pump
Platinum electrode
Replenishment of additive due to rotation
Motion of liquid under the rotating electrode
No motion— diffusion transport only
Additive depletion through inclusion in deposit, etc.

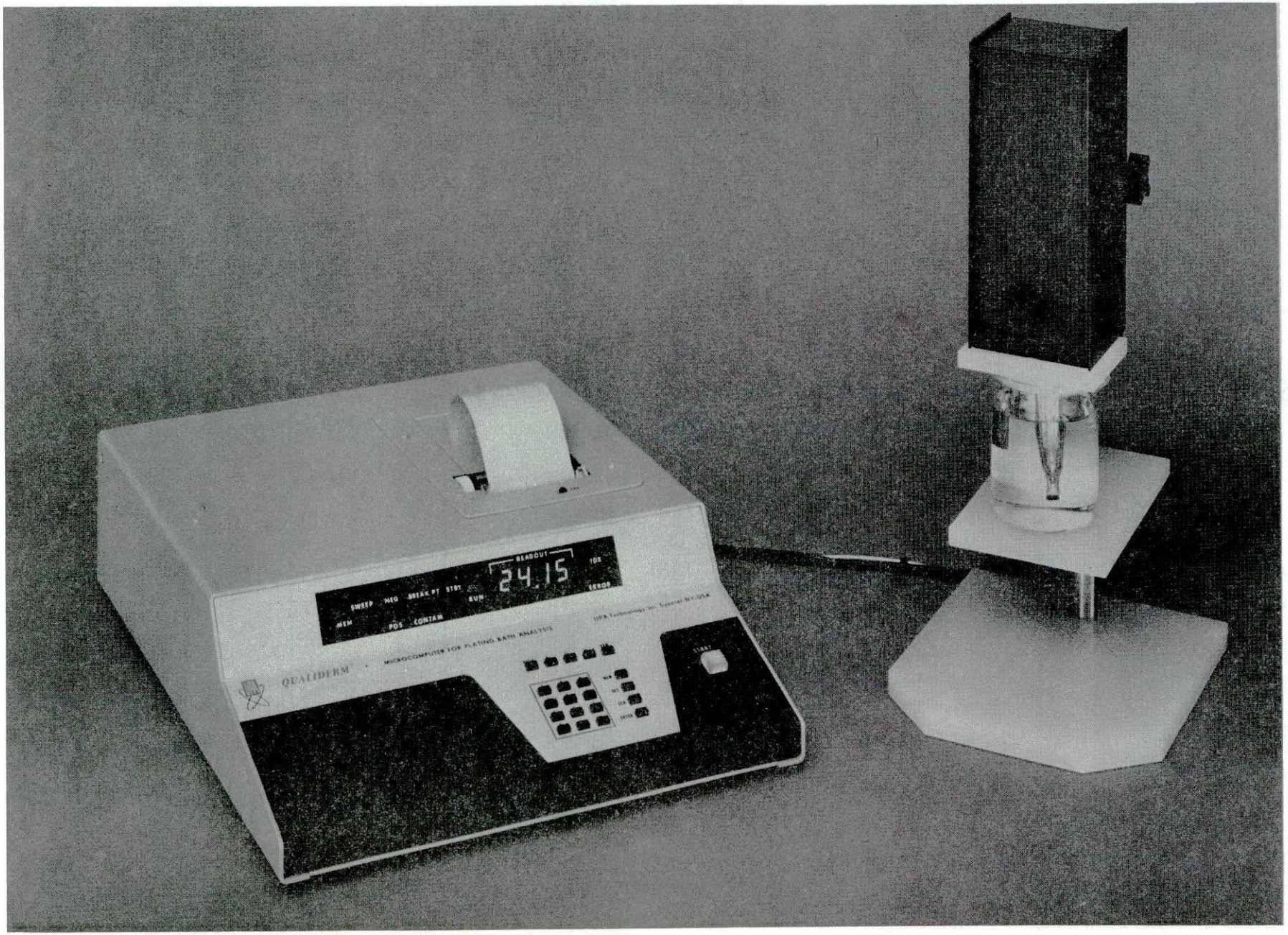
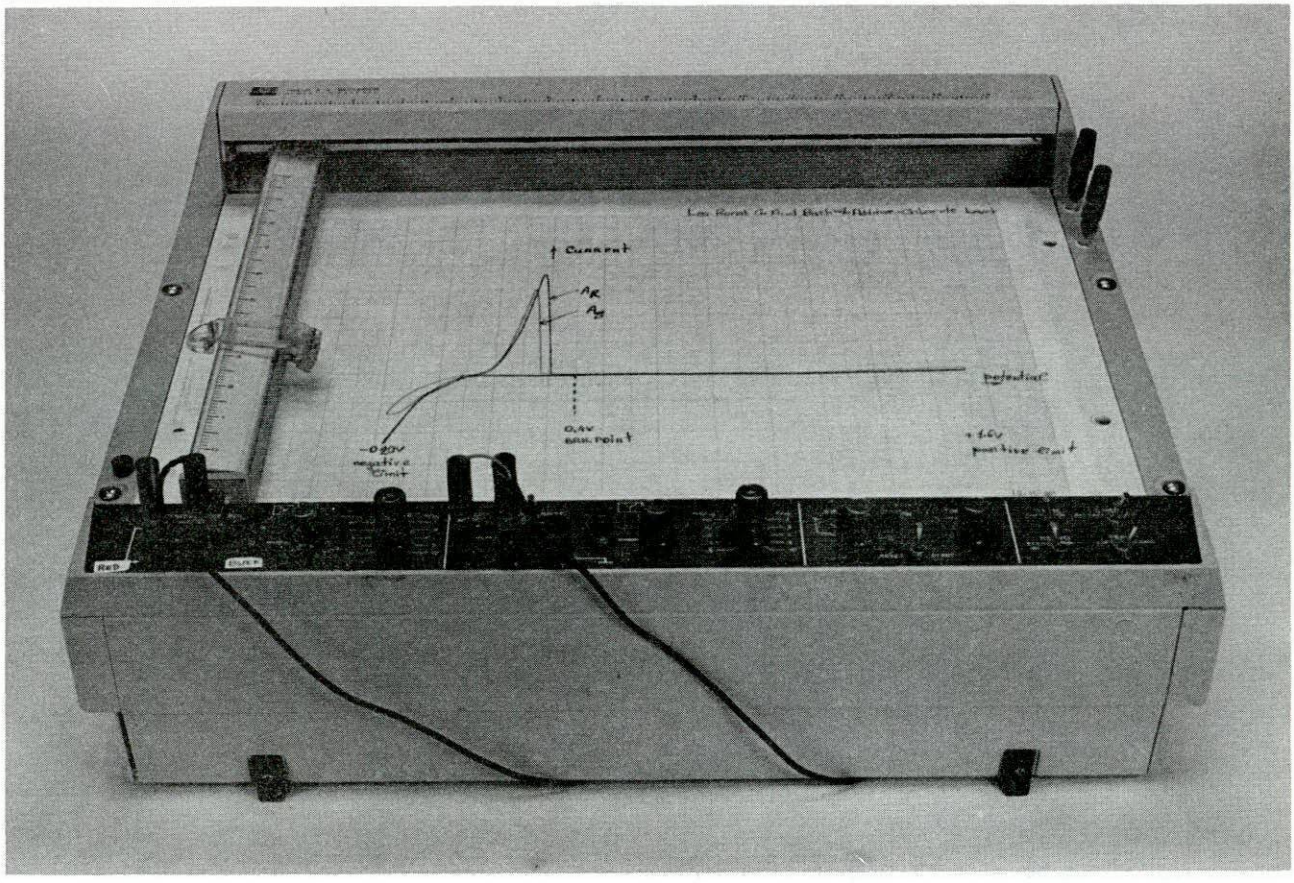

QUALIDERM
MICROCOMPUTER FOR PLATING BATH ANALYSIS
READOUT
24.15
SWEEP
NEG
BREAK PT
STBY
RUN
ERROR
MEM
POS
CONTAM

FIGURE 3

FIGURE 4



G-1

Organic & Chemical Pretreatment Session G

Chemical Pretreatment of Steel for Water-Borne Coatings

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CHEMICAL PRETREATMENT OF STEEL FOR WATER-BORNE COATINGS

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Mr. J. J. McGovern, Automotive Manager

ABSTRACT

The operations from raw part to finished product comprise an entire system. For water-borne finishes, cleaning and conversion coating is a critical segment. While conventional methods do work, special precautions are required to obtain consistently good work. The ability to recognize the source of problems and take corrective action is an important part of operating a successful pretreatment system.

INTRODUCTION

During the past 10 years or so, significant advances have been made in understanding the total finishing process for painted goods. Studies of steel surfaces revealed the detrimental effect of carbon on the durability of the total finish. This has resulted in improved mill practice to give steel with a cleaner surface. Other studies using SEM and ESCA as well as a host of other sophisticated tools have led to an understanding and improvement of zinc phosphate conversion coatings. Organic coatings have likewise been studied and improved. As a result of all this work, some very good systems are available that produce excellent tests on panels.

For the manufacturer to benefit from this work, it has to be transferred to the real world of an operating line. To properly make use of the quality processes available, the user must look at his system as a whole-from raw steel to finished product and each step in between. Like the proverbial chain, each link is very important. As we consider the conversion coating part of the system, we must not ignore the other segments of the system. If there is trouble, it may be caused elsewhere. In turn, the conversion coating part should not create problems. When considering conversion coatings, remember that solvent based finishes may cover some mistakes but water-borne coatings are very unforgiving. Where solvent coatings may cover minor amounts of oil or fingerprints, water-borne coatings can leave bare metal. Solvent systems may cover residues but water systems will not. Where solvent systems cover, water-borne systems pull back. In short, a marginal paint preparation line will not work with water based systems.

The usual response to all of this is to blame the pretreatment, to blame the "chemicals". But, these are the same ingredients that helped produce such wonder panels. Experienced supplier service personnel will tell you that time after time over 90% of the problem lies elsewhere. This is not a self-serving statement. The best steel, the best chemicals, the best finishes cannot overcome bad practice on the process line.

PROCESS

A typical zinc phosphate coating system used to prepare sheet metal for an organic coating consists of several operations or stages. Each stage is separated from the next stage by an inactive area or vestibule. As the part moves along on the conveyor, it will be sprayed with solution for 60 to 120 seconds in each stage. The wet part then passes through the vestibule to the next stage. The stages in sequence are: clean, rinse, zinc phosphate, rinse, acidulated rinse. Some lines may have additional rinse stages. In particular, a deionized rinse is frequently used after the acidulated rinse prior to using a water-borne organic coating. After the pretreatment, the conveyor takes the part to a dry off oven. The part should now be ready for coating. In this process, each stage is important. To get satisfactory preparation, each stage must be working properly. This includes the vestibules and the dry off oven. When the pretreatment is no longer satisfactory, it is time to start looking.

TROUBLE SHOOTING

All lines have trouble at some time. As an operator of a finishing line, you must be intimate with its innermost workings. So, when there is a problem, you, the operator, are in the best position to apply corrective action. Do not be too hasty in assigning fault. Like Sherlock Holmes, you must not only see but you must observe. Experience will show you that the true solution to a problem is often quite simple if you avoid panic long enough to truly observe. Unfortunately, action is often sought for the sake of action and you miss the time to observe. So, when the finished ware does not meet quality requirements, start observing and start asking questions. First of all, did the line ever really produce suitable quality? Many lines are used for years to produce marginal or poor work. If the problem seems more recent, was the change sudden or did the ware gradually lose quality. What is sometimes noticed suddenly may have been going on for some time. Only the awareness is sudden.

As you trouble shoot the line, start with basics. Here it pays to be a skeptic. Do not necessarily take anyone's word that something is so. Check and recheck. Above all, do not neglect the time honored check of temperature and chemical concentrations in the various stages. Has the line speed been changed? This could significantly shorten dwell time in the various stages. You will find that a significant number of problems are solved right at this point.

The next area of investigation involves the mechanical parts of your system. What is the general condition of your line? One of the most frequent mechanical problems is caused by the slow deterioration of spray nozzles and their pipes. Nozzles become worn, or more frequently, clogged. This is a problem that may not be readily apparent since the operating spray zone in a stage may seem to be full of sprayed material when viewed from an end. One clue to problems with nozzles is patterning on large sheet metal pieces. A more difficult clue involves racks of small parts where some are poorly coated. If they are all in the same area of the rack, this may indicate a few bad nozzles. The most difficult problem is a general deterioration of all nozzles resulting in general poor spray impingement on the parts. This may or may not show up as a slight change in pressure. But who remembers what the pressure should be? Here there is no substitute for the tedious examination of all spray nozzles as well as header lines. It is a difficult maintenance job at best. This is particularly so when a few hundred nozzles are involved. Yet this is an extremely important part of keeping up the performance of the washer.

Another problem, usually easy to detect, is work ruined by drippage. There is nothing more disheartening than a drip mark in the middle of a large, otherwise well prepared, piece of sheet metal. However, drippage may be intermittent and the source hard to detect. Here again, careful observation is important. Are the drip marks really the result of flash drying between stages? Is the drippage coming from above or is fluid from parts dripping on parts racked below? Is the drippage coming from the conveyor chain or the shroud? Is the chain well shielded? Are

misdirected spray nozzles hitting the chain? Sometimes drippage will come from poorly designed exhausts that allow condensation to run back into the equipment. There even have been cases where drippage has come from the outside through holes in the shroud. Is the drippage taking place in the dry off oven? Since the source of drips is so illusive and may occur in several unrelated areas, it is frequently necessary to make a number of corrections in a line.

Correcting this type of problem often ends up in upgrading the quality of the entire conversion coating system, including dry off ovens. Note that another drippage problem may also take place in the paint bake oven when water-borne coatings are used. The water removed from the coating condenses somewhere in the oven and then drips on the parts.

No solution to a conversion coating problem can be complete unless you examine your water supply. It is not only hardness that determines water quality. Total dissolved solids is an important factor. In addition to hardness, this includes chlorides and sulfates. If the total dissolved solids is high, even if hardness does not interfere with the cleaning and conversion coating, procorrosive salt deposits may be left on the work. The salts will be particularly concentrated where the water beads. The drippage discussed previously may also be rich in total solids so that it not only mars the surface but creates a procorrosive condition under the organic coating. Even deionized water can be a problem. If you treat your deionizer as a magic black box, it can cause trouble. When you exceed the capacity of the deionizer and forget to regenerate the unit, you will get total dissolved solids problems. In addition, you can get bacterial or algae problems which will mar the finished work. The deionizer, like any portion of your line, requires care and maintenance on a regular basis. If you take care of your equipment, it will take care of you.

SUMMARY

As you can see, there are many pitfalls in properly preparing work for painting on an industrial scale. However, since many plants do it every day, the task is not impossible. Modern processes do exist that are excellent preparations prior to painting. However, for consistent performance, they and the equipment used to apply them, require attention. It requires that maintenance be performed conscientiously on a regular, scheduled basis. Remember that the cost of doing this is far less than the cost of inferior work or the necessity of reworking or scrapping parts.

G-2

Organic & Chemical Pretreatment Session G

Ecological/Energy Impact on Phosphate Coatings

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ECOLOGICAL/ENERGY IMPACT ON PHOSPHATE COATINGS

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The ecological trend involving the replacement of solvent paint systems with water-based paint systems has led to significant changes in the area of zinc phosphate treatments. The use of cathodic or anodic electrodeposited primers affects the zinc phosphate coating characteristics in a manner distinguishable from that of solvent primers. In particular, the phosphate coating characteristics given below are significantly affected by the water-base paint systems, and subsequently play a predominant role in providing adequate corrosion resistance and paint adhesion.

Solubility in Alkaline Environment
Solubility in Acid Environment
Coating Composition
Zinc Phosphate Crystal Structure
Coating Conductivity
Zinc Phosphate Crystal Size
Coverage

The introduction of cathodic electrodeposited primers provided substantial improvement in corrosion resistance over prior primer paint systems; however, new test procedures other than salt spray had to be developed in order to provide results that correlated to actual outdoor exposure testing. At the present time, several testing procedures exist that produce a "scab" type of corrosion in a scribed paint film, in contrast to the standard paint delamination or creepage that is observed after salt spray testing. As a result of the difficulty in assessing the quality of the phosphated coating under paint via cyclic scab testing procedures, it was decided to investigate the corrosion properties of a phosphate coating via electrochemical surface analysis in order to gain a better understanding of the mechanisms governing underfilm corrosion.

The use of electrochemical analysis of zinc phosphate coatings as a means to characterize the coating properties has been previously studied by several investigators.(1)-(4). Since the primary modes of corrosion are the anodic dissolution of the coating (or metal substrate) and the cathodic reduction of oxygen or water, our investigation of zinc phosphate coatings involved both anodic and cathodic polarization techniques; in contrast to prior studies where cathodic polarization was primarily studied. A schematic of our experimental apparatus is shown in Figure 1.(5). Our study involved variation of the potential between a Saturated Calomel Electrode (SCE) and the metal substrate, with concomitant measurement of the resultant current between the metal substrate and counter electrodes. Further, the change in the steady-state potential (E_{SS}) of the substrate, when immersed in a dilute solution of an electrolyte, also provided an insight into the corrosive nature of the phosphate coating.

The presence of a zinc phosphate coating, or modification of the phosphating process via final rinse variation, temperature, etc. may affect

both the anodic and cathodic corrosion modes simultaneously or independently. The phosphate coating, however, provided a reduction in the corrosion current in most cases, and thus reflected the "insulating" nature of zinc phosphate coatings. Figure 2 illustrates the results of our cathodic and anodic polarization of phosphated and non-phosphated steel and galvanized steel.(5) From Figure 2, one observes that the steady-state potential of the phosphated steel substrate has shifted to a more negative value, thus reflecting a more passive surface condition. Further, the corrosion current of the phosphated steel sample is less than that of non-phosphated steel. Summarizing, on steel substrates the phosphate coating will "dissolve" first during corrosion, thus providing cathodic protection to the steel substrate. The phosphate coating on galvanized steel provides additional resistance to corrosion, but with a different mechanism from that of steel. Again, the corrosion current on the galvanized steel is less with the phosphated coating; however, the resultant steady-state potential has shifted toward a more positive value. The shift of the steady-state potential in the positive direction implies that the phosphate coating has increased the corrosivity of the galvanized steel; however, the corrosion current of the phosphated galvanized steel has decreased. In summary, a phosphate coating on galvanized steel protects the galvanized substrate by inhibiting the dissolution of the galvanized substrate during corrosion, even though the phosphate coating does not provide cathodic protection to the galvanized steel substrate (i.e., dissolve first during the corrosion process). One may conclude that the phosphate coating acts as a physical barrier in its protection of the galvanized steel substrate.

The zinc phosphate treatment of aluminum is complicated by the existence of several aluminum alloys, each of which has specific characteristics that affect the zinc phosphate/aluminum interaction. Further, the electrochemical analysis of zinc phosphated aluminum substrates is also complicated by the rapid formation of the protective aluminum oxide film, whose solubility is pH dependent. Since cathodic polarization affects the pH of the electrolytic solution used in the electrochemical surface analysis, the analysis of the zinc phosphated aluminum substrate was performed at several pH values, as shown in Figure 3.(5) From Figure 3, one may note that the pH of the electrolytic solution substantially affects the anodic polarization behavior, and the corrosivity of the phosphated aluminum surface decreases as the pH of the electrolytic solution decreases. Therefore, one may conclude that the main factors contributing to the resultant corrosion reistance of a phosphated and painted aluminum substrate will depend upon the solubility (or stability) of the aluminum oxide film and/or the zinc phosphate coating at the pH which results from the corrosion process at the paint defect. Since the zinc phosphate coating solubility is also pH dependent, it cannot be stated precisely whether or not the phosphate coating provides anodic or cathodic protection to the aluminum substrate.

In the majority of cases where aluminum will be treated with a zinc phosphate coating, steel and galvanized steel are also being processed simultaneously. In the processing of these substrates, special attention must be directed at the cleaning of these substrates prior to phosphating. The cleaner must be sufficiently alkaline to remove the oils, smut, dirt,

etc, from the steel and galvanized steel substrates, without excessively attacking the aluminum substrate. Further, the phosphating bath would require the addition of fluoride compounds to prevent the build-up of soluble aluminum in the zinc phosphate bath, which would inhibit the coating formation on steel. The electrochemical analysis of the effect of fluoride concentration in a zinc phosphate bath upon the coating formation on an aluminum substrate is given in Table I. The current produced from both cathodic and anodic polarization of the phosphated aluminum substrate within 50 millivolts of the steady-state potential was measured and averaged. As one may note, as the fluoride concentration in the phosphating bath increased, the coating weights increased with a simultaneous decrease in the crystal size and polarization current.

A major ecological improvement associated with zinc phosphate processing would be the elimination of a chrome-based final rinse. The electrochemical behavior of an iron phosphated surface was found to be affected by the chemical nature of the final rinse. Further, through experimentation, it was discovered that certain final rinse solutions rendered the surface activity, as measured via the Polarization Current, comparable to that caused by a chrome-based final rinse. In continuing our experimentation, it was determined that the Polarization Current can be correlated to subsequent salt spray performance of the painted substrate (solvent type paint), as shown in Figure 4. In addition, the Polarization Current was also correlated to subsequent Cyclic Scab Test (see Appendix A) results using a paint system comprising a water-base cationic electrodeposited primer (Figure 5). Testing of the non-chrome final rinse solutions under production conditions is proceeding at this time.

As is well known, savings in energy costs can be obtained through the use of "low" temperature processes, where "low" temperature usually refers to processes that operate at temperatures below 110°F. Several "low" temperature iron phosphate processes are available in the Fabricated Metals Industry, where the requirement for paint adhesion may exceed that of corrosion resistance (e.g., office furniture). In those industries where optimum corrosion resistance of the painted substrate is mandatory (i.e., Automotive Industry), a zinc phosphate or calcium/zinc phosphate coating would be necessary to meet this demand. Although "low" temperature zinc phosphate solutions have been developed in the past, these systems were inadequate to provide the necessary corrosion resistance with the water-base electrodeposited primer paint systems that are being utilized today. Past "low" temperature zinc phosphate coatings usually contained manganese, produced heavy coating weights (i.e., 250-300 mg/ft^2) on low carbon steel, and exhibited a tendency to be "powdery". Further, processing difficulties were usually encountered, such as excessive sludge formation and erratic coating behavior. Through experimentation it was determined that the following parameters substantially affected the resultant quality of a "low" temperature zinc phosphate process:

- Cleaner Composition
- Crystal Refinement Stage
- Bath Composition
- Coating Composition
- Temperature Fluctuations

As a result of the decrease in operating temperature (from 125 to 95°F), the rate of acid attack at the metal surface is reduced, which in turn minimizes the resultant pH change at the metal surface/bath solution interface. Since the pH change at the interface is minimized, the deposition of the zinc phosphate coating is also reduced unless adjustments are made in the processing parameters. One primary adjustment in the processing parameters would be the incorporation of an "activating" rinse prior to phosphating. The presence of an "activated" metal surface via the use of Jernstedt salts provides compensation for the minimal acid attack at the metal surface. The activation of the metal surface may also be provided by the cleaner as long as the degreasing capability of the cleaner stage is not substantially reduced.

It was determined in our investigation that substantial modification of the constituents in the zinc phosphate bath was required in order to produce a zinc phosphate coating that provided the quality with cathodic electrodeposited paint systems that was comparable to the "iron-enriched" zinc phosphate coatings which are being employed in the Automotive Industry currently. Further, it was also determined in our investigation that the incorporation of manganese into the zinc phosphate bath was not required to provide adequate coating formation at 90 to 95°F or to improve the performance. The effect of bath acidity upon coating formation on steel is shown in Figure 6, where "R" refers to the ratio of Total Acidity to Free Acidity (see Appendix B). As one may note, as "R" increases, the rate of coating formation increases.

Finally, the characteristics of our low temperature zinc phosphate coating on galvanized steel was determined using Auger Depth Profile Analysis, as shown in Figure 7 (6). The coating studied in Figure 7 was applied to the galvanized steel surface via immersion. As one may note in Figure 7, a substantial amount of nickel was found throughout the coating, which we believe represents a major factor in providing optimum corrosion resistance and paint adhesion on galvanized steel. Additional surface analysis of our low temperature zinc phosphate coating on steel (spray application) has also shown the presence of nickel in significant amounts. In summary, the presence of nickel in a zinc phosphate coating plays an important role in providing the optimum adhesion and corrosion resistance of a painted and galvanized steel substrate.

In conclusion, the continuing ecological and energy restrictions in the coatings industry will significantly affect zinc phosphate coating technology. As quality requirements continue to increase, so does the need for a better understanding of the complete function that a zinc phosphate coating performs under paint in helping to prevent the loss of paint adhesion and subsequent corrosion of the base metal.

APPENDIX A

CYCLIC SCAB TEST PROCEDURE

a). 15 Minute Immersion - 5% NaCl

b). 1 Hour, 15 Minutes drain in Ambient Atmosphere

c). 22 Hours, 30 Minutes at 85% R.H., 120°F

(a) + (b) + (c): 1 Cycle
5 Cycles per week
Test Duration: 20 Cycles

APPENDIX B

Total Acid Titration: Sample Size 10 milliliter

Sample titrated with 0.1 Normal NaOH to Phenolphthalein Endpoint

Free Acid Titration: Sample Size 10 milliliter

Sample titrated with 0.1 Normal to Brom Phenol Endpoint

TABLE I

FLUORIDE EFFECT ON ZINC PHOSPHATE COATINGS ON ALUMINUM

Fluoride Concentration	Crystal Size (microns)	Ct.Wts(Avg) mg/ft^2	Polarization Current* (microamps/cm^2
30-40 ppm	50-60	40	24
150-200 ppm	20-30	90	16
Over 350 ppm	5-10	180	4

*Measurements performed at a pH of 7.5

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6. Union Carbide, Tarrytown, N.Y., Central Scientific Laboratory.

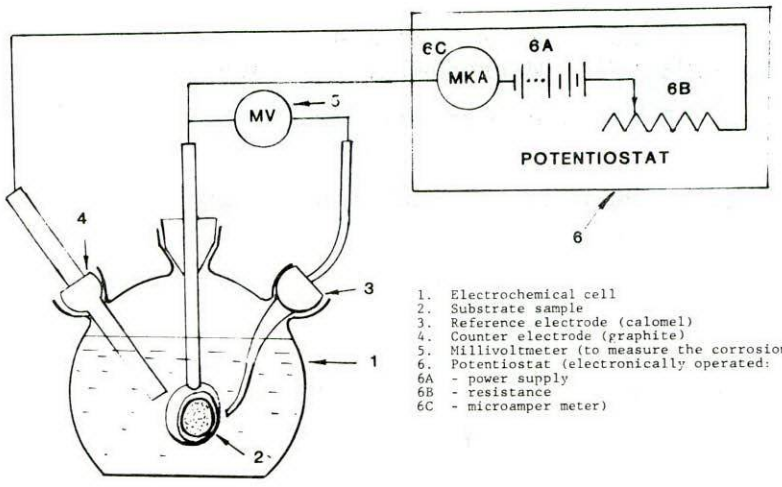
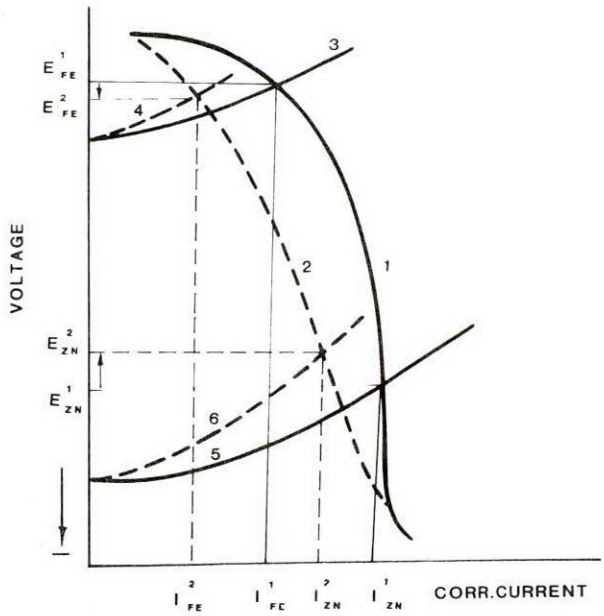
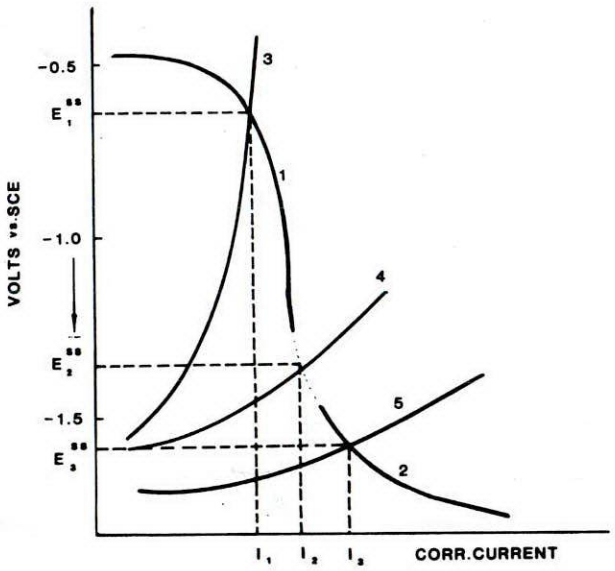


Figure 1. Electrochemical Measurement Apparatus.



1. Oxygen reduction on non-phosphated metal
2. Oxygen reduction on phosphated metal
3. Anodic dissolution of non-phosphated steel
4. Anodic dissolution of phosphated steel
5. Anodic dissolution of non-phosphated galvanized steel
6. Anodic dissolution of phosphated galvanized steel

Figure 2. Formation of Steady-State Potentials on Steel and Galvanized Steel Substrates.



1. Oxygen reduction
2. Hydrogen evolution
3. Dissolution of aluminum at pH from 3 to 5
4. Dissolution of aluminum at pH from 7 to 9
5. Dissolution of aluminum at pH = 10 and more.

Figure 3. Formation of Steady-State Potential on Aluminum.

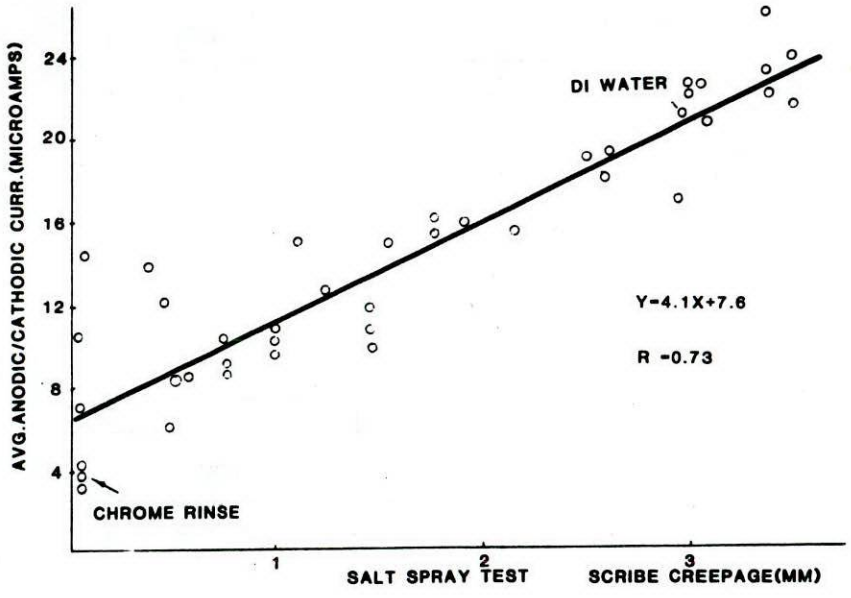


Figure 4. Linear Diagram of Potentiodynamic and Salt Spray Tests.

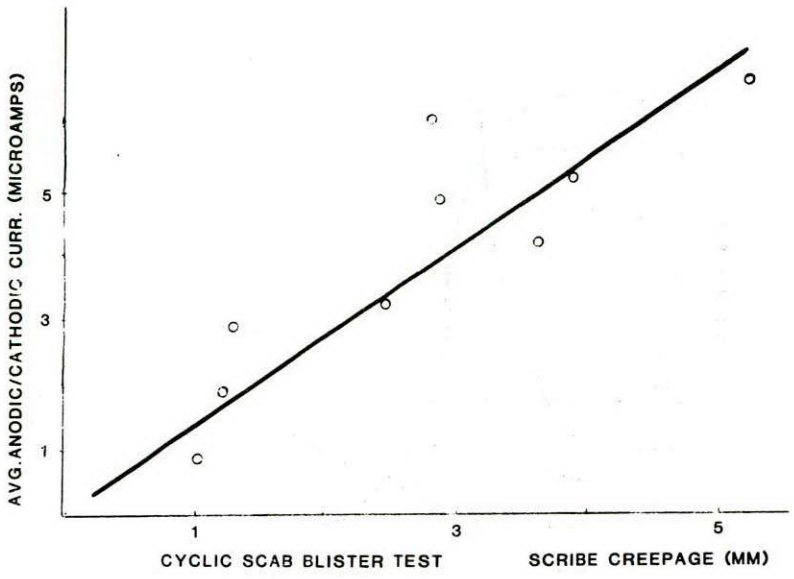


Figure 5. Linear Diagram of Potentiodynamic and Cyclic Scab Blister Test.

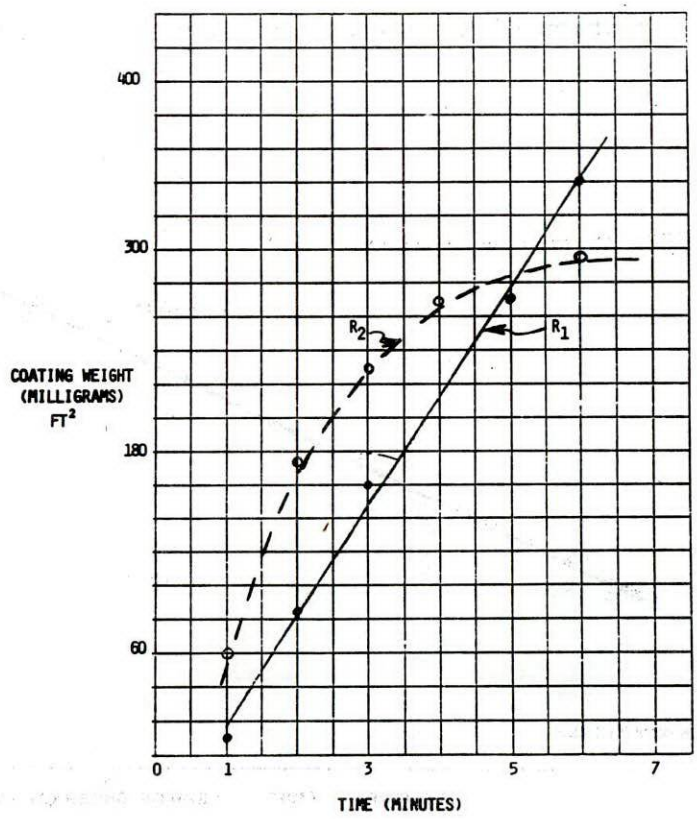


Figure 6. Bath Acidity Effect Upon Coating Formation at 93°F.

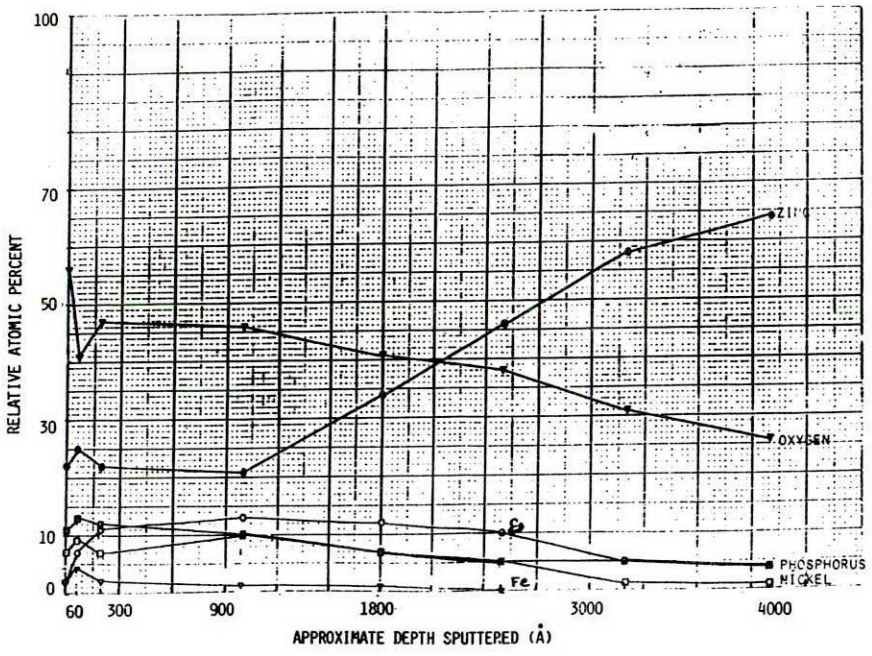


Figure 7. Auger Depth Profile of Phosphate Coating on Galvanized Steel.

G-3

Organic & Chemical Pretreatment Session G

Compliance with Solvent Emission Regulations Without Change in Resins, Pigments or Basic Equipment

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COMPLIANCE WITH SOLVENT EMISSION REGULATIONS WITHOUT CHANGE IN RESINS, PIGMENTS OR BASIC EQUIPMENT

by

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Birmingham MI 48010

Approximately 50% of all industrial coatings are applied by use of equipment designed to handle paints of conventional viscosity of approximately 60 centipoises (25 seconds #4 Ford cup or 27 seconds #2 Zahn cup). The comparatively low viscosity is usually achieved by reducing or thinning of paints to 25 to 35 vol% Non-Volatiles (NV). These paints, however, do not comply with Governmental Regulations since they contain between 4.3 and 5.5 lb VOC per gallon paint minus water, depending upon the density of the VOC, as computed by use of Equation 1 (see Appendix) and schematically presented in Figures 1 and 2a.

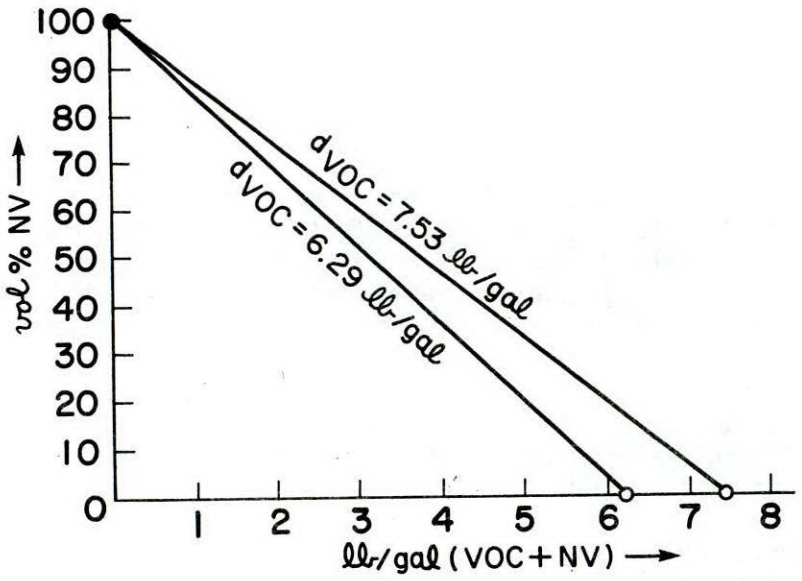

FIGURE 1

Influence of d_{VOC} on allowable vol% NV

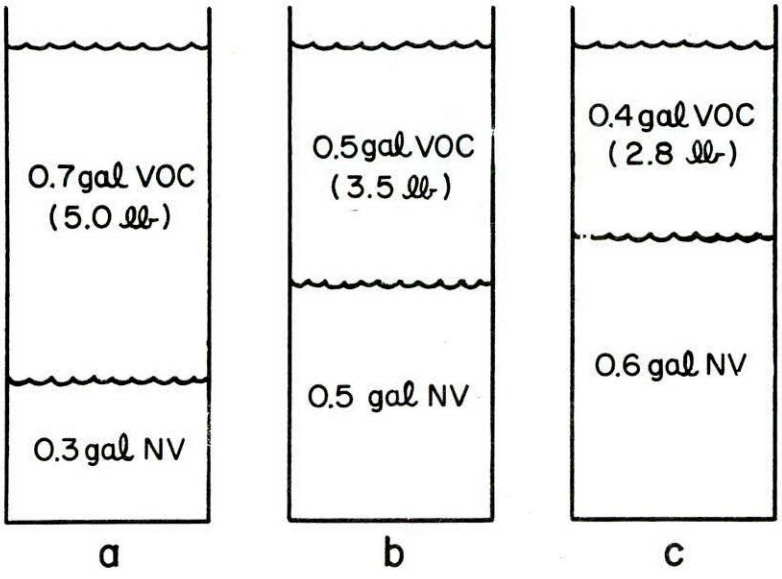

FIGURE 2

Volume fraction of VOC
and
lb VOC/gal(VOC+NV)

Most State Implementation Plans mandate the use of paints of not more than 2.8 lb VOC and up to 3.5 lb VOC for General Metal Finishing, in other words, approximately 45 to 60 vol%NV (see Figure 2b). Paints of these solid contents are of higher viscosity than conventional materials, which, in many cases necessitates considerable capital expenditure for new spray painting equipment.

Conventional hand spray guns result in very low transfer efficiency, probably not higher than 30% for general merchandise and not more than 40% for such large objects as automobile and truck bodies (1).

Many State Implementation Plans require transfer efficiencies of 50% t.e., and some states require 65% t.e., which, for these high viscosity paints, can be achieved only by use of electrostatic centrifugal atomization.

The large expenditures for new equipment can in many cases be avoided by the use of a recently developed class of paint solvents, which has lifted conventional handspray equipment from obsolescence into renewed interest.

Compliance Solvents

A unique opportunity for complying with governmental paint-solvent emission regulations was introduced on July 8, 1977 through a U.S. Environmental Protection Agency notice in the Federal Register (2): "...volatile organic compounds of negligible photochemical resistance that should be exempt from regulation under State Implementation Plans...(are)... Methane, Ethane, 1,1,1-Trichloroethane, Freon 1,1,3..." This notice was later confirmed and reconfirmed 4 more times during the next three years (3) and expanded to include several more solvents, of which methylene chloride is of interest to the paint and finishing industries.

The exempt chlorinated hydrocarbons are now called Compliance Solvents. Their use has virtually changed the description of allowable paints from "not exceeding certain specified weights of VOC per volume of paint minus water" to "paint minus water or compliance solvents" (lb VOC/gal [VOC+NV]). Since 1979 the majority of states, including California, have exempted 1,1,1-trichloroethane and methylene chloride from emission restrictions.

Compliance Paints

Compliance paints may be looked upon as High Solids paints thinned with 1,1,1- and/or methylene chloride to the low viscosity of conventional materials. Indeed, some paint manufacturers sell a paint concentrate, which the customer reduces with compliance solvents.

Another way to look at compliance paints is to state that they are conventional paints in which a certain amount of solvents (like xylene, VM&P, butanol, etc.) have been replaced by compliance solvents.

In either case, compliance paints are solvent borne materials of conventional viscosities, and can be formulated while retaining the resins and pigments currently used by a customer.

A rapidly increasing number of U.S. resin and paint manufacturers supply materials formulated by use of compliance solvents.

Toxicity and Carcinogenity Tests

1,1,1-trichloroethane and methylene chloride have been subjected to many tests involving thousands of animals. Some of these tests have been reported in a U.S. Environmental Protection Agency Report (4, page 174); "...interim results of carcinogenic tests... of methylene chloride...were negative...", and (4, page 207); "...a National Cancer Institute bioassay of 1,1,1-trichloroethane found no correlation...(with)...any cancers..." Several studies gave 1,1,1- and methylene chloride a clean bill of health (see 5,6, and 7).

The Occupational Safety and Health Act (OSHA) allows equal or larger Time Weighted Average exposure of workers to 1,1,1- and methylene chloride (CH_2Cl_2) than for other commonly used solvents. The toxicity Threshold Limit Values for compliance solvents are higher or equal to most other

solvents, as shown in Table 1. Thus, the wastes and sludges of all currently used paints are considered toxic, and are subject to all applicable waste disposal regulations.

Table 1

OSHA EXPOSURE[a] and TOXICITY[b] STANDARDS

SOLVENT	3[h] TWA ppm	TLV ppm
1,1,1-	350	350
CH_2Cl_2	500	200
Toluene	200	100
MEK	200	200

a Fed. Register 39-23540, 6-27-74
b Am. Conf. Gov'mt. Hygienists 1976

Archer and Stevens (8) conclude from these and many other data: "...although chlorinated solvents do not differ dramatically from hydrocarbons under OSHA regulations covering worker exposure, they offer safer working conditions when flamability hazards are of concern..."

Availability

A number of U.S. manufacturers produce 1,1,1-trichloroethane and methylene chloride. Their combined production capacity is estimated as 1,250 million lbs 1,1,1- and 900 million lbs methylene chloride annually. The 1980 sales were estimated as 570, and 530 million lbs respectively.

In as much as the metal finishing industry is concerned, much of these two chlorocarbons are used for metal preparation, either directly or in combination with phosphates.

Methylene chloride is also used as a paint stripper.

These solvents are stabilized as needed for the above mentioned applications. However, to date, only the Dow Chemical Company has developed grades of 1,1,1-trichlorethane and methylene chloride specifically stabilized for coating purposes. It is a reasonable assumption that - if successful - plenty of motivation will be provided for the utilization of existing production capacity of other chlorcarbon manufacturers.

Solvent Emission Regulations

One of the most environment-conscious states is California which exempts the use of 1,1,1- and methylene chloride from regulations. The current law, in form of Rule 1107 has been summarized as follows (9): "...beginning in January 1983 all users of coatings which are applied to miscellaneous metal parts and products, must limit the amount of VOC in the baking finishes they use (baked at temperatures in excess of 194°F) to 360 g/L as applied (3.0 lb/gal) paint minus water or compliance solvents. For air drying coatings, or coatings that are force dried at temperatures below 194°F, you will

be limited to 420 g VOC/L (3.5 lb/gal) of coating as applied. However, by January 1984, in the Los Angeles basin, you must reduce these Volatile Organic Compounds to 275 g/l (2.3 lb/gal) of baking enamel as applied, and to 340 g/L (2.8 lb/gal) for air dried paint as applied..."

The unit 340 g VOC per liter paint minus water or compliance solvent (2.8 lb/gal) does not lend itself directly to translation into lb VOC emitted while coating a given size of production. The unit most directly related to a metal finishing operation is "lb VOC per gallon of Non Volatiles." The conversion of lb VOC per gallon of paint minus water or compliance solvents to lb VOC/gal NV is facilitated by Equation 2 see Appendix or see (10, page 21) .

California Rule 1107 imposes not only 340 g VOC/liter (2.8 lbs) but also demands a transfer efficiency of 65%, in other words, electrostatically aided handspray. Equation 3 see Appendix or see (10, page 37) is helpful for the computation of the VOC emitted, as shown in Example A of Appendix. For instance, when 1604 ft^2 are painted 1 mil thick at 65% t.e. by use of a paint of 2.8 lb VOC/gal (VOC+NV), assuming d_{VOC} as 7.0 lb/gal, 7.23 lb (3.28 kg) VOC are emitted. In other words, in California, according to Rule 1107, 7.23 lb VOC are allowed.

A paint of 2.8 lb VOC/gal (VOC+NV) contains approximately 60 vol%NV (d_{VOC} = 7.0) according to Equation 1 and also according to Figures 1 and 2c.

If the transfer efficiency is increased to 95% by use of centrigugal electrostatic atomization, two important advantages are gained:

a) The cost of paint is reduced by about 1/3.
b) Since the allowable emission remains unchanged, paints of lower vol%NV can be used according to the Equivalence Concept (11). These, less concentrated paints, are easier to atomize.

Again, using the equations of the Appendix, the following data are obtained: At 95% transfer efficiency a paint of 3.5 lb VOC/gal (VOC+NV) and at 40% t.e. a paint of 2.0 lb VOC/gal (VOC+NV) are equivalent to the 2.8 lb VOC paint, in other words, in all 3 cases, not more than the allowable 7.2 lb VOC are emitted per gallon of NV applied. However, 95% transfer efficiency means automatic centrifugal electrostatic atomization, requiring considerable investment of capital. 40% t.e. requires an approximately 70 vol% NV paint, very difficult to handle with paint heaters and centrifugal guns. Yet, such a 70 vol% NV paint with proper composition of its 30 vol% VOC, can be reduced by use of 1,1,1-trichloroethane to any desired viscosity, to allow easy handling.

Of particular interest is reduction to a 30 vol% NV concentration dissolved in VOC plus 1,1,1-trichloroethane because such paints are of the viscosity for which conventional air atomizing guns are designed. Figure 3 shows that low viscosity compliance paints are available for any type of atomizing. equipment.

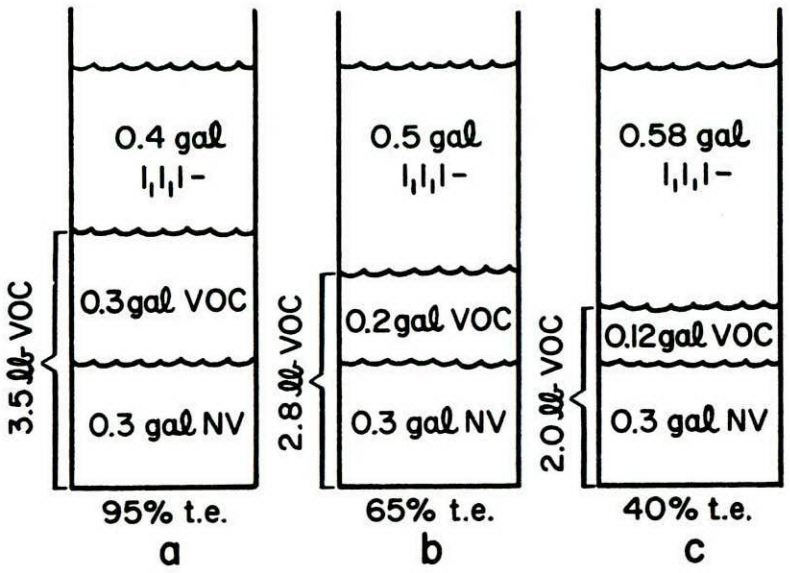

FIGURE 3

Equivalence Principle.
Adjustment of paint to conventional viscosity
and VOC Emission for various %t.e.

Continued Use of Existing Equipment

Governmental Regulations are concerned with the quantity of environmentally objectionable VOC associated with the volume of NV. Figure 1 shows the gradual increase of NV caused by stricter regulations. Hand in hand with increased NV goes higher and higher viscosity, demanding higher fluid pressures and heating devices. A break-through occurred when it was realized that paint viscosity can be lowered through the use of environmentally inoffensive diluents, called compliance solvents, such as 1,1,1-trichloroethane.

These paints can be formulated at, for instance, 30 vol%NV with varying quantities of VOC. At this constant volume of NV, their viscosity varies very little. The relative quantities of VOC and 1,1,1- can be changed, to comply with the individual requirements of the user.

Large companies may find cost advantages in investing in automatic booths, using centrifugal electrostatic atomization which results in up to 95% t.e. (Figure 3a)

Small companies, which currently use air atomizing hand guns, can continue to use these with minor changes in equipment, usually ranging from no cost

to several thousand dollars only. A paint which emits into the air not more than the allowable 7.2 lb VOC at 40% t.e. is schematically presented in Figure 3a. The viscosity of this and other compliance paints is approximately 60 centipoises (25 seconds #4 Ford cup or 27 seconds #2 Zahn cup), and there is little doubt that the large number of manufacturers who operate today by use of air atomized hand spray will welcome the opportunity to continue the use of this technique through incorporation of 1,1,1- into their paints.

Equipment Changes

Essentially one change has to be made for both air drying and baked compliance paints:

> The contact between paint and aluminum has to be avoided (12). This demand is not confined to appliance paints only. In fact a literature study revealed that the earliest notice about the danger of paint components in contact with aluminum appeared in 1934, when it was pointed out that alcohols react with aluminum under liberation of explosive hydrogen gas (13).

The other change applies only when direct fired ovens are currently used:

> The contact between compliance solvent vapor and direct flame has to be avoided to prevent the formation of hydrochloric acid vapors. The necessary change consists in using fresh air to supply the flame (9, page 6).

A good number of cases are on record where the necessary changes have been accomplished at expenditures of less than $5,000.

Revival of Air Drying Paints

Particularly in times of high cost and shortage of energy, air drying materials are of great interest. Also, the quality of air drying materials has improved over the years. Yet, ambient temperature of forced cure (up to 195°F) is not too widely used. The reason is that air drying materials have required large amounts of VOC. Most State Implementation Plans allow more VOC for air drying paints, usually between 3.5 and 4.5 lb VOC/gal (VOC+NV). Even this large allowance does not produce typical air drying lacquers of sufficiently low viscosity. The addition of 1,1,1-trichloroethane, however, results in easy to handle paints, in compliance with Solvent Emission Regulations.

These air drying compliance paints are now being re-accepted by industry and reports begin to appear in the literature (14).

Summary

1,1,1-trichloroethane and methylene chloride, sometimes called "Compliance Solvents", are exempt from Governmental Regulations in the majority of

states, including such key areas as California, Connecticut, Indiana, New York, Ohio, etc.

The definition of allowable paints can be understood as limiting the "lb Volatile Organic Compounds per gallon of paint minus water or Compliance Solvents." lb VOC/gal (VOC+NV) .

Compliance paints contain exempt chlorinated solvents, replacing part of their VOC, or may be looked upon as High Solids materials thinned with Compliance Solvents to conventional viscosity.

The use of Compliance Solvents brings the opportunity of retaining a currently used system of resin and pigments while accomplishing compliance with such strict emission regulations as California Rule 1107 for 1982 and 1984.

The changes in the formulation of compliance paints are restricted to changes in the solvent balance only.

The cost of converting from conventional paints to compliance paints is much less than the cost of converting to other allowable paints.

Air drying lacquers, complying with Emission Regulations, are beginning to be re-accepted by industry.

Appendix

Equation 1

Computation of vol%NV from lb VOC per gallon paint minus water.

$$\text{vol\%NV} = \left(1 - \frac{\text{lb VOC}}{d_{VOC}} \times 100\right)$$

where:

vol (VOC + NV) = 1 gal

d_{VOC} = density in lb/gal

Equation 2

Conversion from $\frac{\text{wt. VOC}}{\text{vol (VOC + NV)}}$ to $\frac{\text{wt. VOC}}{\text{vol NV}}$

$$\text{vol VOC} + \text{vol NV} = 1$$

$$\text{vol NV} = 1 - \text{vol VOC} = 1 - \frac{\text{wt. VOC}}{d_{VOC}}$$

$$\frac{\text{wt. VOC emitted}}{\text{gal NV applied}} = \text{wt VOC} \; / \; \left(1 - \frac{\text{wt VOC}}{d_{VOC}}\right)$$

Equation 3

Computation of wt. VOC emitted.

$$\text{wt VOC emitted} = \frac{100}{\%\text{t.e.}} \times \frac{Ap}{K} \times t \times \frac{\text{wt VOC}}{\text{gal NV}}$$

where:

%t.e. = % transfer efficiency

Ap = area painted (ft^2 or m^2)

t = film thickness (mil or μ)

K = 1604 ft^2mil/gal or 1,000 $m^2\mu$/L

$\frac{\text{wt VOC}}{\text{gal NV}}$ = wt VOC associated with 1 gal NV

Example A

How many lb VOC are emitted when 1604 ft^2 are painted 1 mil thick by use of a paint of 2.8 lb VOC/gal (VOC+NV) at 65% t.e. as the California 1107 mandates? Assúme d_{VOC} = 7.0 lb/gal.

Equation 2:

$$\frac{\text{lb VOC emitted}}{\text{gal NV applied}} = 2.8/\left(1 - \frac{2.8}{7.0}\right) = 4.67$$

Equation 3:

$$\text{lb VOC emitted} = \frac{100}{65\%} \times \frac{1604\ ft^2}{1604\ ft^2\ \text{mil/gal}} \times 1\ \text{mil} \times 4.67\ \frac{\text{lb VOC}}{\text{gal NV}} =$$

= 7.2 lb VOC emitted = 3.3kg

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G-4

Organic & Chemical Pretreatment Session G

Considerations When Converting to Water-Borne Coatings for Dip, Flowcoat and Spray Application

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CONSIDERATIONS WHEN CONVERTING TO WATER-BORNE COATINGS FOR DIP, FLOWCOAT, AND SPRAY APPLICATION

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Abstract

The strengths and weaknesses of water-borne coatings will be compared to solvent base coatings for application and physical properties.

Recommendations will be presented on how to initiate an efficient water-borne trial run program and to economically convert an existing solvent system to a water-borne system.

Introduction

Some of you are familiar with water-borne coatings, either having tried to introduce them into your production and were not successful, then reverted back to a solvent system or have been able to adapt a water-borne system to your application line and are now enjoying the benefits.

Problem areas encountered when converting to a water-borne coating may have always been present but the solvent coatings were just more tolerent of these conditions.

Water-borne coatings are replacing solvent coatings which have been in use for many years and have been modified through those years to obtain the accepted application properties and appearance.

Physical and Application Properties of Water-Borne Coatings

Water-borne coatings are more susceptible to contamination and have poorer surface wetting properties than solvent coatings. The presence of oil, dirt or grease on poorly cleaned parts may result in cratering and crawling. Even though the water-borne coating may coat over a contaminated surface and have an acceptable appearance, a loss of adhesion may be seen. Good maintenance of the pretreatment is required to minimize or eliminate this problem.

Water systems are also prone toward pull-away from sharp edges and wash out under holes. This can be eliminated again by good maintenance of the pretreat, mechanically by exhaust in the flash off area and the formulation using additives. The most troublesome of water-borne properties is that of popping and blistering at higher film thicknesses. The use of high boiling

solvents, two zone ovens, and preheating the coated parts are several ways of eliminating the popping and blistering. Viscosity control is more critical since higher viscosities yield higher film thickness which lead back to the blistering and popping problem.

Water-borne coatings are more prone to bubbling and foaming than solvent systems, but with proper formulation, the bubbling and foaming can virtually be eliminated and not cause any application problems.

Water based coatings are more sensitive to temperature and humidity than solvent coatings but this can be controlled by viscosity adjustment, small amounts of co-solvent, in-line heaters and chillers and adequate exhausing of the application area. Even though the application and physical properties of water-borne coatings are more sensitive than solvent coatings, they can be no cause for concern if handled properly.

Now that the weaknesses of water-borne coatings have been brought to your attention, we can discuss the numerous strengths of water-based coatings when compared to solvent coatings.

After the conversion from solvent to water has been made, many installations have experienced improved mileage and lower application costs. Since the coating is water soluble, it is possible to eliminate the dry off oven for dip and flow coat applications and, in some instances, spray.

Systems to recover the paint in the dip and flow coat vapor tunnels have become common place. This material is used as a reducer, further lowering the application cost of water-borne systems. It is also possible to formulate lower cure coatings for customers and decreasing oven temperatures by as much as 75 degrees. Where the same color is being applied by spray and dip or flow coat, it is feasible to use the same material, thereby reducing material inventory.

The water-borne coatings can also be formulated to a low solvent level and to a high flash point to meet various EPA and fire regulations.

Application of Water-Borne Coatings

When a dip coating is compared to flow coat, there are strengths and weaknesses to be considered for both types of application. Dip coatings will tend to have less film variance on a part than will flow coat. There are less rejects with dip than flow coat which are caused by plugged or misdirected nozzles. Color change, where required, is easier and less expensive with a dip system. Several tanks on rails can be

rolled into place beneath the conveyor, but to change colors for flow coat requires pumping out of the material and flushing before the new color can be introduced to the system. Water-borne coatings are prone to bubbling and foaming in flow coat applications and at times it can be very difficult to control. The dip tank, on the other hand, has less agitation and consequently less bubbling. Dip tanks require a larger volume of paint than flow coaters which makes for a longer time to turn the material over. This requires a closer monitoring of the paint for amine and co-solvent.

As previously mentioned, water-borne coatings are more susceptible to contamination, and there is the possibility of dumping a dip tank if the cause cannot be found and corrected. On the other hand, if the flow coater were to become contaminated, the tank could be recharged with a minimum of production time and at less cost.

Water-borne coatings are being applied successfully by air and airless guns with and without electrostatic and by all types of high speed rotational electrostatic equipment. There are installations using the lower speed 3600 RPM disc with satisfactory results.

When compared to solvent coatings, water-borne coatings applied by electrostatic spray have given improved wrap and penetration. With some lines, this has eliminated the need for touch-up or reinforce. Better atomization, due in part to the high speed rotational electrostatic equipment, yields improved hiding at a lower film thickness.

The prime disadvantage of applying water-borne in various installations is the requirement of making application equipment changes and the isolation of the electrostatic applicators. Color change may pose a problem for high volume lines where limited floor space and color change time are factors. It is more difficult to obtain high film builds with water-borne coatings as they are more susceptible to humidity and temperature changes. This condition can be controlled by varying the RPM's of the rotational applicator, gun air pressures, voltage, and distances to the ware. As with dip and flow coat systems the application properties of spray coatings can be controlled by small amounts of co-solvent, viscosity adjustments, paint temperature, and ambient temperature and humidity control.

Planning a Water-Borne Program

Once it is been decided that a water-borne program is to be initiated, the initial preparations are for a trial run. First contact your pretreat and paint suppliers so that the specifications can be reviewed and paint samples requested.

When the water-borne paint has been approved to your paint specifications, the next step is to have the supplier make a line survey. After the line survey is completed, the supplier should submit his recommendations and modifications necessary for his product to be successfully applied. Usually, the addition or changes needed for a trial run involve a minimum of expense. Dip tanks and flow coaters will require little, if any, modifications. One or more air mixers may be needed for agitation as water-borne coatings are more prone to settling. The addition of in-line filters is recommended since the changing from solvent to water and back to solvent will generate some dirt. The water-borne coating will loosen the solvent coating no matter how much scraping and flushing is done. Spray systems will require some sort of isolations and possibly a change in application equipment.

The paint supplier should also furnish a procedure for clean-up. This would include the steps necessary to prepare the dip, a flow coater, or spray system for loading with the water coating and also the steps for converting the system back to solvent after the trial is over.

The length of trial will be dependent on the time allocated, type of application, and the objectives of the trial. Spray trial runs offer the most flexibility and can be as short as a five hook run and are easily taken in and out of the system. Flow coat trials are more time consuming as they involve more clean-up before and after the trial. These are normally started and terminated on a weekend. Dip tanks with their larger volume of paint are normally loaded on weekends and if acceptable will continue to run.

After the short trials, the extended run of 15 to 30 days is usually undertaken. This allows for an observation of paint stability, mileage, and application with temperature and humidity changes.

Conversion from Solvent to Water-Borne

After having made several trial runs there will be an indication of what modifications will be needed to convert the solvent system to a water-borne system.

Dip tanks need few, if any, modifications for use with water-borne coatings.A weir and headers may be the only additions. As previously mentioned, air mixers and in-line filters are recommended as is DI water for reducing the coatings. Hangers may need to be redesigned to change the flow pattern if blistering and popping were a problem that could not be resolved.

During the initial flow coat trial runs, it may become evident

that the coverage and penetration are not satisfactory. Flow coaters normally require more risers and the addition of nozzles if only copper tubing is being used since water-borne coatings are generally applied at higher viscosities and have less tendency to break up and provide good coverage. If a large number of risers and nozzles are added, then it may be necessary to obtain a larger pump. The vapor tunnel may require modification to control the temperature and humidity. As mentioned for dip tanks, a hanger redesign may be required to eliminate heavy film build areas. Electrostatic Spray application of water-borne coatings require the isolation of the paint supply and the supply lines to the applicator.

If disc application is being used, it may require a hanger redesign of change in the loop to meet the distance to ware requirements when changing from a large diameter, lower-speed disc, to a smaller diameter, high-speed disc.

Conclusion

Because of the different parameters involved, i.e., type ovens, line speed, flash time, hanger design, type product, and product specifications, nearly every customer has a water-borne coating tailor made to his requirements.

One may observe a water-borne line in operation to obtain an idea of the application properties but the only positive way to determine if a water-borne system will meet your requirements is to have an extended trial run on the production line.

G-5

Organic & Chemical Pretreatment Session G

An Evaluation of Autodeposition

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AN EVALUATION OF AUTODEPOSITION

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Abstract

The results of an investigation of autodeposition as a corrosion protective coating are presented. The chemistry and interesting features of the process, along with particulars of its stages, are covered. Autodeposition is evaluated against criteria desirable for a coating and an application process. Then, the results of a process parameter investigation through specific case salt spray testing are summarized.

Introduction

Autodeposition was investigated as a means of improving the corrosion protection for certain sheet metal parts. Based on the conclusions of this investigation, it was recommended that an autodeposition paint system be installed to coat these parts.

The decision to thoroughly study autodeposition was made following very good salt spray results and the realization that this type of system could be less expensive than the previously considered cathodic electrodeposition system. Input from a company which has operated an autodeposition paint system since 1976 increased interest in this type of coating system. It was learned that relatively little test data was available for this coating, thus an extensive evaluation and test program, including a process parameter investigation for the less costly and less known autodeposition system was planned.

Description of Autodeposition

This waterborne process, which depends on chemical reactions to achieve coating deposition, has been in commercial use since 1973. Since that time approximately one billion square feet of surface area have been treated. There are two installations in the United States at which sheet metal headlamp housings and car frames are coated.

The autodeposition coating bath consists of a latex emulsion resin, hydrofluoric acid, hydrogen peroxide (oxidizing agent), and deionized water. Theoretically, the percent solids in the bath may vary widely, but for commercial applications it generally ranges from 5 to 12 percent. The bath viscosity is close to that of water. No organic solvents are present in the

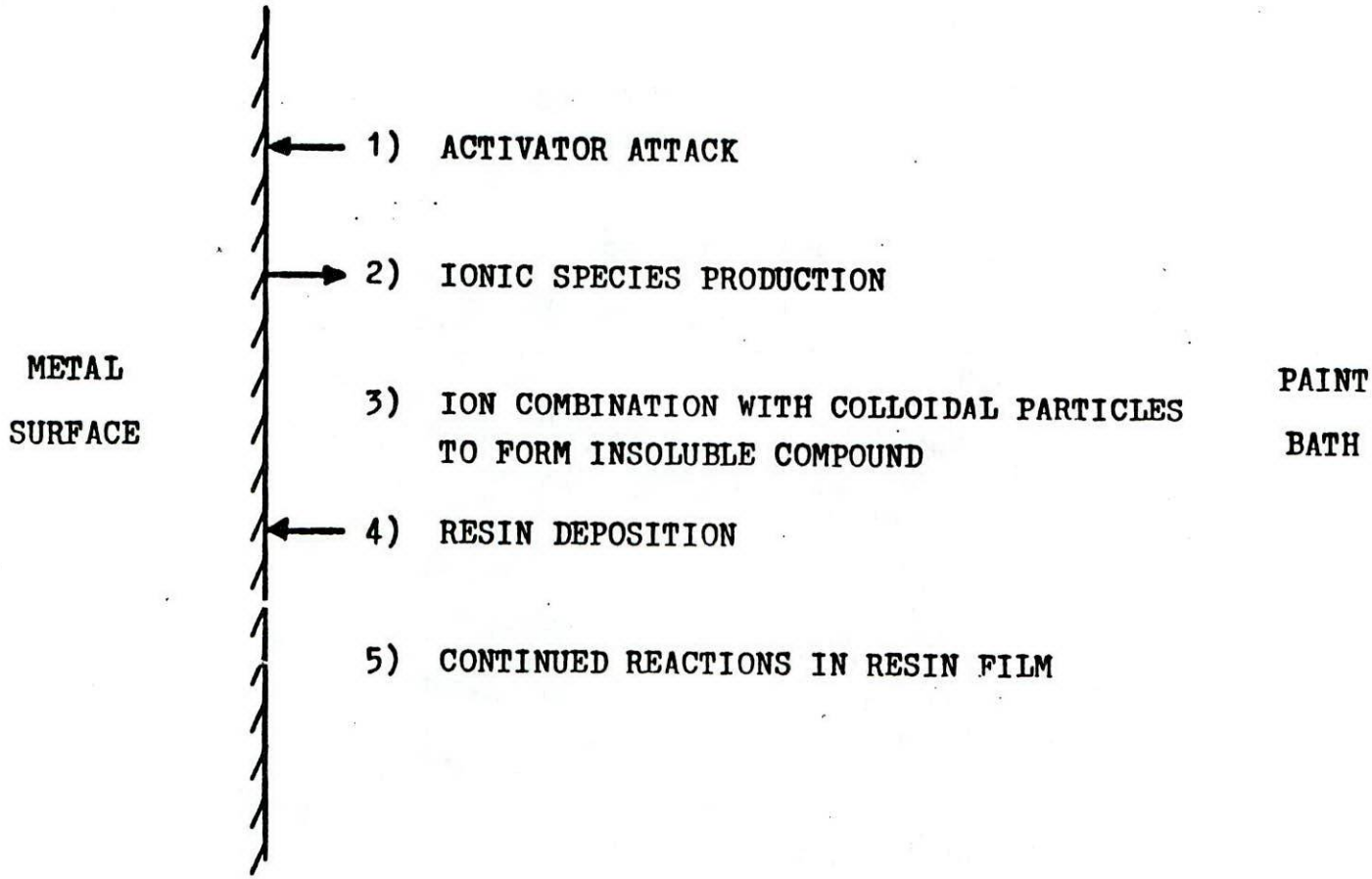
coating bath; however, in certain systems a small amount of low vapor pressure coalescent may be present. Another feature of the bath is its acidic nature; the pH is typically between 2.6 and 3.5.

The chemical reactions in the coating which effect deposition proceed by the mechanism shown in figure 1. Proton attack etches the steel surface and metallic iron is oxidized to the ferrous ion (Fe^{+2}). Hydrogen peroxide oxidizes the ferrous ion, producing the ferric ion (Fe^{+3}). The ferric ion acts as a destabilizing agent for the colloidal latex particles in the bath, causing their deposition onto the metal surface. The newly deposited coating is adherent yet porous, and so chemical activators can rapidly permeate it to reach the surface of the metal.

The thickness of the autodeposition film is time rate dependent. The coating continues to grow as long as ionic species are produced at the coating metal interface. As shown in figure 2, the rate of film growth is initially very rapid, but the deposition rate slows as deposited particles begin to interfere with the diffusion of the activators to the metal surface. The film thickness will continue to grow as long as a part is in the coating bath, although after long immersion this growth becomes negligible. Different patterns of growth result from such factors as the particular latex involved and the resin solids content.

Another interesting feature of autodeposition is the uniform thickness of the deposited coating, even on commercial metal surfaces with varying degrees of chemical activity. In an autodeposition bath, local anodes (sites of high chemical activity found at sheared edges, cut threads, deformed areas, etc.) are coated first since this is where ionic species are generated most rapidly. Once these active sites are coated, the local cell polarity is reversed, and they become cathodic in relation to the surrounding uncoated areas. The polarity continues to reverse during coating and the result is further deposition where the coating is thinnest, since this is where activator diffusion occurs most readily. Thus, for autodeposition the film build is continuously balanced and consequently the deposited coating has uniform thickness.

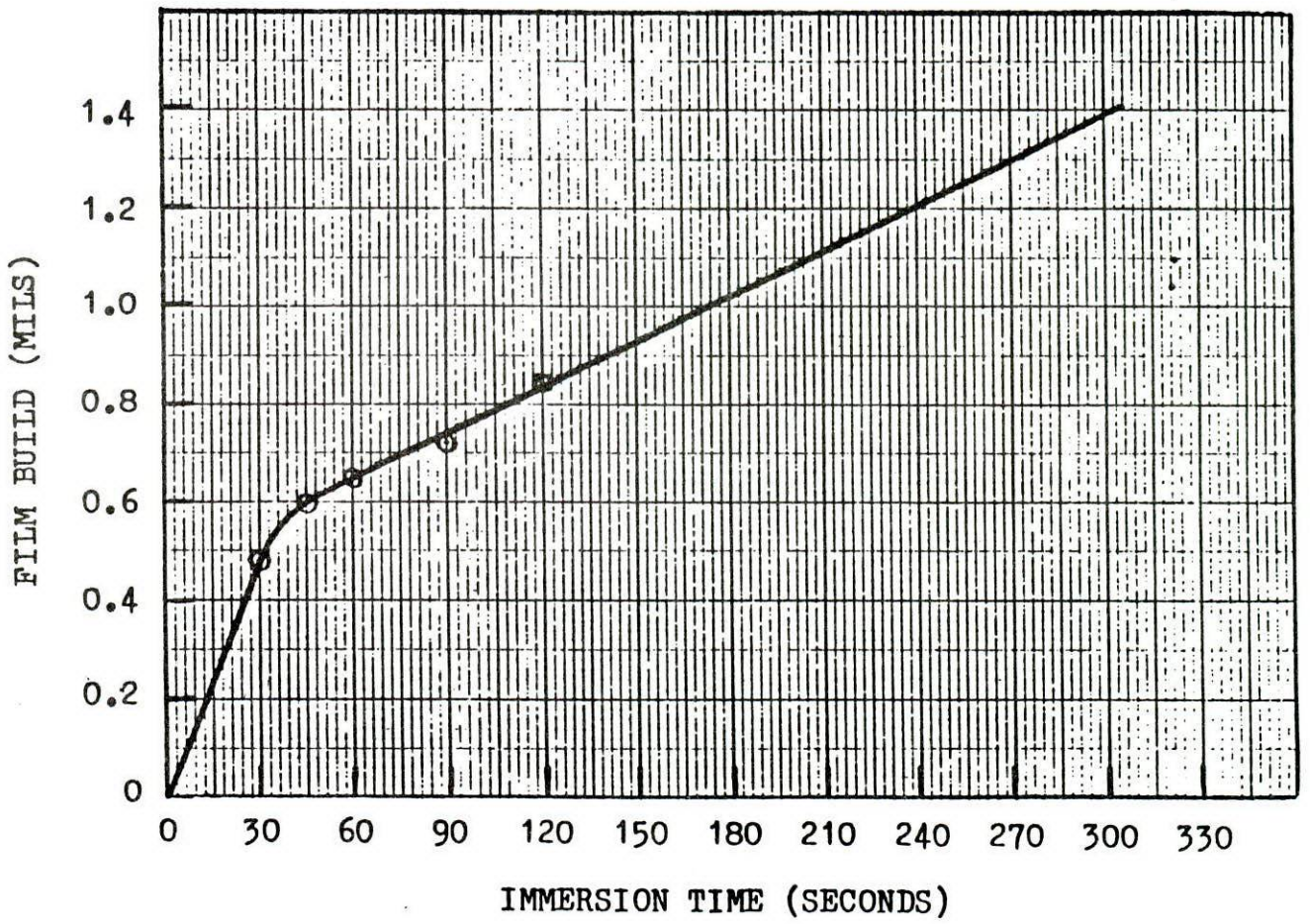
The coating deposited by autodeposition displays an unusual characteristic for a latex paint. Coated parts can be water rinsed shortly after removal from the paint bath with very little material loss. On leaving the paint bath, the coating consists of two layers. One of these is a very cohesive, reacted layer, while the other is composed of undeposited excess colloid and activator from the paint bath. The chemicals in this second layer continue to react, which results in deposition of the drag-out resin and increased film thickness. Figure 3 indicates that resin lost in the water rinse following coating



Provided by Amchem Products, Inc.

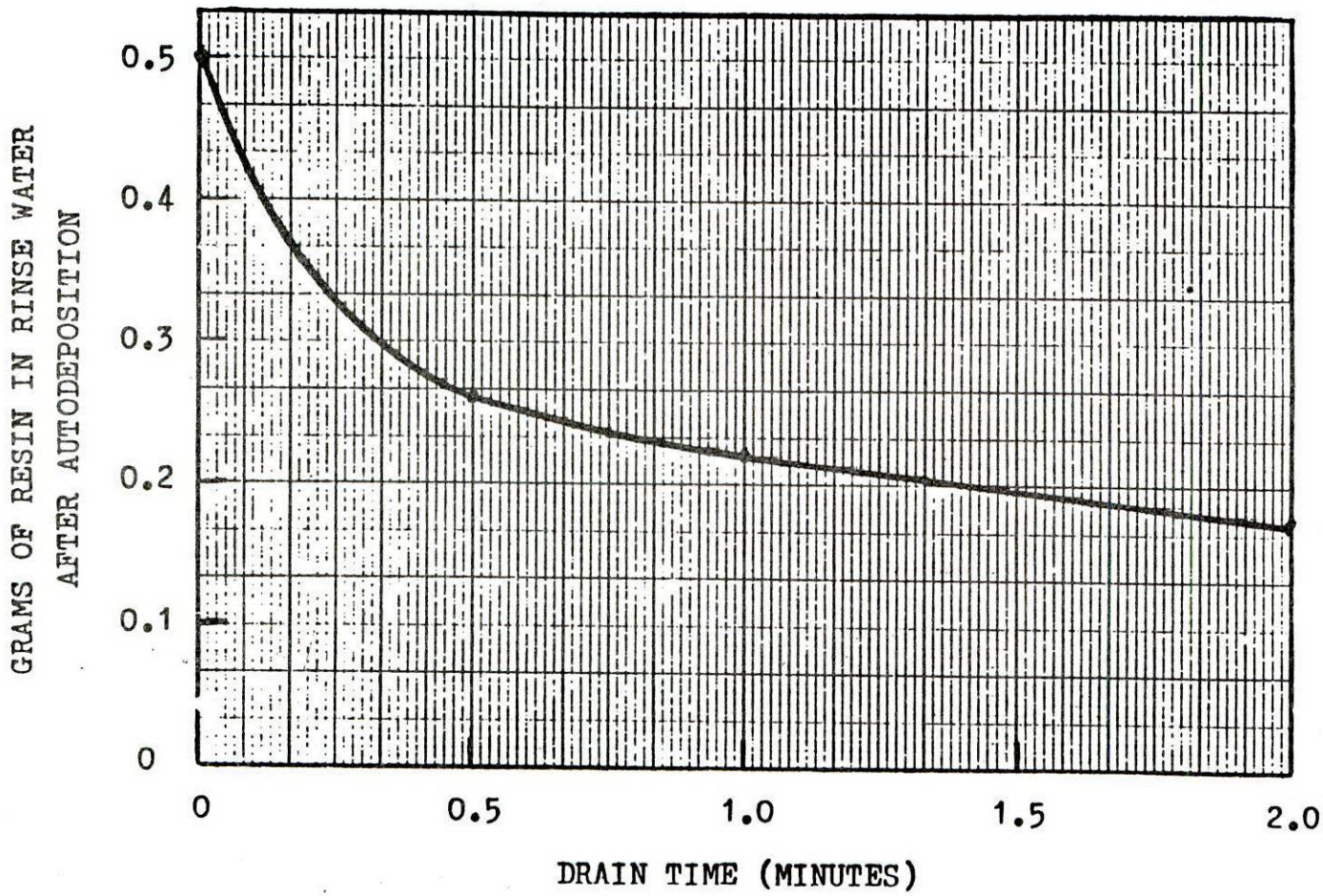
PROPOSED REACTIONS AT METAL SURFACE
AND PAINT BATH INTERFACE

FIGURE 1



FILM BUILD WITH TIME FOR AUTODEPOSITION COATING (6% SOLIDS)

FIGURE 2



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RESIN LOSS WITH DRAIN TIME

FIGURE 3

decreases with the exposure to air time prior to rinsing. This feature of autodeposition minimizes the loss of resin due to drag-out and results in both a favorable coating efficiency and low demand on a waste treatment facility.

A final characteristic of autodeposition, one of the most important, is that it does not require a separate metal conversion coating, such as a phosphate. This is possible since the adhesion of the deposited coating is extremely good due to strong interactions between the metal and the organic film. This elimination of a phosphate stage leads to savings in floor space and operating costs.

An autodeposition system consists of the following major stages: 1) Clean, 2) Rinse, 3) Coat, 4) Rinse, 5) Chrome Rinse and 6) Cure. Descriptions of each of these stages provide a better understanding of the process and its requirements.

A cleaning stage is typical of all metal finishing processes. Oils and shop dirt must be removed from parts prior to coating. This is especially true for autodeposition, because any contamination may inhibit activator diffusion and prevent deposition. Also, this system contains no organic solvents to help dissolve oils. Therefore, it is recommended that both spray and dip cleaner stages be employed to insure the thorough cleaning necessary for good coating adhesion. Impingement of the spray cleaner dislodges the majority of the soil, while the more concentrated dip cleaner removes any soil which may remain, particularly in recessed areas.

The cleaning stage is followed by multiple rinses to prevent alkali contamination of the coating bath. The conductivity of the drippings from the parts should be reduced to well below values attainable with plant water. Thus, a short deionized water rinse is required just prior to the coating bath to prevent build-up of ionic contaminants.

The coating stage is next. The chemical makeup of this bath has already been covered, but other aspects of the stage are worth mentioning. First, the temperature of the bath should be maintained at a relatively constant 20°C (68°F). This requires a heat exchanger, even though the autodeposition reaction is not exothermic. Control of the bath temperature aids in determining the etch rate of the ionic species, which in turn affects the deposition rate. Maintaining the bath at the specified temperature helps stabilize film build and insures high quality. Secondly, the coating bath requires agitation to hold the resin and pigment in suspension. To accomplish this, variable speed mixers with propellers are mounted along the sides of the coating tank. The paint tank should be sized for an average material turnover rate of approximately once per month. Another

suggestion is that a sludge removal system be employed to prevent buildup. Figure 4 shows one possible system, along with other coating tank features. This system incorporates a lance for cleaning the bottom of the tank, a weir in which to accumulate sludge, and a tank bottom that slopes to a collection trough. Sludge is pumped from this trough and the bottom of the weir to drums for disposal. The tanks should also be dragged occasionally to remove fallen parts.

An immersion tap water rinse follows the coating stage. A dip rinse is preferred since the freshly deposited film is fairly soft (about 30 to 40 percent solids) and could be damaged by spray impingement. Unreacted paint bath material on the parts and racks is removed in the rinse. This minimizes resin contamination of the next stage, the acidic chrome rinse, and in turn reduces replenishment and treatment costs. Removal of the unreacted material from the parts also decreases the possibility of streaks or other patterns which may appear if this material is allowed to dry.

The last stage before curing is an acidic chrome rinse. This proprietary solution containing hexavalent chromium serves basically as an inhibitor. It is baked into the resin film and improves both coating adhesion and corrosion resistance.

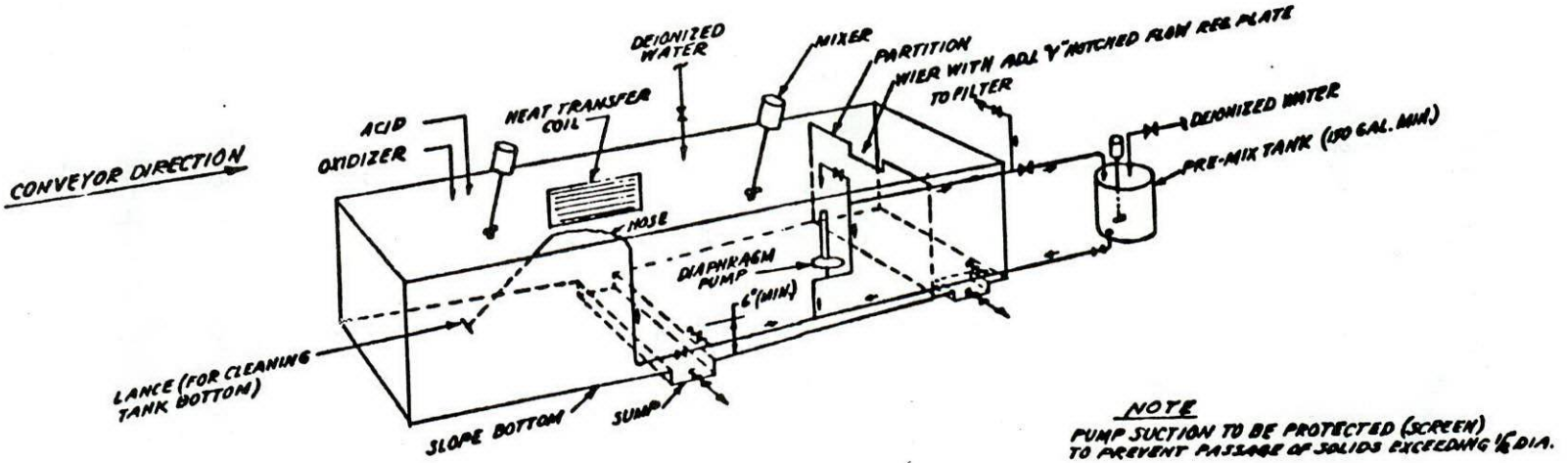
The coating is cured in a two zone oven. Parts are in the first zone 10 to 15 minutes at 110° - 120°C (230° - 248°F) to evaporate water from the wet coating. Full curing occurs during the 10 to 20 minutes the parts are in the second zone, which is held at about 140° - 180°C (284° - 356°F). The objective is to reach a peak metal temperature of approximately 174°C for about eight minutes to obtain optimum cure. The exact cure cycle depends on the part geometry and on the desired corrosion resistance.

Evaluation of Autodeposition

In an attempt to determine the production reliability of autodeposition, a company which has operated this type of paint system for over five years was contacted regarding their experience. Below is a short description of that system and a summary of their response.

The system applies a 0.7 - 0.9 mil coating to sheet metal housings using three parallel monorail conveyor systems. The parts average 0.86 square feet in surface area. The line runs two shifts per day, five days a week. It is capable of coating approximately 12,000 parts per hour.

There has been almost no system downtime due to the auto-deposition process itself. Normally, process problems due to



Provided by Amchem Products, Inc.

SCHEMATIC OF AN AUTODEPOSITION COATING TANK

FIGURE 4

deviation from the established paint bath conditions have had the effect of reducing the appearance quality, usually by streaks or reduced coating gloss, but very rarely have they resulted in unacceptable corrosion resistance. A small number of racks are stripped each month, resulting in each rack being stripped on the average of once every three years. Although it is recommended that the coating tank be drained and cleaned, and about one third of the bath be replenished each year, the system was once operated for almost two years before the maintenance procedure was required. The quality of the coating did not drop until the end of the two year period. The experience with this autodeposition system was described as a good one. This information led to the conclusion that the autodeposition process is sound and dependable.

The criteria for a corrosion protective coating and its application process against which autodeposition was evaluated were: basic test requirements for an underhood class finish, product requirements and production requirements. The performance of the coating is reported in the form of brief test results.

Coated parts were evaluated by conducting the following tests:

1) Tape adhesion test
2) Humidity test and tape adhesion test
3) Neutral salt spray test
4) Chip resistance (gravelometer) test

The coating easily passed both tape adhesion tests with no peel back occurring in either case. It received a rating of very good to excellent for the salt spray test, with less than one percent red rust. Chip resistance test specimens were given a 5B rating and so the coating handily passed this test also.

Coated parts were installed on vehicles for durability tests in which they received two years of simulated corrosion. The coating was in very good condition on all parts tested with no significant red rust. The requirement for this test was that the coated parts receive a rating of eight or better on a corrosion rating from scale of zero to ten where ten signifies no red rust. The coating easily met this requirement since the returned parts were assigned a rating of nine.

The coating was further evaluated in the following product requirement areas:

1) Coating thickness
2) Brittleness
3) Bend effect

4) Brake fluid resistance

5) Gasoline resistance

6) Corrosion resistance

7) Corrosion creepback

The coating thickness was specified to be no less than 0.3 mil. Numerous thickness checks on well over 100 parts coated to a nominal film build of 0.7 to 0.8 mil revealed that the coating thickness never dropped below 0.5 mil. For the brittleness test, a furrow was scribed to the base metal on a coated part using a dime. The coating met the requirement that it not flake beyond the width of the furrow. Sample coupons coated by autodeposition were subjected to the bend test over a 0.25 inch mandrel. Results of the test were excellent at the required bend angle of 5°, and so the bend angle was gradually increased up to 350°. Results were excellent even at this angle, with no noticeable changes in the coating. A piece of a coated part was immersed in brake fluid and another in unleaded gasoline at room temperature for 30 minutes. In both cases no rub-off of paint onto a soft cloth occurred. Thus, the coating passed both solvent resistance tests. Furthermore the tested parts were required to show no more than five percent red rust after a 96 hour salt spray test. In anticipation of an increase in the salt spray exposure time, coated parts were also tested to 168 and 240 hours; results showed 1 to 2 percent and 1 to 3 percent red rust, respectively. This data indicated that the autodeposition coating could meet the 96 hour test, and it would continue to meet corrosion resistance requirements if the salt spray exposure time were increased to 240 hours. Coated parts were also vertically scribed, subjected to salt spray for 240 hours (96 hours required) and then immediately blown dry. The failure distance, measured from the scribe line was not to exceed 3.0 millimeters. It ranged from 0 to 0.5 millimeters.

The coating satisfactorily met these four remaining product requirements:

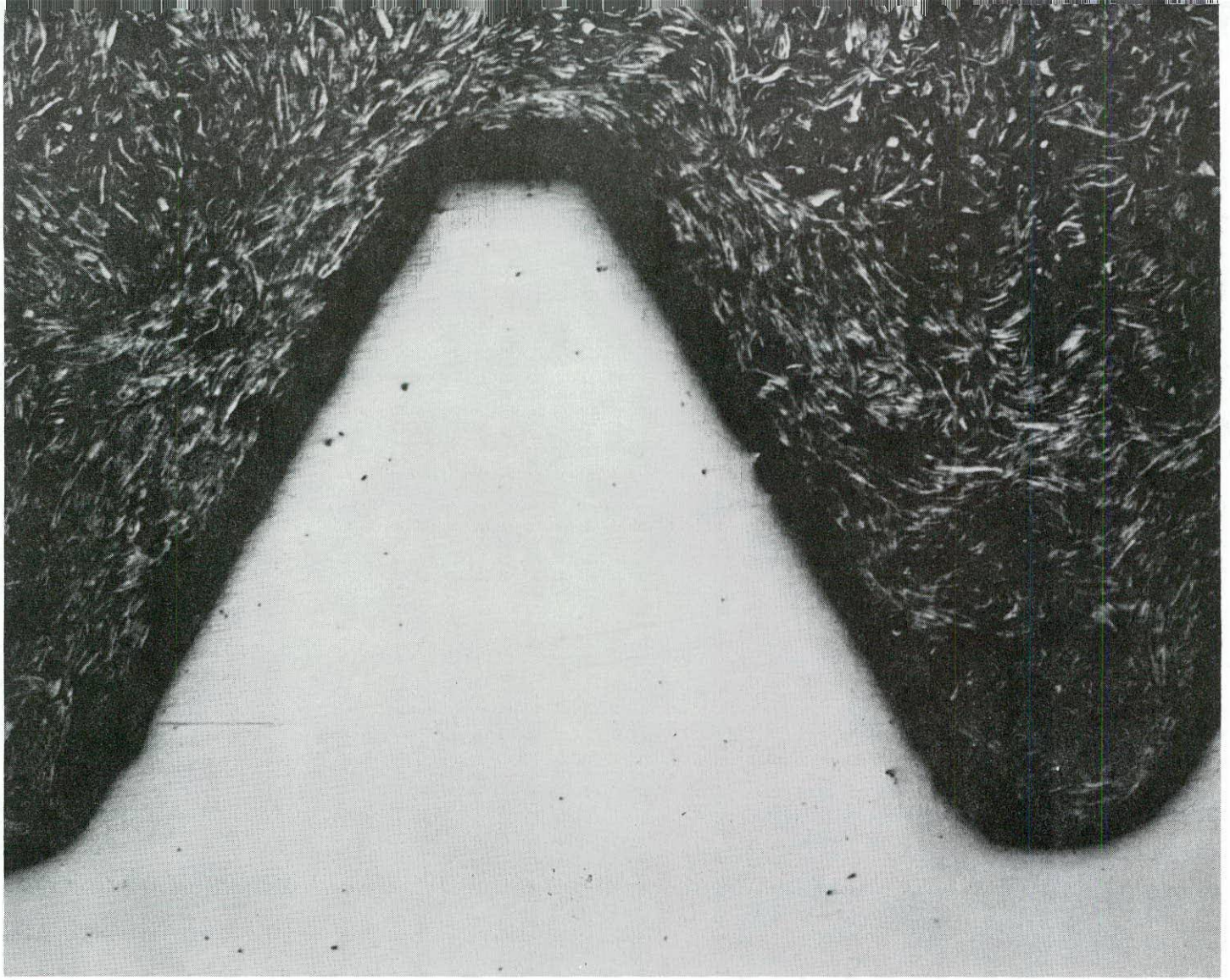
1) Good appearance

2) Uniform and proper film thickness

3) Scratch resistance

4) Coating of entire part

The appearance of autodeposition coated parts conveyed the desired high quality image. Numerous coating thickness checks indicated good uniformity. This is shown in figure 5, which is a cross section of a coated, threaded part. The coating also appeared to be scratch resistant enough to be acceptable after parts have received normal in-house handling. Two thousand autodeposition coated parts were handled as would be typical in



CROSS SECTION OF AN AUTODEPOSITION COATED THREAD

FIGURE 5

house and then assembled on a production line. Overall, the coating sustained only minor scratches. Finally, due to the nature of the process, the entire part is coated both inside and out, since wherever the paint bath contacts the metal surface coating deposition results.

The highest priority production requirement was that the system be economical in terms of capital investment, while at the same time be dependable. In conjunction with a paint system equipment supplier, an estimated cost comparison between a cathodic electrodeposition system and an autodeposition system was developed. As a conservative estimate, it appeared that the autodeposition system would cost about 10 percent less to purchase and install than the previously considered cathodic electrodeposition system.

Operating costs, including energy, chemicals, maintenance and rack stripping, were considered also. Energy costs, estimated for 1984, were calculated in terms of the projected steam, natural gas and electricity usage for both types of systems. The autodeposition system was estimated to require 44 percent less energy to operate than a cathodic electrodeposition system. The projected chemical treatment costs were calculated to be approximately $20 per 1,000 square feet of surface area treated. This was considered a reasonable cost for the corrosion protection provided by the autodeposition coating.

With regard to the maintenance demands of the previously mentioned autodeposition system, it was learned that the vast majority of the maintenance is routine in nature, such as monthly cleaning of tanks. Thus, this type of system appeared to have standard maintenance requirements. Projected rack stripping costs were relatively low, since racks would need to be stripped on the average once every two to three years. This would be possible since the coating would collect very slowly on the racks due to coating dragout, which would be minimized by the bath's low resin solids content and accompanying low viscosity.

The remaining production requirements, which require little explanation, are listed below. The system should:

1) Minimize floor space
2) Minimize operating labor
3) Be capable of handling high production volumes
4) Present few environmental concerns
5) Minimize safety hazards in the plant

An autodeposition system saves floor space by not requiring a phosphate stage or a dry-off stage prior to coating. As for labor, one person could operate the line itself. The system would also be capable of treating the required volume of parts

per day. An autodeposition system would involve treatment of free fluorides and hexavalent chromium, as well as disposal of paint sludge. Since the coating is waterborne and contains virtually no organic solvents, there would be minimal air pollution compared to conventional paint systems. It was concluded that an autodeposition system would not create any major environmental problems. Also, since it is a waterborne process, it would not be a fire hazard. Finally, since deposition occurs via chemical reactions rather than electrical attraction, autodeposition would be less hazardous than systems which require high DC voltage levels.

A process parameter investigation was conducted through specific case salt spray testing to further increase the confidence level for the autodeposition process. Two duplicate sets of parts were prepared by the coating supplier for 28 different specific cases. Each part was stamped prior to treatment with an identification number from which the processing it had experienced could be traced. The cases were chosen to learn the effect on corrosion resistance for process parameter variations in the following areas:

1) Coating thickness
2) Chrome rinse
3) Overcure
4) Undercure
5) Reduced cure time
6) Paint solids
7) Low redox potential
8) Low level of free fluorides
9) Low chrome concentration in chrome rinse
10) Rusty parts

The cases tested are specifically described in figure 6, which also shows the corresponding identification numbers.

Six coating thickness checks were taken per part and then a set of parts for each specific case was assembled on the production line. This assembly procedure was followed to simulate the condition of the coating after it had received the nicks, scratches and silicone fluid exposure typical on the production line. The parts were exposed to a neutral salt spray for 240 hours. An evaluation of each assembly was made after 96, 168, and 240 hours of exposure. A summary of these evaluations is shown in figure 7. The large majority of the ratings were very good, with parts showing only slight red rust (less than five percent of the total part surface). The major surfaces of the parts were to exhibit almost no red rust. The

FIGURE 6

DISCRIPTIONS OF SPECIFIC CASE TEST VARIATIONS

Test I.D. Number	Description of Test Variations
2051	Coating thickness 0.9-1.0 mil
2057	Coating thickness 0.4-0.5 mill
2060	30 second chrome rinse
2062	60 second chrome rinse
2064	90 second chrome rinse
2108	No chrome rinse
2068	Overcure-time stage 1: 15 min. @ 248°F; stage 2: 40 min. @ 356°F.
2066	Overcure-time stage 1: 30 min. @ 248°F; stage 2: 20 min. @ 356°F
2091	Overcure-time stage 1: 15 min. @ 248°F; stage 2: 8 hrs. @ 356°F
2071	Overcure-temp. stage 1: 15 min. @ 248°F; stage 2: 20 min. @ 456°F
2069	Overcure-temp. stage 1: 15 min. @ 356°F; stage 2: 20 min. @ 356°F
2084	Undercure temp. stage 1: 15 min. @ 120°F; stage 2: 20 min. @ 180°F
2079	Undercure-temp. stage 1: 15 min. @ 248°F; stage 2: 20 min. @ 248°F
2085	Undercure-coating thickness 0.4-0.5 mil stage 1: 15 min. @ 120°F; stage 2: 20 min. @ 180°F

FIGURE 6

DESCRIPTIONS OF SPECIFIC CASE TEST VARIATIONS (CONT.)

Test I.D. Number	Description of Test Variations
2088	Undercure-coating thickness 0.9-1.0 mil stage 1: 15 min. @ 120°F; stage 2: 20 min. @ 180°F
2078	Reduced cure time stage 1: 10 min. @ 248°F; stage 2: 10 min. @ 392°F
2171	Reduced cure time stage 1: 12 min. @ 248°F; stage 2: 18 min. @ 356°F
2173	Reduced cure time stage 1: 10 min. @ 248°F; stage 2: 15 min. @ 356°F
2073	Reduced cure time stage 1: 10 min. @ 248°F; stage 2: 20 min. @ 356°F
2075	Reduced cure time stage 1: 15 min. @ 248°F; stage 2: 10 min. @ 392°F
2097	Reduced cure time stage 1: 9 min. @ 248°F; stage 2: 9 min. @ 392°F
2096	Four percent paint solids
2099	Eight percent paint solids
2102	Low redox potential 275-325 mV
2104	Low free fluoride concentration
2106	Three percent chrome rinse concentration
2089	Rusty parts-no pickle
2169	Rusty parts-dip pickled at 160°F

FIGURE 7

EVALUATIONS OF SPECIFIC CASE TEST RESULTS

(Scale from 0 to 10 where ten signifies no rust.)

Test I.D. Number	96 Hr.	168 Hr.	240 Hr.	Comments
2051	9	9-	9-	Slight staining
2057	9	9-	8+	Dull finish
2060	9	9	9	
2062	9	9	9	
2064	9+	9	9	Very good gloss
2108	6	3	1	Severe red rust
2068	9	9	9	
2066	9+	9	9	
2091	9+	9	9	
2071	9	9	9-	
2069	9+	9	9-	
2084	6	4+	3	Severe red rust
2079	8	7	6	Moderate staining and blistering
2085	3	2	1	Severe red rust
2088	7	5	4	Moderate red rust
2078	9	9-	9-	
2171	9	9	9-	
2173	9	9	8+	
2073	9+	9	9	
2075	9+	9	9	
2097	9+	9	9	

FIGURE 7

EVALUATIONS OF SPECIFIC CASE TEST RESULTS (CONT.)

Test I.D. Number	96 Hr.	168 Hr.	240 Hr.	Comments
2096	9+	9	9	Slightly duller finish
2099	9+	9	9	Very good gloss
2102	9+	9	9	
2104	9	9	9-	
2106	9+	9	9	
2089	9+	9	8+	
2169	9+	9	9	

comments in figure 7 refer to the appearance of the entire assembly, and for the cases with no comments, it should be understood that their red rust was not located on major surfaces. Results after the 240 hour salt spray exposure are briefly discussed below.

The first two specific case salt spray tests involved variations in the nominal coating thickness of 0.7 to 0.8 mil. A thicker, 0.9 to 1.0 mil coating, and a thinner, 0.4 to 0.5 mil coating, were tested. The thicker case showed slight staining of the coating from rust run-down, but the interlock area of the assembly looked very good. The thinner case had a duller finish and about twice the amount of red rust in the part interlock area. As expected, the thicker coating resulted in better corrosion protection and appearance.

The second group of specific case tests dealt with the influence of the chrome rinse. Cases were processed with 30, 60 and 90 second chrome rinse dips. The results for the 60 second case were considered representative of those for the proposed process. There was no significant difference in the salt spray performance for the 30 and 60 second dip cases. The 90 second dip case did have better gloss and less red rust. The case of no chrome rinse was tested to confirm the requirement for and influence of the chrome rinse. Very severe red rust resulted for this case. These results revealed that the chrome rinse has a very strong influence on the corrosion protection of the coating, and it is indeed a requirement for an autodeposition paint system.

Several cases of overcured samples were also investigated to determine if excessive cure time or temperature would reduce corrosion resistance. Two cases were prepared with twice the cure time for the first and second oven stages, respectively. These cases were to simulate possible short-term stoppage of the conveyor with parts in the oven. The results indicated that the corrosion resistance of the coating was not significantly affected in either circumstance. The case with double the time in stage one did, however, exhibit slightly less rust. Parts were also prepared to simulate coated parts which had received an extended cure time in the second stage. The coating for this case performed comparably well and appeared to be only slightly adversely affected; it had just a few more rusty nicks.

Two cases involving an increase in cure temperature were tested. For the first of these, the temperature in the second oven stage was raised to 456°F, 100°F over the proposed cure temperature, to simulate an improper temperature setting. For the second variation, the first oven stage was set at 356°F, the same temperature as the one proposed for stage two. This case simulated results for either a single stage oven, or an improper

temperature setting. Salt spray results were generally good for both cases, but there did appear to be an increase in the number of rust spots on the major surfaces of the parts. Thus, both cases presented acceptable corrosion protection, although it was not as good as that for the recommended process.

Four specific cases involved undercured samples. The first of these was prepared by setting the temperatures in the oven stages to 120°F and 180°F, rather than the recommended 120°C and 180°C. This case was to simulate results for an improper oven temperature setting. Test results were very poor, with approximately 75 percent red rust and severe blistering. Different results were obtained for the second case, for which both oven stages were set at 248°F, the recommended temperature for stage one. This case simulated a possible mistaken temperature setting for the second stage, approximately 100°F lower than the recommended 356°F. Moderate blistering and staining of the coating primarily influenced the rating of this case, which showed red rust areas comparable to that of results for the recommended process. The outcome of these tests reinforced the belief that undercure due to a low second stage temperature results in blistering and staining of the coating.

The next two undercure cases were prepared utilizing the same oven temperatures as for the first undercure case, but in these cases the coating was thin (0.4 to 0.5 mil) and thick (0.9 to 1.0 mil), respectively. Severe and moderate red rust results indicated that the thin coating provided less corrosion protection than the thick coating for these cure temperatures.

One of the most important variations in the proposed process was a reduced cure time. The recommended cure cycle was 15 minutes at 248°F for stage one, and 20 minutes at 356°F for stage two. The first variation tested reduced the time in each stage to 10 minutes, and increased the temperature of stage two to 392°F. The results for this case were given a rating of nine minus. These favorable results were much better than expected, and led to the testing of the next two variations. For these cases, the recommended oven temperatures were maintained, but the time in stages one and two were decreased to 12 and 18 minutes, and 10 and 15 minutes, respectively. Results for these were rated as nine minus and eight plus. A slightly higher amount of red rust accounted for the lower rating for the latter case. The favorable outcomes for these two cases indicated that the recommended cure time could be reduced. Further testing was planned to reinforce this assumption and to determine a possible cure cycle.

The three remaining cure variations all involved some modification of both time and oven temperature. The time in stage one was reduced to 10 minutes for the first of these cases, while the temperature was raised to 257°F (an increase of 9°F);

stage two's time and temperature remained unchanged. This variation in the cure cycle did not appear to adversely affect the corrosion resistance of the coating from that of the proposed cure. Results were similar for the next case, for which the first cure stage followed the recommendation, but the second cure stage was altered to 10 minutes at 392°F. As in the previous case, the cure temperature was increased while the time was decreased. These results further indicated that the cure time could be reduced without a significant decrease in the corrosion resistance of the coating. For the final reduced cure time case, the two stages were set at 248°F and 392°F, but the time in each stage was reduced to 9 minutes. This case was tested to give some indication of the margin of acceptance for the first reduced cure time case. If results for the last variation had been a failure, it would have been assumed that those for the first were fairly close to failure. As it occurred, the results for the last were good, and from this, the assumption followed that the results for the first reduced cure time had not been close to failure. Furthermore, from the data it appeared as if the first cure stage may be reduced by 5 minutes, while remaining at 248°F, without adversely affecting the coating's salt spray performance. Similarly, it seemed safe to drop the second cure stage by 5 minutes, while maintaining a 356°F cure temperature. A further modification of the second cure stage to 10 minutes at 392°F was decided to have good potential. An example of a new possible cure is 10 minutes at 248°F followed by 12 to 15 minutes at 392°F.

Two variations of the recommended six percent paint solids were tested, four percent and eight percent. The corrosion resistance of the coating appeared not to be significantly affected by these variations of the paint bath solids, based on the salt spray results for the three cases. One noticeable difference between the three variations (four, six and eight percent paint solids) was the amount of gloss, which increased with the amount of paint solids. This result was predictable, since a higher solids bath is more likely to produce a denser wet coating which is effectively self healing. In contrast, the lower solids bath would probably produce a more permeable coating. A second difference was found in the two extreme variations in the form of average coating thickness. Six thickness checks were taken on each of the four parts for the two cases. The average coating thickness was 0.76 mil and 0.89 mil for four and eight percent solids, respectively. Thus, both gloss and coating thickness increase with the percent solids in the paint bath.

The next two cases also involved variations in parameters for the coating bath. The recommended oxidation/reduction, or redox, potential for the bath was 350 to 400 millivolts, but a case was prepared with a redox potential between 275 and 325

millivolts to simulate a neglected bath condition. The results were reassuringly good, and it was concluded that this variation did not decrease the coating's corrosion resistance. For the second case, parts were coated in a paint bath which exhibited a low level of free fluorides, approximately 130 microamperes. It was recommended that this reading be maintained within 170 and 240 microamperes. This case also simulated a neglected paint bath. The favorable results indicated that similar reductions in free fluoride levels would not diminish the corrosion protection of the autodeposition coating.

Another specific case was chosen to deal with a variation in the concentration of the chrome rinse from the recommended four percent to three percent. This case was designed to simulate neglect of the reaction rinse stage which might result in dilution of the solution's concentration. From the salt spray results, it appeared that a slight reduction in the concentration of the chrome rinse would have no effect on the corrosion resistance of the coating.

The final two specific case tests concerned the processing of rusty parts. One case was prepared according to the proposed process, except the acid pickle and the following rinse were omitted. Prior to coating, these parts showed large areas of light rust. One such area was located on the upper left side of a part. Careful examination revealed red rust breaking through the coating in this area. Consequently, the corrosion resistance exhibited for this case was slightly below that of the final case, which was prepared according to the recommended process including immersion in a heated acid pickle. These results indicated the need for the acid pickle and showed expected typical salt spray performance for rusty parts which have received the pickle.

In summary, twenty-three of the twenty-eight process variations tested showed little or no significant effect on the corrosion resistance of the coating. The ratings for these cases were all eights or nines. Only five of the cases tested showed a moderate or severe effect on the coating's corrosion resistance. Three of these had received the same severe undercure, another was undercured by different means, and the fifth case had received no chrome rinse. The occurrence of undercured samples in production could be prevented by installing temperature monitoring equipment, and parts would always receive a chrome rinse dip if the tank were charged. Thus, little concern was developed for the five cases with poor salt spray results. On the other hand, the ability of the autodeposition coating to provide satisfactory corrosion protection, even when the process is altered slightly, was established.

The effects on the corrosion resistance of the coating in the specific case salt spray tests are summarized below:

A. No significant reduction in corrosion resistance

2060	30 second chrome rinse		
2062	60 second chrome rinse		
2064	90 second chrome rinse		
2068	Overcure-time	stage 1:	15 min. @ 248°F;
		stage 2:	40 min. @ 356°F
2066	Overcure-time	stage 1:	30 min. @ 248°F;
		stage 2:	20 min. @ 356°F
2091	Overcure-time	stage 1:	15 min. @ 248°F;
		stage 2:	8 hrs. @ 356°F
2073	Reduced cure time	stage 1:	10 min. @ 257°F;
		stage 2:	20 min. @ 356°F
2075	Reduced cure time	stage 1:	15 min. @ 248°F;
		stage 2:	10 min. @ 392°F
2097	Reduced cure time	stage 1:	9 min. @ 248°F;
		stage 2:	9 min. @ 392°F
2096	Four percent paint solids		
2099	Eight percent paint solids		
2102	Low redox potential 275-325 mV		
2106	Three percent chrome rinse concentration		
2169	Rusty parts-dip pickled at 160°F		

B. Slight reduction in corrosion resistance

2051	Coating thickness 0.9-1.0 mil		
2057	Coating thickness 0.4-0.5 mil		
2071	Overcure-temp.	stage 1:	15 min. @ 248°F;
		stage 2:	20 min. @ 456°F
2069	Overcure-temp.	stage 1:	15 min. @ 356°F:
		stage 2:	20 min. @ 356°F
2078	Reduced cure time	stage 1:	10 min. @ 248°F.
		stage 2:	10 min. @ 392°F

2171 Reduced cure time stage 1: 12 min. @ 248°F;
stage 2: 18 min. @ 356°F

2173 Reduced cure time stage 1: 10 min. @ 248°F;
stage 2: 15 min. @ 356°F

2104 Low level of free fluorides (120-130 uamps)

2089 Rusty parts-no pickle

C. Moderate reduction in corrosion resistance

2079 Undercure-temp. stage 1: 15 min. @ 248°F;
stage 2: 20 min. @ 248°F

2088 Undercure-coating thickness 0.9-1.0 mil
stage 1: 15 min. @ 120°F;
stage 2: 20 min. @ 180°F

D. Severe reduction in corrosion resistance

2108 No chrome rinse

2084 Undercure-temp. stage 1: 15 min. @ 120°F;
stage 2: 20 min. @ 180°F

2085 Undercure-coating thickness 0.4-0.5 mil
stage 1: 15 min. @ 120°F;
stage 2: 20 min. @ 180°F

Summary

It was concluded that autodeposition is a satisfactory means of improving the corrosion protection for the parts evaluated.

Autodeposition rated very well against the criteria established for a coating and its method of application. It was judged sound and dependable based on over five years of experience. The coating met all underhood class finish tests and product requirements, and the process satisfied the production requirements. Finally, the process parameter investigation established the ability of the autodeposition coating to provide acceptable corrosion protection, even when the process is varied slightly.

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*This paper is based in large measure on the fifth year Bachelor of Mechanical Engineering thesis of Mary Jo Wooten, General Motors Institute, Flint, MI, 1982.

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Private communication from Mr. Terry A. Neubauer to Mr. Frank Glick, December 18, 1981.

G-6

Organic & Chemical Pretreatment Session G

Automatic Control for Prepaint Systems

David Boyd and William Roberts
Diversey Wyandotte Corp
Wyandotte, MI

AUTOMATIC CONTROLS FOR PREPAINT SYSTEMS

David Boyd and William Roberts
Diversey Wyandotte Corporation
1532 Biddle Avenue
Wyandotte, Michigan

One of the most critical parameters of a high quality coating line is the quality of the precoat system. This is becoming more evident as line speeds increase finished parts and end users refuse to purchase poor quality. If the prepaint chemicals are not collectively within the manufacturing limits required to produce high quality parts, the coating cannot meet quality standards set by your customer. A poorly engineered prepaint system will result in increasing scrap, with a resulting decrease in profit dollars.

Recent advances in microelectronics have allowed us to develop compact, reliable, very sensitive equipment, capable of effectively controlling prepaint systems within very close tolerances.

In the past, these systems were maintained by manually determining the chemical solution concentration and adding the chemicals as required. This solution checking and addition of chemical would be performed 2-4 times per day, as dictated by production and the people involved. Another procedure involved simply feeding the chemical into the working bath at a set rate over an eight hour day. Both procedures produced poor results, especially on fast lines, lines run intermittently and operations suffering from drastic personnel cutbacks.

The problem of maintaining the prepaint system under these adverse conditions, and produce high quality results has been accomplished by a third approach electronically connecting the solution control unit with an electronic sensing device that continually measures the chemical concentration, and "calls for" chemical feed only when required to maintain a very precise working solution. This provides continual solution control and activates the feed unit adding the right amount of chemical to maintain the optimum concentration, only when actually needed. This is accomplished by measuring the electrical resistance (or its reciprocal, the electrical conductivity) of the working solutions, which is proportional to the chemical concentrations.

Concentration control of chemical solutions is based on the electrical resistance of solutions varying with concentrations. It is this variation in resistance that is measured and used by the solution control unit to maintain a uniform chemical concentration.

The resistance of chemical solutions is measured with a Wheatstone bridge circuit. The basis of the Wheatstone bridge is known variable resistance on one side and the unknown resistance of the solution on the other side. The variable resistance is adjusted until it just equals the resistance of the chemial solution as indicated by no current flow. The variable resistance reading equals the resistance of the chemical solution, as

measured by the sensing device.

The sensing device consists of two conductive surfaces having a definite size and definite distance between them. The standard probe, having a constant of 1, measures the conductivity of 1 cu. centimeter of the chemical solution. Materials of construction vary from stainless steel to nickel to platinized surfaces along with the various others necessary to withstand the corrosive effects of the particular chemical solution being measured.

All of these units operate by passing the current through the sensing device in the chemical solution. The current, or what remains after overcoming the resistance of the chemical solution, returns to solution control unit.

The current returning from the sensing device is then rectifed from AC to DC and is amplified so that the change in current can be more easily measured. Amplified current can then actuate the relay which will turn on or turn off a pump, solenoid valve, feeder, or other device through the electronic solution control equipment.

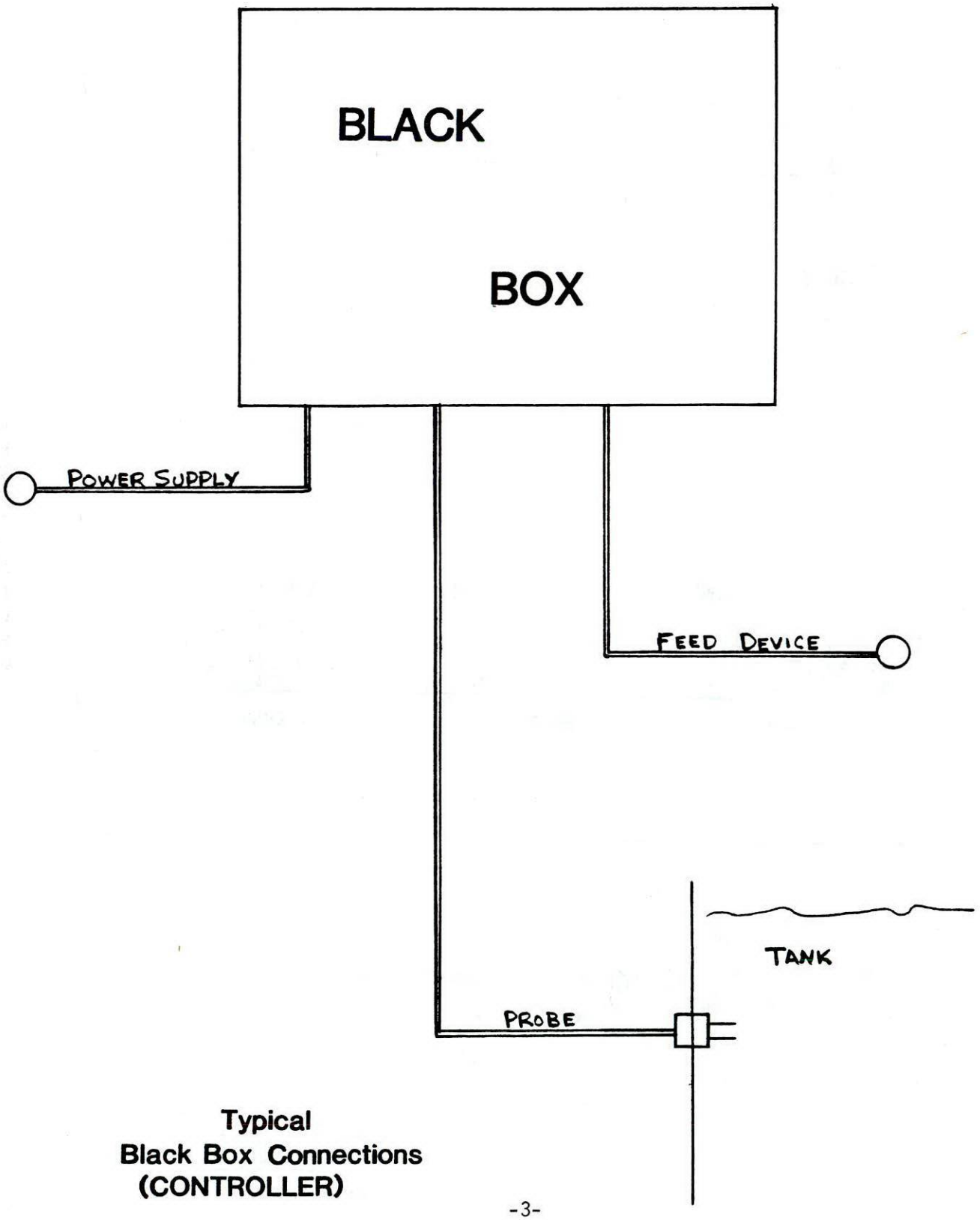
The unit used to control the concentration of cleaning solution is usually called an electronic solution control unit. This operates a relay which can activate a pump, solenoid valve, or other electrical device to feed product to the solution or stop feeding product to the solution as measured by the sensing device.

When the temperature of a solution increases, the resistance of the solution decreases. When controlling the concentration of chemical solutions, a temperature increase of the solution using a fixed setting results in a decrease in concentration. This is because the controller attempts to maintain a uniform resistance and as the resistance decreases with the increase in temperature, the concentration must decrease to compensate or maintain a uniform resistance. Therefore, an adjustment is required when the temperature of the solution is changed.

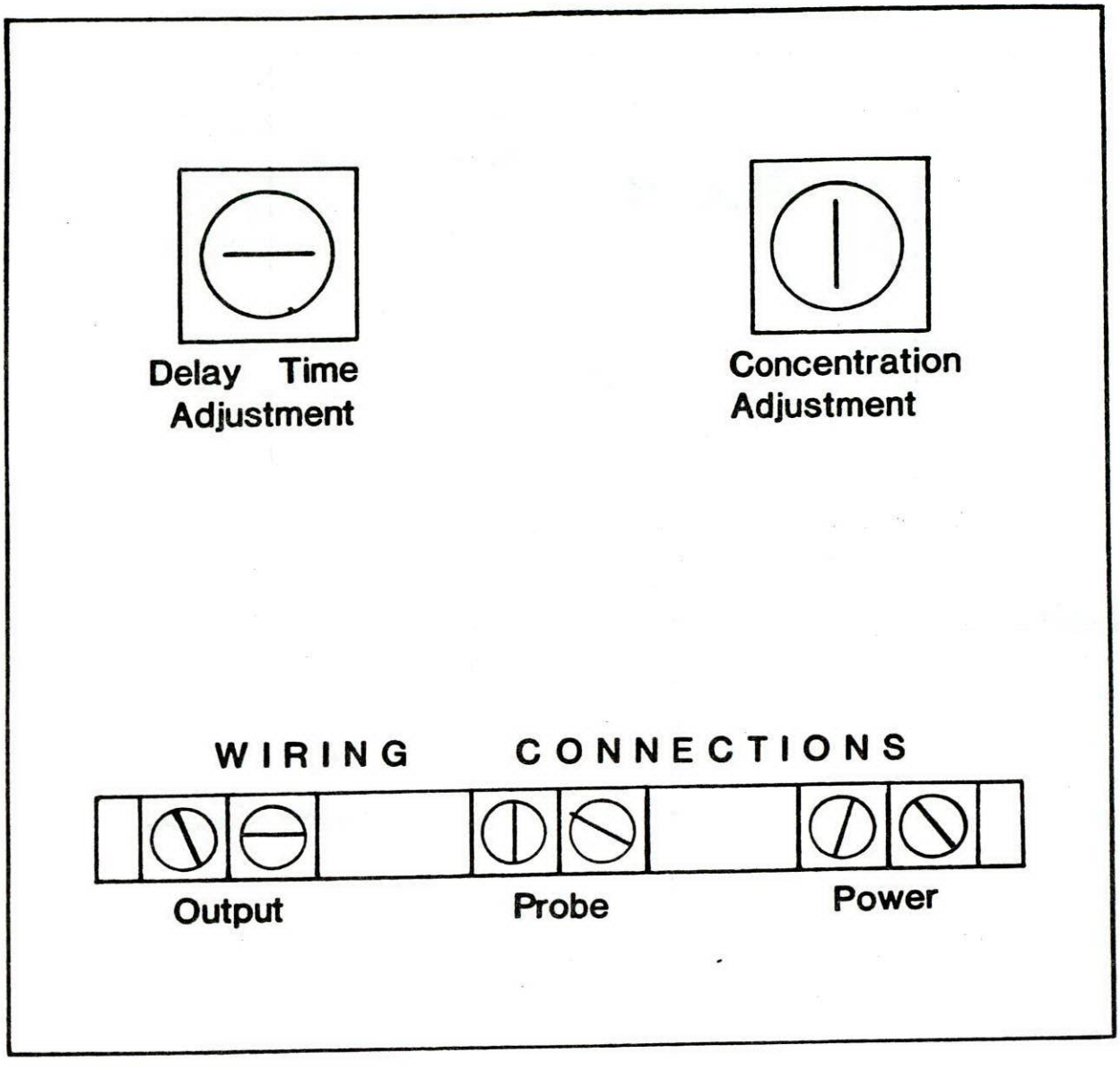
This practical application of microelectronics can be used to efficiently monitor and control systems of multiple one stage washers using prepaint chemicals from a single bulk supply tank, to a standard five stage spray washer using cleaner, phosphate, and seal. Proper installation and maintenance of these units results in:

1) Reduced overall cost.
2) Increased efficiency and output.
3) Lower chemical inventories.
4) Minimize human intervention.
5) Uniform quality.
6) More effective labor utilization.
7) Increased profits.

With the advent of increased manufacturing rates, higher quality standards, automated systems (robotic's) and computer programming, automatic chemical solution control is a necessity to remain competitive in a very competitive world.



Typical
Black Box Connections
(CONTROLLER)



Typical
Controller Adjustments
(Black Box)

H-1

Electroless Plating Session H

The Relationship Between Stress and Adhesion of Electroless Nickel-Phosphorus Deposits on Zincated Aluminum

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The Relationship Between Stress And Adhesion Of Electroless Nickel-Phosphorus Deposits On Zincated Aluminum

Glenn O. Mallory
Allied-Kelite Div., Witco Chemical Corp.
Los Angeles, CA 90012

ABSTRACT

Several factors affecting the adhesion of electroless nickel-phosphorus deposits on zincated aluminum were studied. The two most important factors affecting adhesion were found to be the formation of a zinc rich zone (ZRZ) at the Ni-Al interface and deposit stress. Additionally, deposits that have high internal tensile stress are shown to induce adhesion failure when the ZRZ is relatively thick. The induction time for electroless nickel deposition is shown to be related to the thickness of the zinc film. The structure and composition of the Ni-Al interface were determined by AES analysis.

Two models for adhesion failure of the electroless nickel plated aluminum are proposed.

INTRODUCTION

Metallic coatings, such as nickel, applied to aluminum alloys by electrolytic or electroless deposition provide properties that include corrosion protection, abrasion and wear resistance, solderability, and enhanced aesthetic appeal. Additionally, the chemical and physical properties of electroless nickel-phosphorus deposits provide several more advantages over electrodeposited nickel. Electroless nickel (EN) will deposit uniformly over complex shapes. Electroless Ni-P deposits in the as-plated condition have hardness values in the range of 500 to 600 VHN compared to 200 to 300 VHN for typical nickel electrodeposits. Electroless Ni-P alloys generally exhibit superior resistance to chemical attack when compared to "pure" nickel deposits. However, aluminum and its alloys are anodic to the metals that are commonly plated onto it. Galvanic corrosion of the aluminum can occur when the substrate is exposed to a hostile environment through pores in the plated deposit. Electroless nickel plating provides a coating with inherent low porosity.

Concomitant with the enhanced properties obtained when aluminum is plated with nickel is the difficulty encountered in plating the substrate. Aluminum has a natural affinity for oxygen, hence there is an oxide film always present on the aluminum surface. The kinetics for formation of the oxide is such that if the film is removed it reforms immediately regardless of the surface preparation process. This "permanent" oxide film interferes with the formation of metallic bonds between the aluminum substrate and the metal deposit. The aluminum must be protected from re-oxidation between the removal of the oxide and the deposition process. The oxide film can be replaced by simple immersion deposition of another metal on aluminum. This thin metallic film, usually zinc, must be resistant to oxidation. The conventional method of applying the zinc film involves immersing the aluminum substrate in an alkaline zincate solution.

The alkaline zinc immersion process was first described by Hewitson in 1927[1]. Several years later, modifications of the process were reported by Korpium[2] in 1939 and Perner[3] in 1942.

The overall alkaline zinc immersion process can be characterized as follows:

1. Dissolution of aluminum (anodic)

(1) $Al + 3OH^- = Al(OH)_3 + 3e^-$, $E^0 = 2.31$

$Al(OH)_3 = H_2AlO_3^- + H^+$

2. Deposition of zinc (cathodic)

(2) $Zn(OH)_4 = Zn^{++} + 4OH^-$

$Zn^{++} + 2e^- = Zn^0$, $E^0 = -0.763$

$H^+ + e^- = 1/2H_2$

There are two general types of alkaline zincate solutions:

1. Concentrated

Zinc oxide — 40-100 grams per litre

Sodium hydroxide — 400-550 grams per litre

2. Dilute

Zinc oxide — 5-20 grams per litre

Sodium hydroxide — 50-120 grams per litre

These two general formulations have been further modified by the addition of various metal ions such as iron, nickel, lead or copper, along with various chelating agents; e.g., gluconates, tartrates, etc.[4] Several proprietary products are available that are based on these modifications.

A study of the corrosion of zincated, plated aluminum by W. G. Zelley[5] led him to the conclusion that the best results are obtained with the thinnest immersion zinc deposits practicable.

Keller and Zelley[6] showed the effect of temperature and alloy on the weight of the immersion zinc film formed on the aluminum alloy. Figure 1 shows the variation in weight of zinc deposited with temperature. The higher the temperature, the more zinc deposited.

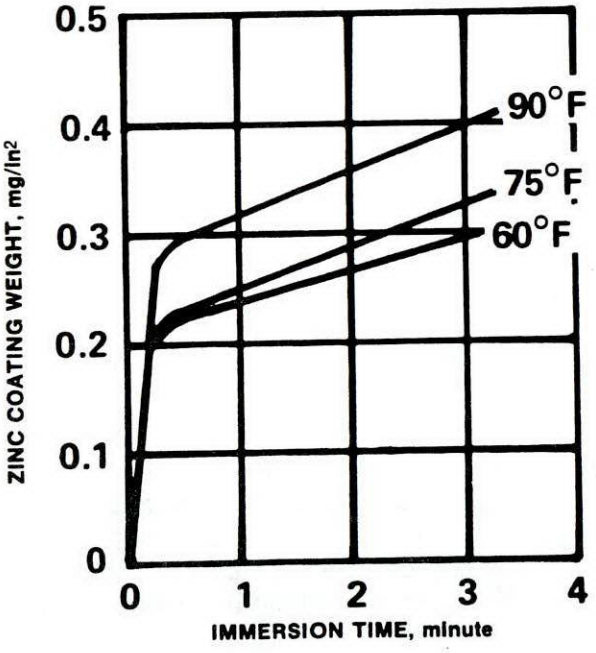

Figure 1. Effect of temperature of zincate solution on weight of zinc film deposited on 1100-H18 aluminum sheet.

Figure 2 shows the effect of the alloy on the zinc immersion coating weight. This effect is due to the differences in potential between the aluminum alloys and zinc in the zincate solution. The greater the potential difference, the heavier the zinc deposit.

For those alloys that yield a zinc film that is heavier than desired, the double zinc immersion process described by Korpium[2] can be used to produce thinner deposits. A typical process sequence involves:

1. Solvent clean
2. Mild alkaline clean
3. Rinse
4. Deoxidize
5. Rinse
6. Zincate for 60 seconds at room temperature
7. Rinse
8. Remove zinc film in 50% nitric acid
9. Rinse
10. Final zincate for 30 to 60 seconds at room temperature

In 1949, Heiman[7] reported an acid zinc immersion system for plating on aluminum. He proposed a solution containing zinc sulfate and hydrofluoric acid, for example:

$ZnSO_4 \cdot 7H_2O$ — 720 grams per litre
HF (48%) — 17.5 mL per litre

Heiman recommended operating this solution at room temperature with immersion times up to one minute. The acid zinc immersion process can also be characterized by an anodic step and a cathodic step as follows:

1. Anodic

(3) $Al + 6F^- = AlF_6^{---} + 3e^-, \quad E^0 = 2.07$

2. Cathodic

(4) $Zn^{++} + 2e^- = Zn, \quad E^0 = -0.763$

$H^+ + e^- = 1/2H_2$

Figure 3 shows the variation of weight of zinc deposited from an acid zinc immersion bath on aluminum alloys 2024, 6061 and 7075. The order of increasing deposit weight as

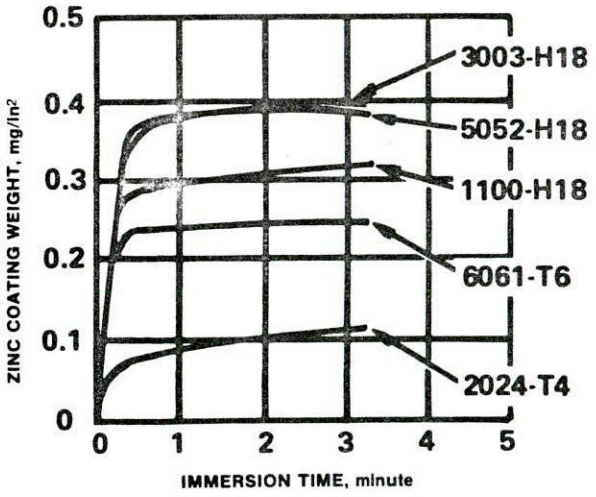

Figure 2. Weight of zinc film obtained from the alkaline zinc immersion process.

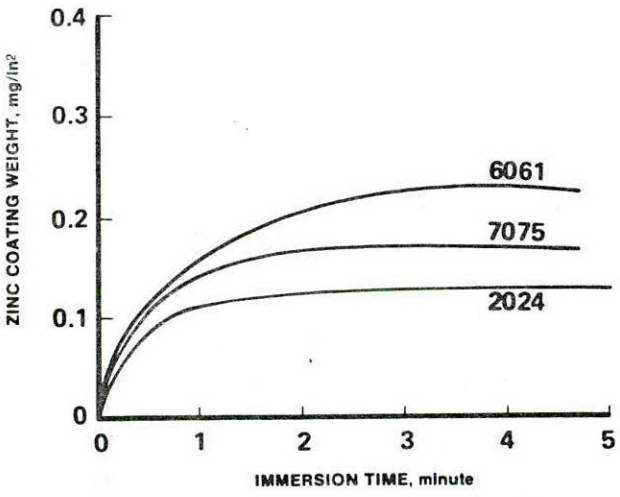

Figure 3. Weight of zinc film obtained from acid zinc immersion bath.

with the alkaline zincate systems is: 2024 < 7075 < 6061. By comparing the weight results obtained for alkaline zincate solutions and the acid Heiman solution, it is seen that much shorter immersion times are required for alkaline zincates than for acid zinc solutions.

In spite of the development and availability of well-researched commercial immersion zinc processes, electroless nickel deposits are known to develop poor adhesion to zincated aluminum surfaces. Blackwood et al[8] state that adhesion is directly related to the zincating solution, the composition of the aluminum alloy, and the electroless nickel bath itself. Yarkosky and coworkers[9] claim that adhesion failure results from the increase in total acidity of the plating bath. Other investigators indicate that the adhesion of the coating to the substrate is influenced by the nature and magnitude of the internal stress of the EN deposit. In general, a tensile stress in the coating will decrease its adhesion, corrosion resistance and sometimes the fatigue strength of the substrate. The objective of this paper is the study of the nature of the internal stress of EN deposits and its effect on the adhesion of the deposits to zincated aluminum.

EXPERIMENTAL

Aluminum Substrates

Five aluminum alloys were used in this study: 1100, 2024, 3003, 5086 and 6061. Alloy 1100 was used in all Auger Electron Spectroscopy (AES) analyses because of its purity. That is, the dissolution of an aluminum substrate in the zincate solution will leave traces of the alloying constituent at the interface of the zinc film and the aluminum. AES analysis cannot discriminate between copper from dissolution of alloy 2024 or residual copper from the copper bearing zincate solution. The aluminum helices used on the spiral contractometer stress tests were alloy 3003. Adhesion, AES and salt spray tests were run on either 4 in × 2 in × .030 in or 6 in × 4 in × .020 in panels. The composition of each alloy is given in Table 1.

Table 1. Nominal Composition Of Aluminum Alloys; Essential Elements (Percent By Weight)

Alloy	Cu	Mn	Si	Mg	Zn	Fe	Cr
1100	—	—	—	—	—	—	—
2024	4.5	0.6	0.5	1.5	0.2	0.5	0.1
3003	0.1	1.2	0.6	—	0.1	0.7	—
5086	0.1	0.5	0.4	4	0.25	0.5	0.1
6061	0.25	0.1	0.6	1.0	0.25	0.7	0.25

Process Cycle

1. Clean in proprietary acid cleaner
2. Cold water rinse
3. Acid etch
   - HNO_3 — 50% by vol.
   - H_2SO_4 — 25% by vol.
   - NH_4HF_2 — 120 g/L
   - Water — Balance
4. Cold water rinse
5. Zincate, 30 seconds
6. Electroless nickel plate

Zincate Solutions

Three zincate solutions were used to prepare the aluminum for plating. The formulations of the alkaline zincate solutions are recorded in Table 2. The immersion time in the zincate solutions was 30 seconds.

Table 2. Formulations Of Test Zincate Solutions A, B and C

Material	Concentration, g/L A	B*	C*
NaOH	100	500	100
ZnO	15	100	15
CuCN	—	20	—
KCN	—	45	—
$FeCl_3 \cdot 6H_2O$	1.5	—	—
Sodium Gluconate	5	—	5
Catechol	5	—	5

* See Reference 4

EN Plating Bath

A 4-litre plating bath was used for all plating tests. The surface area-to-solution volume ratio was kept at 30 cm^2/litre (except for stress tests) to minimize the effects of changes in bath composition during the course of the plating test. The composition of the reference plating solution used in this investigation is given below:

Bath Composition		
Ni	—	0.1 M
Lactic Acid	—	0.3 M
Acetic Acid	—	0.25 M
Sodium Acetate	—	0.25 M
$NaH_2PO_2 \cdot H_2O$	—	0.3M
pH	—	Variable (4.0-5.2), adjust with dilute NaOH
Temperature	—	88°C
Thiourea	—	As required
Lead	—	As required

The stabilizers were added to the reference solution as required. The acetic acid/acetate buffer system was used to minimize pH changes during each experimental run. The pH did not vary more than 0.03 pH units from any given initial value. All panels were plated to a thickness of 25 μm (1.0 mil).

Stress Tests

The type and magnitude of internal stresses in EN deposits were determined with a Brenner-Senderoff Contractometer. In essence, the method of measuring the stress is based on plating the outside of a helix, which in operation has one end fixed and the other

end is allowed to move as the stress develops. The free end transmits its movement to an indicating needle through gears that magnify the needle movement. As the helix is EN plated, the stress in the deposit causes the helix to wind more tightly if the stress is compressive or unwind if the stress is tensile. The internal stress can be calculated from the amount of needle deflection and other data. For the stress calculation, the calibration constant of the helix must be known, and consists essentially of determining the force required per degree of dial deflection.

The range of the instrument is approximately 20,000 psi tensile (or compressive) when the stud in the gear is in line with the axis of the gears. This range can be doubled for a solution in which stress is known to be highly tensile (or compressive) by positioning the gear to the left for tensile solutions or to the right for compressive solutions.

The calculation of stress, σ, from the angular deflection, δ, is based on the equation,

$$\sigma = \frac{ET(T+t)\rho\delta}{6\pi\ DLt} \tag{5}$$

where,

E = modulus of elasticity of substrate
T = thickness of helix
t = thickness of deposit
ρ = pitch of the helix
δ = angular deflection
D = outer diameter of helix
L = length of helix

Stress measurements taken at operating temperature of the plating bath are related to the intrinsic stress. Stress measurements made after the contractometer system has cooled to room temperature are reported as the total or residual stress.

Potential-Time Measurements

Potential-time (E-t) tests were performed using a PAR Model 350 corrosion measurement system adapted for chronopotentiometric measurements.

Adhesion Tests

Adhesion failure was determined visually. That is, the surface of plated panels were examined for any evidence of blisters, cracks or exfoliated deposits. Blister formation during plating and salt spray testing was also monitored. The type of failure (cohesive or adhesive) was determined by AES analysis.

The simplest and most common test of adhesion is the bend test. However, there are many variables other than stress that affect adhesion in this method of testing. Hence, the bend test was used sparingly and only when it was felt that a qualitative check was necessary.

AES Analysis

All AES analytical tests were performed by Surface Science Laboratories, Inc., Mountain View, California.

DISCUSSION

Zinc Film Formation

Data derived from studies on the weight of zinc film deposited versus time for the three experimental zincate solutions closely parallels the results obtained by other investigators.

The concentrated zincate solution (B) produces the heaviest zinc films on all alloys. The inhibited dilute zincate solution (A) yields the thinnest deposits. The uninhibited dilute zincate solution (C) produces deposits that are, weightwise, between those of A and B. In general, the weight of films obtained from solution C are closer to deposits from solution A than solution B.

Wyszynski[10] showed that the rate of zinc film growth from uninhibited zincate solutions was much greater than that yielded by inhibited (Fe-complex) solutions. Lashmore[11] demonstrated that small additions of metal ions, e.g., Fe^{+3}, to zincate solutions have a major effect on the zinc immersion reaction. He found that in the presence of a ferric complex, the dissolution of aluminum occurs at a rate of nine atoms of aluminum for each zinc atom deposited. In the absence of the iron-complex, three atoms of aluminum dissolve for every two atoms of zinc deposited. Typical weight versus time curves for the experimental zincates are shown in Figure 4. The aluminum alloy is 1100.

Zinc Film Dissolution

Dissolution of the zinc film occurs when the zincated aluminum substrate is immersed in the EN plating bath. However, zinc metal is not simply dissolved chemically and then dispersed throughout the bulk of the EN solution. Zinc and other metal ions are reduced and codeposited with nickel into the EN deposit. This is demonstrated by AES analysis over the Ni-P/aluminum substrate interface. A zinc rich zone (ZRZ) is shown to exist between the bulk EN deposit and the aluminum surface. The elemental components and thicknesses of the ZRZ's are given in Table 3.

Table 3. Elemental Composition And Thickness Of Residual ZRZ

Zincate Solution	ZRZ Thickness, Å	ZRZ Elemental Composition					
		Zn	Ni	P	Al	Fe	Cu
A	665	+	+	+	+	+	0
B	2500	+	+	+	+	0	+
C	1500	+	+	+	+	0	0

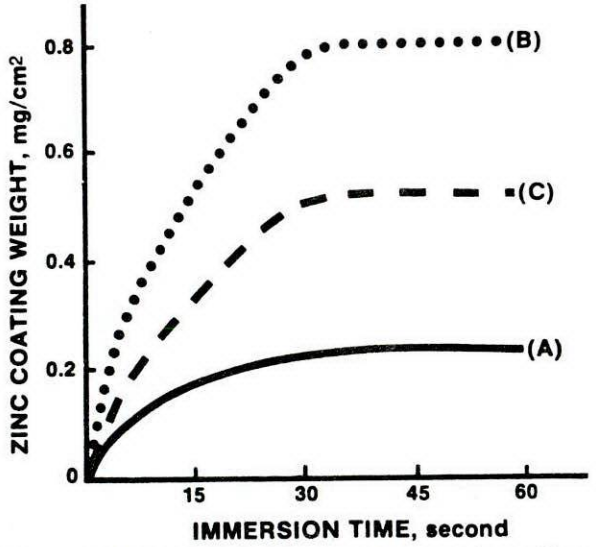

Figure 4. Weight of zinc film obtained from the three zincate solutions on alloy 1100.

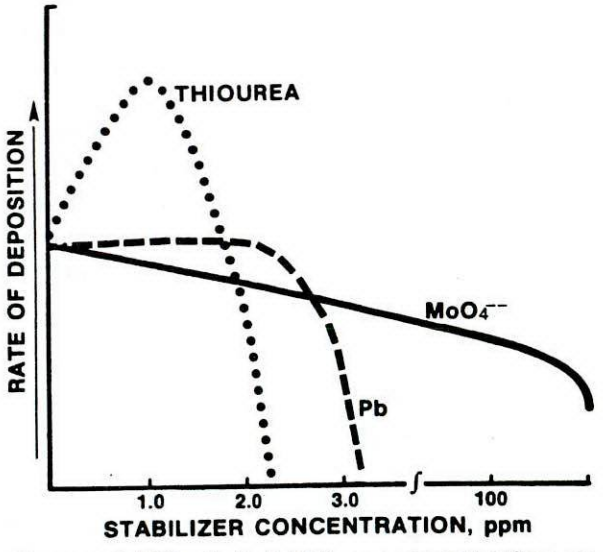

Figure. 5. Effect of stabilizer concentration on rate of electroless deposition.

Zinc Rich Zones (ZRZ)

The thickness and composition of a ZRZ depends mainly on three factors:

1. Composition of the zincate solution
2. Composition of the aluminum alloy
3. Chemistry of the EN plating bath

The results given in Table 3 reflect the effect of the composition of the zincate solution on the formation of the residual ZRZ. The EN plating bath contained no stabilizers and the aluminum substrate was 1100 alloy (certified to be 99.9% pure).

Comparison of ZRZ thicknesses show that the concentrated zincate (solution B) results in the thickest ZRZ, followed by solution C. Dissolution of the zinc film formed from solution A yields the thinnest ZRZ. It should be noted that solutions A and C differ only in that A contains the iron-complex.

In Figure 2 it was seen that the weight of zinc deposited in a given time period was influenced by the aluminum alloy being processed. It can be safely stated that alloys which catalyze the formation of heavy zinc films will also retain the thickest ZRZ.

The addition of certain stabilizers to the EN plating bath has a pronounced effect on mass transport during the dissolution-codeposition reactions involving the zinc film at the interface. AES depth profiles of solution A's ZRZ showed the zinc to be much thinner when 1 ppm thiourea was added to the EN plating bath. No change in zinc thickness was observed when the stabilizer was 1 ppm lead. The addition of oxy-anion stabilizers, e.g., IO_3^- or MoO_4^{--}, lead to an expanded ZRZ. These results are tabulated in Table 4.

Table 4. Effect Of Stabilizers On ZRZ Thickness

Zincate Solutions	ZRZ Thickness, Å			
	Neat	Thiourea	Pb	MoO_4
A	665	250	670	900
B	2500	1400	2300	2900
C	1500	800	1400	1800

The effect of the stabilizers on the rate of nickel deposition is shown in Figure 5. At its optimum concentration, thiourea has a marked accelerating effect on the deposition rate. It is assumed that when thiourea is added, the rate of EN deposition exceeds the rate of zinc dissolution relative to the rate without thiourea. In this case, the perpendicular distance the zinc ions migrate from the aluminum substrate is minimal, resulting in a thin ZRZ. Lead as a stabilizer has little or no effect on the deposition rate up to its critical concentration, hence no change in ZRZ from the zero stabilizer case. The oxy-anion stabilizers tend to reduce EN deposition rate in the concentration range where they are effective stabilizers, allowing the zinc ions to diffuse a greater distance from the aluminum surface, thereby expanding the ZRZ.

Induction Time for EN Deposition

The time required for establishment of the steady-state mixed (deposition) potential, E_d, is call the induction time. When EN plating zincated aluminum, the induction time was observed to be dependent on several variables. These factors include the weight of the zinc film, the aluminum alloy substrate, and the chemistry of the plating bath. The first two variables are interdependent. The weight of the zinc film on a particular aluminum alloy depends on the type of zincate solution used. On the other hand, the aluminum alloy

The concentrated zincate solution (B) produces the heaviest zinc films on all alloys. The inhibited dilute zincate solution (A) yields the thinnest deposits. The uninhibited dilute zincate solution (C) produces deposits that are, weightwise, between those of A and B. In general, the weight of films obtained from solution C are closer to deposits from solution A than solution B.

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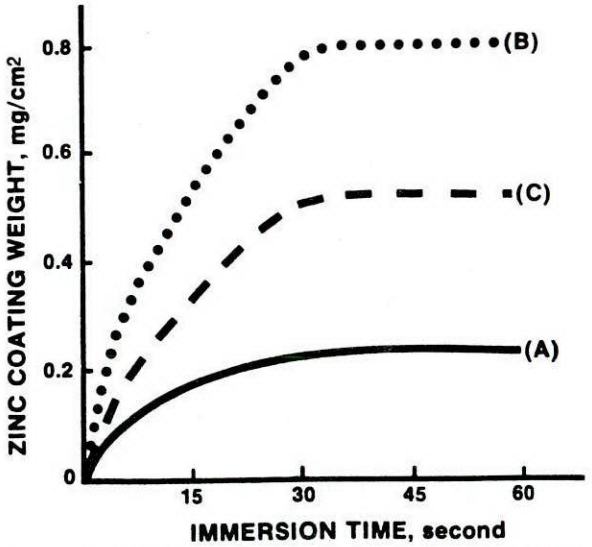

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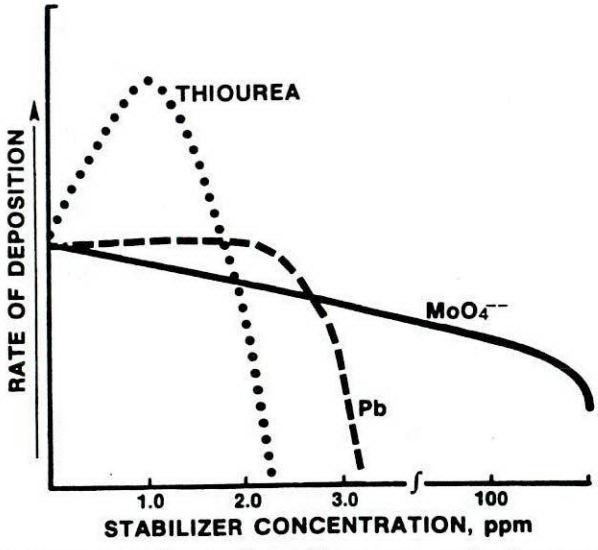

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2. Composition of the aluminum alloy
3. Chemistry of the EN plating bath

The results given in Table 3 reflect the effect of the composition of the zincate solution on the formation of the residual ZRZ. The EN plating bath contained no stabilizers and the aluminum substrate was 1100 alloy (certified to be 99.9% pure).

Comparison of ZRZ thicknesses show that the concentrated zincate (solution B) results in the thickest ZRZ, followed by solution C. Dissolution of the zinc film formed from solution A yields the thinnest ZRZ. It should be noted that solutions A and C differ only in that A contains the iron-complex.

In Figure 2 it was seen that the weight of zinc deposited in a given time period was influenced by the aluminum alloy being processed. It can be safely stated that alloys which catalyze the formation of heavy zinc films will also retain the thickest ZRZ.

The addition of certain stabilizers to the EN plating bath has a pronounced effect on mass transport during the dissolution-codeposition reactions involving the zinc film at the interface. AES depth profiles of solution A's ZRZ showed the zinc to be much thinner when 1 ppm thiourea was added to the EN plating bath. No change in zinc thickness was observed when the stabilizer was 1 ppm lead. The addition of oxy-anion stabilizers, e.g., IO_3^- or MoO_4^{--}, lead to an expanded ZRZ. These results are tabulated in Table 4.

Table 4. Effect Of Stabilizers On ZRZ Thickness

Zincate Solutions	ZRZ Thickness, Å			
	Neat	Thiourea	Pb	MoO_4
A	665	250	670	900
B	2500	1400	2300	2900
C	1500	800	1400	1800

The effect of the stabilizers on the rate of nickel deposition is shown in Figure 5. At its optimum concentration, thiourea has a marked accelerating effect on the deposition rate. It is assumed that when thiourea is added, the rate of EN deposition exceeds the rate of zinc dissolution relative to the rate without thiourea. In this case, the perpendicular distance the zinc ions migrate from the aluminum substrate is minimal, resulting in a thin ZRZ. Lead as a stabilizer has little or no effect on the deposition rate up to its critical concentration, hence no change in ZRZ from the zero stabilizer case. The oxy-anion stabilizers tend to reduce EN deposition rate in the concentration range where they are effective stabilizers, allowing the zinc ions to diffuse a greater distance from the aluminum surface, thereby expanding the ZRZ.

Induction Time for EN Deposition

The time required for establishment of the steady-state mixed (deposition) potential, E_d, is call the induction time. When EN plating zincated aluminum, the induction time was observed to be dependent on several variables. These factors include the weight of the zinc film, the aluminum alloy substrate, and the chemistry of the plating bath. The first two variables are interdependent. The weight of the zinc film on a particular aluminum alloy depends on the type of zincate solution used. On the other hand, the aluminum alloy

influences the weight of the zinc film formed from a given zincate solution (see Figure 2). The discussion that follows is limited to the experimental data obtained for one aluminum alloy, 1100. The results are typical of all the aluminum alloys studied.

Potential-time (E-t) curves for the zincated 1100 alloy are shown in Figure 6. The (E-t) curves exhibit a sudden change of potential when E_d is reached. The time necessary to reach the deposition potential is termed the induction time. The induction time depends on the weight of the zinc film formed.

The initial potentials of zincated aluminum in the EN plating bath are always more negative than E_d.

The zinc dissolution reaction takes place during the induction period. This reaction is accompanied by the immersion deposition of nickel. That is,

$$\begin{aligned} \text{Zn dissolution reaction:} \quad & Zn^0 = Zn^{++} + 2e^- , \; E^0 = 0.763 \\ \text{Ni immersion deposition:} \quad & Ni^{++} + 2e^- = Ni^0 , \; E^0 = -0.250 \\ \text{Overall reaction:} \quad & Zn^0 + Ni^{++} = Ni^0 + Zn^{++} , \; E^0 = 0.513 \end{aligned}$$

The initial potential measured when zincated aluminum is immersed in the EN plating bath is equivalent to the potential reading obtained when zinc foil (99.99) is immersed in the EN solution. The potential, in the latter case, changes in the direction of E_d for the EN reaction. Since zinc is not catalytic to EN deposition, E_d is never attained. However, the potential drift to more positive values does indicate that the displacement reaction between zinc metal and nickel ions is proceeding. (E-t) curve for zinc foil in the EN plating solution is shown in Figure 7.

The previous discussion on zinc film dissolution indicated that the zinc metal is not simply dissolved but is subsequently codeposited with nickel into the EN film, forming a zinc rich zone, the ZRZ. The question arises as to how the thermodynamic driving force for zinc dissolution can coexist with the driving force for zinc deposition, both in the same electrode potential. The answer may lie in the Nernst relationship for the zinc reaction:

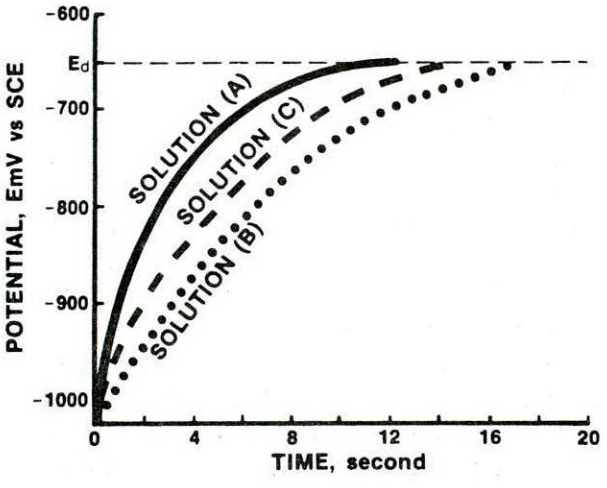

Figure 6. Potential-time curves for electroless nickel deposition on zincated aluminum.

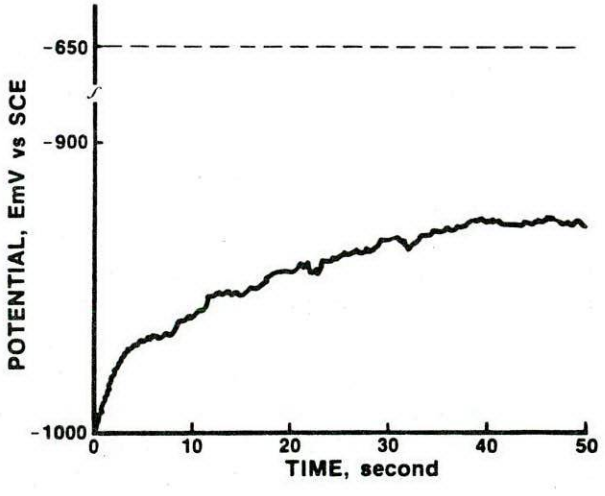

Figure 7. Potential-time curve for zinc foil immersion in EN plating bath.

(6) $Zn^{+2} + 2e^{-} = Zn^{0}, \quad E^{0} = -0.763$

(7) $$E = E^{0} - \frac{RT^{0}}{nF} \ln \frac{[Zn]}{[Zn^{+2}]}$$

or

(8) $$E = E^{0} - \frac{RT^{0}}{nF} \ln [Zn] + \frac{RT^{0}}{nF} \ln [Zn^{+2}]$$

where,

E^{0} = standard potential for the zinc reaction
R = gas constant
T' = temperature °K
F = Faraday's constant
n = number of electrons transferred
$[Zn]$ = activity of zinc metal
$[Zn^{+2}]$ = activity of zinc ions

setting the activity of the solid zinc metal phase equal to unity, we obtain the equation (at 90° C),

(9) $E_{Zn} = -0.763 + 0.036 \log [Zn^{+2}]$

Initially, there will be very little zinc dissolved in the diffusion layer close to the metal substrate. In this case, $[Zn^{+2}] <<< 1$, giving a large negative value for $\log [Zn^{+2}]$. E_{Zn} will be substantially more negative than E^{0}, and a large thermodynamic driving force for zinc dissolution will exist.

As zinc dissolves into the diffusion layer, $[Zn^{+2}]$, the zinc activity will rise rapidly increasing the value of E_{Zn}. As E_{Zn} increases so will the mixed potential between zinc dissolution and nickel deposition, as seen in the potential-time curves of Figure 6. As E_{Zn} increases, it will attain and exceed the potential of the hypophosphite oxidation reaction. At this point, zinc reduction (deposition) will occur simultaneously with nickel deposition. Zinc will therefore be codeposited with nickel into the EN deposit forming the ZRZ.

Nickel deposited by replacement catalyzes the electroless or autocatalytic deposition reaction. When the deposition potential is reached, the EN reaction proceeds alone.

If the aluminum substrate is exposed to the EN plating solution as a result of zinc dissolution, a concurrent reaction, aluminum dissolution, occurs.

Aluminum dissolution: $Al = Al^{+3} + 3e^{-}, \quad E^{0} = 1.66\ V$

Thermodynamically speaking, aluminum dissolution can trigger nickel and/or zinc immersion deposition at the sites where aluminum is dissolving. However, potential-time studies of the induction period for EN plating bare aluminum reveal that the potentials measured prior to attaining E_d are more positive than for zincated aluminum, as shown in Figure 8. If the zinc film was completely dissolved, exposing bare aluminum alloy to the EN solution, a sudden shift in potential to a value greater than E_d (>650 mV) should occur, followed by a rapid decrease to E_d. Since this does not happen, it must be assumed that the (E-t) curve of Figure 8 is due to the dissolution of the oxide coating on the aluminum or it reflects the change in E_{mix} for the hydrogen evolution-hypophosphite oxidation partial electrode processes that occur prior to metal deposition. Additionally, $|E^{0}_{Al}| > |E^{0}_{Zn}|$ so that (E-t) curves for Al dissolution should be in the same direction as the (E-t) curve for zinc dissolution. (E-t) curves for bare aluminum were similar to Figure 8 regardless of method of preparation of substrate. This implies that the oxide film reforms extremely fast.

The potential-time curve from the initial potential to E_d is smooth, i.e., the functional representation for the (E-t) curve is continuous.

The induction time for zinc dissolution/EN deposition varies with pH as shown in Figure 9. In the absence of EN bath stabilizers the functional relationship can be represented by the expression,

$$\left(\frac{\partial I_0}{\partial pH}\right)_{T^\circ,\ Al,\ Z,\ M} = f\ (pH)$$

where,

I_0 = induction time, no stabilizer case
T° = temperature
Al = aluminum alloy
Z = zincate solution
M = composition of plating bath

f(pH) is a continuously differentiable monotonic function of pH. When thiourea is added to the plating bath, the relationship is given by a straight line whose slope is,

$$\left(\frac{\partial I_s}{\partial pH}\right)_{T^\circ,\ Al,\ Z,\ M} = \text{constant}$$

I_s is the induction time for the stabilized case.

The importance of induction time studies will become apparent when the relationship between deposit stress, adhesion, and ZRZ are discussed.

Stress And Adhesion

In general, all electroless nickel deposits are in a state of internal stress. The stress may be compressive so that the deposit would like to expand parallel to the surface. In extreme cases of compressive stress, the deposit will buckle up on the substrate. Alternatively, the deposit may be in tensile stress, i.e., the coating would like to contract. The extremum of tensile stress is when stress forces are sufficiently large so that the elastic limit of the deposit is exceeded and it breaks up.

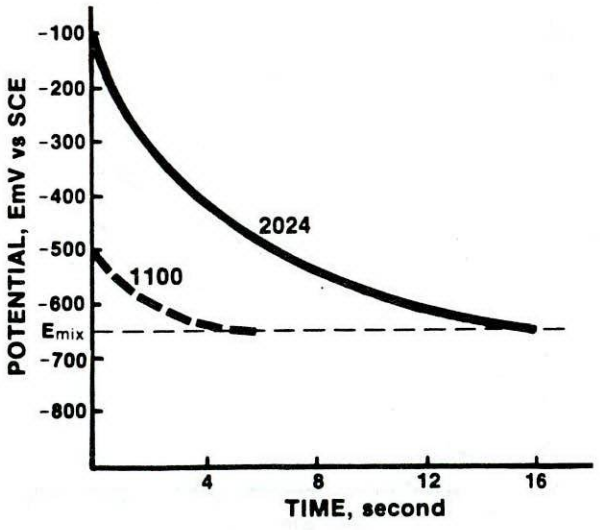

Figure 8. Potential-time curves for electroless nickel deposition on bare aluminum alloys.

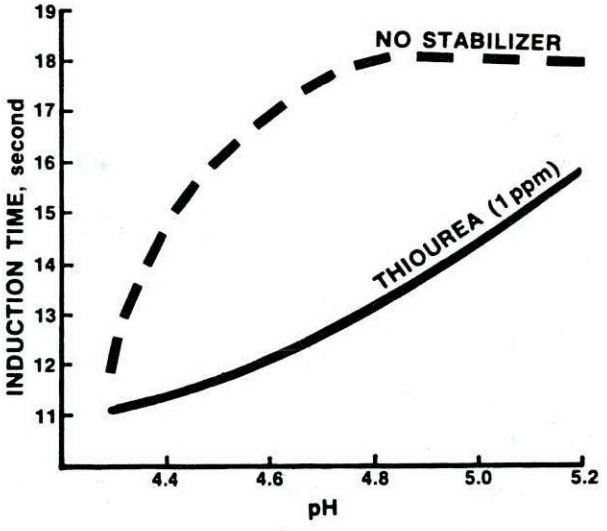

Figure 9. Effect of bath pH on induction time (zincate solution B).

Movement of the deposit relative to the substrate (loss of adhesion) will take place only if the adhesive bond between deposit and substrate is broken. When there is a loss of adhesion between the deposit and substrate, it is often found that the "free" deposit will curl up. This behavior indicates that the coating is stressed.

The internal stress in the EN deposit, σ_T, is the sum of two components, i.e.,

$$\sigma_T = \sigma_{intrinsic} + \sigma_{thermal}$$

The intrinsic stress, σ_i, results from crystal and lattice growth defects introduced into the deposit during deposition. The expression used to calculate σ_i was given in equation (5).

When the coefficients of thermal expansion of the EN deposit, α_d, and the substrate, α_s, are different, cooling the system produces the second component of σ_T, the thermal stress σ_H. This necessitates the addition of a correction term to equation (5) to account for the difference in the expansion coefficients, as follows:

$$(10) \qquad \sigma_H = (\alpha_d - \sigma_s)\left[\frac{E(\Delta\tau)\,(T + t)}{(T + t)^2 + 3Tt}\right]$$

where $\Delta\tau$ is the difference between the plating bath temperature and room temperature.

The type and magnitude of the thermal stress contribution depends on the term $(\alpha_d - \alpha_s)$. When $(\alpha_d - \alpha_s)<0$, the contribution is compressive; if $(\alpha_d - \alpha_s)>0$, the contribution is tensile in nature. When electroless nickel plating aluminum, $\alpha_s>\alpha_d$, $(\alpha_d - \alpha_s)<0$ and σ_H is compressive.

Relationships such as stress versus pH of EN bath, stress versus phosphorus content of deposit, and plating bath pH versus P content of deposit have been well studied, particularly when EN plating ferrous alloy substrates. Parker and Shah[12] reported stress data for EN plating several metal alloys including beryllium and aluminum. Their results are given for measurements taken at room temperature.

The effect of pH on the stress of Ni-P films (deposited on aluminum from the experimental plating bath) is shown in Figure 10. The intrinsic stress of EN deposits on aluminum varies with pH in a similar fashion to σ_i for deposits on ferrous alloys. That is, when the pH of the plating bath is greater than 4.7, σ_i is tensile; for pH values less than 4.7, σ_i is compressive. To illustrate this fact, σ_{i304} is included in Figure 10. It can be assumed

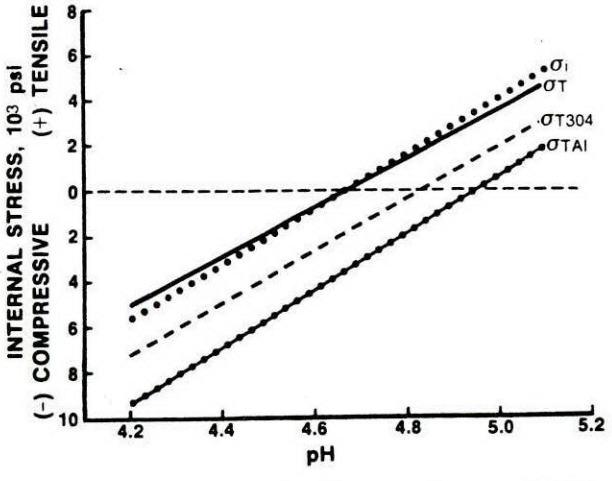

Figure 10. Effect of pH on stress of EN deposits.

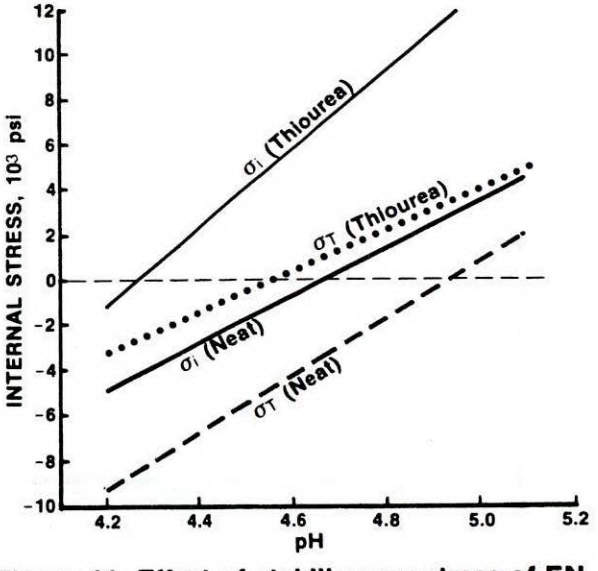

Figure 11. Effect of stabilizer on stress of EN deposits as a function of pH.

that the substrate has only second-order effects on the intrinsic stress of the deposit. The curve depicting the variation of the total (residual) stress lies in the compressive region for all values of pH studied. The effect of the difference in thermal expansion coefficients is shown by comparing the two curves σ_{TAl} (aluminum) and σ_{T304} (304 stainless steel). The expansion coefficients have a first-order effect on σ_T.

The addition of a stabilizer to the plating bath can influence changes in the stress of the resultant deposits. One ppm thiourea added to the EN plating bath shifts both σ_i and σ_T to more tensile values as shown in Figure 11. This increase in tensile stress can have a deleterious effect on adhesion.

With one exception, most investigators overlooked or ignored the effect of bath aging (regenerations) on the stress in EN deposits. By adding orthophosphite to several test solutions, Baldwin and Such[13] were able to simulate the accumulation of the product of hypophosphite oxidation that occurs during plating. They achieved a tensile stress of 17,000 psi at a phosphite concentration of 120 g/L. The EN film was deposited on a copper-plated steel substrate. Performing similar experiments in this laboratory with aluminum substrates, the intrinsic stress was increased to 15,000 psi tensile (Figure 12). Equivalent results were obtained by actually regenerating the bath a sufficient number of cycles to accumulate 160 g/L orthophosphite (curve 2 in Figure 12).

Finally, stress can be affected by changes in the concentration of complexing agent in the plating bath, as illustrated in Figure 13. At constant temperature, Ni^{+3}, $H_2PO_2^-$, and pH, σ_i is shifted to more compressive values when the concentration of lactate anion is increased from 1 to 6 times the molar concentration of nickel. It should be noted that increasing the concentration of complexing agent did not ameliorate the effect of the thiourea addition and return σ_i to lower stress values.

An absolutely necessary property of EN deposits is their adhesion to the substrate. The adhesion must be such that the deposit is not removed from the substrate by mechanical or thermal forces acting on the plated article. Adhesion can be defined as the force required to separate the deposit from the substrate. If the separation occurs at the interface, it is termed adhesive failure. If separation occurs within the substrate or within the deposit, it is termed cohesive failure.

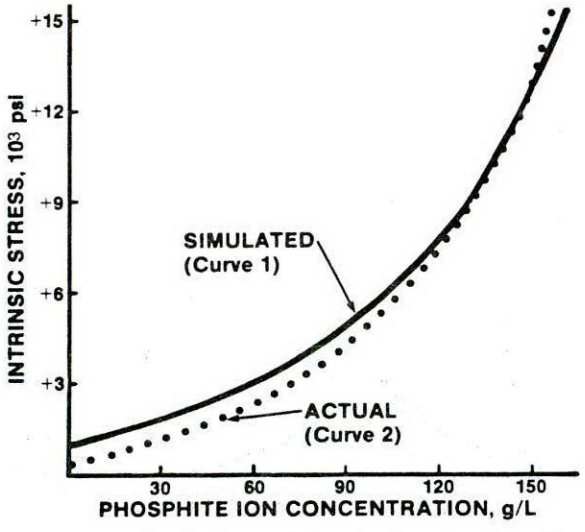

Figure 12. Variation of intrinsic stress with phosphite ion concentration.

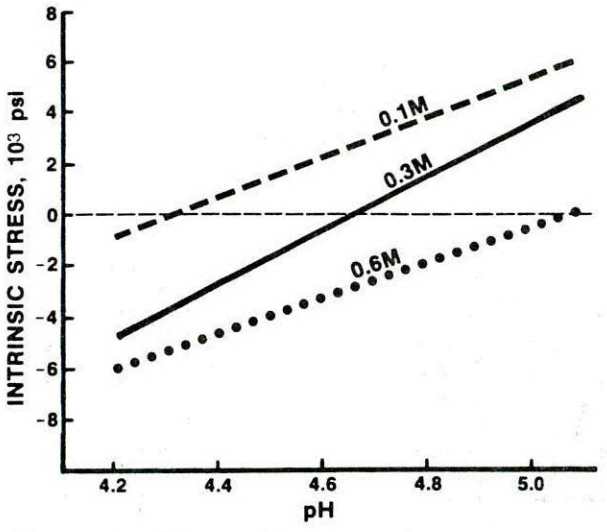

Figure 13. Effect of lactate anion concentration on intrinsic stress as a function of pH.

Auger spectrographic analysis of EN deposits that have separated from aluminum substrates indicate that either adhesive or cohesive failure can occur. Cohesive failure is predominant in the ZRZ. Analysis of both faces of the separation is required to determine which type of failure has occurred. This is represented schematically in Figure 14. Figure 14 shows that for adhesive failure the amount of zinc and nickel found in the substrate face is insignificant, while the ZRZ is intact on the deposit face only. For cohesive failure, remnants of the ZRZ is observed on the deposit face and the substrate face.

One method of determining adhesive failure is the visual observation of blister formation during plating. In this case, it was found that the intrinsic stress of the deposits exceeded (+) 12,000 psi tensile. Adhesive failure also occurred when the residual stress, σ_T, was greater in absolute value than (-) 10,000 psi compressive. Cracked deposits and blisters that form during salt spray testing are related, but not limited, to adhesive failure due to compressive stress.

Cohesive failure occurs to a lesser extent than adhesive failure. The conditions that lead to the formation of a very thick and brittle ZRZ, lead to cohesive failure. This type of failure occurs when the cohesion forces in the weak ZRZ are much less than the stress forces in that region. Under these conditions, fractures will occur in the ZRZ. Additionally, the binding forces between substrate and deposit (including ZRZ) must be greater than the internal stress forces causing the fractures in the ZRZ.

SUMMARY OF EXPERIMENTAL RESULTS

AES analysis at the interface of the aluminum substrate/Ni-P deposit (including ZRZ) shows that the zinc concentration in the ZRZ can assume two concentration profiles. The distribution of zinc in the ZRZ is shown in Figure 15. Curve 1 in Figure 15 shows the zinc concentration to have a Gaussian distribution over the thickness of the ZRZ. The zinc concentration gradient skewed toward the substrate is represented by curve 2. Adhesive and cohesive failure are related to the distribution profiles.

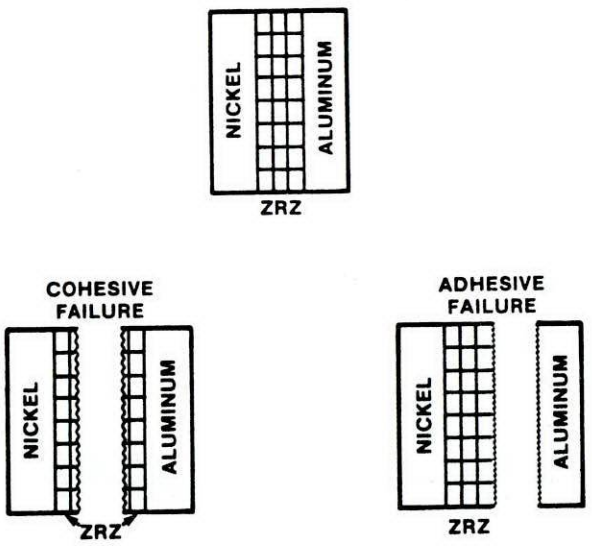

Figure 14. Schematic representation of adhesive and cohesive failure.

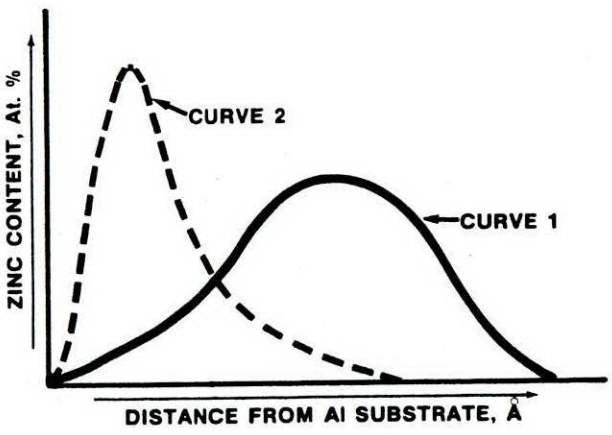

Figure 15. Zinc distribution in ZRZ.

Adhesive Failure

When the zinc distribution is diffuse and Gaussian in form, a high stress is required for adhesive failure. In this case, the intrinsic stress usually exceeds 15,000 psi tensile. Adhesive failure of Gaussian-distributed zinc occurs most frequently in ZRZ layers that are residue from zincate solution B.

The induction-time becomes important when considering adhesive failure of deposits plated on zincates from solutions A and C. The zinc films produced by zincate solutions A and C are much thinner than those from solution B. Small induction times result in higher zinc concentrations near the aluminum/ZRZ interface (curve 2, Figure 15). Factors that increase the rate of deposition, e.g., thiourea, and high pH, well exacerbate this condition. The type of stress required to cause adhesive failure in these cases could be either tensile or compressive. If the intrinsic stress is greater than 10 ksi tensile, failure will occur. If the intrinsic stress lies in the range 5 to 10 ksi, and the residual stress is near (-) 10 ksi compressive, adhesive failure will also result. Increasing the induction time by any method expands the ZRZ and causes the zinc concentration to be more diffuse in the ZRZ (Gaussian). A much greater stress force is required for failure.

Cohesive Failure

This type of failure occurred in ZRZ layers obtained from zincate solutions B and C. The zinc distribution in this case has the form given in Figure 16. A very brittle, high-zinc content layer with low tensile strength is formed in the ZRZ. When internal stress exceeds the tensile strength of this layer, separation occurs.

The conditions that lead to the type of cohesive failure discussed above usually occur when the EN plating solution has been regenerated several times, solution dragout has been excessive and the complexing agent concentration is low. The buffer capacity of the solution is lowered because of dragout and the pH drops rapidly during plating. Apparently, factors such as rate of zinc dissolution, induction time, pH, and rate of deposition are coupled in a manner that allows the formation of the brittle zinc layer in the ZRZ. These conditions also induce high internal stress in the deposit.

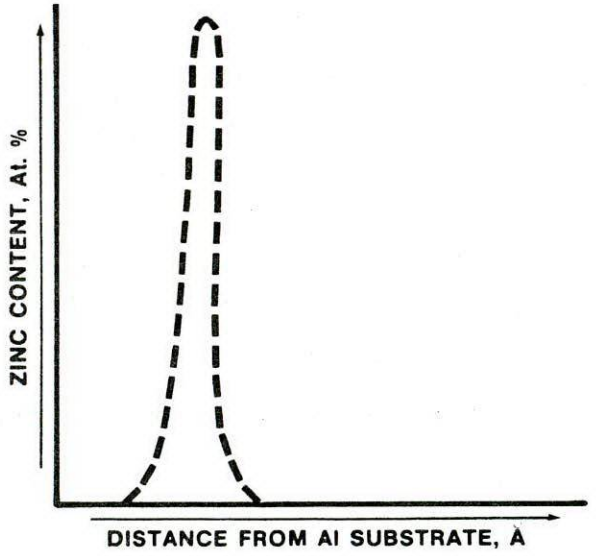

Figure 16. Zinc distribution in ZRZ (cohesive failure).

CONCLUSION

The type of zincate solution used in the EN plating of aluminum has a pronounced effect on the subsequent adhesion of the EN deposit. Each zincate deposits a zinc film of characteristic thickness and composition. These films lead to the formation of a zinc rich zone in the EN deposit next to the aluminum substrate. The zincate of choice is one that ultimately yields the thinnest ZRZ.

The distribution of zinc in the ZRZ is influenced by the chemistry of the EN plating bath. EN solutions that lead to diffuse zinc distribution are preferred. Stabilizers that shorten induction time should be avoided if possible.

Plating bath conditions that yield deposits of high stress are to be avoided. The internal stress can be monitored using the Brenner-Senderoff Contractometer. This allows for the determination of the intrinsic and residual stresses.

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H-2

Electroless Plating Session H

Performance of Electroless Deposits for EMI/RFI Shielding Applications

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PERFORMANCE OF ELECTROLESS DEPOSITS FOR EMI/RFI SHIELDING

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Environmental pollution of all types is a wide-spread modern problem. Government regulations have recently focused on a new area, electromagnetic interference due to uncontrolled emissions from electronic and electromagnetic devices. The Federal Communications Commission has set forth a series of regulations under Docket 20780 to control EMI and RFI, that is radio frequency interference.

The processes used for plating on plastics would seem to be a viable technique for RFI shielding. The basic techniques for applying electroless copper or any of the electroless nickels to plastics are well-known at the present time. Yet, little hard scientific data has appeared on the ability of these electroless coatings to work as EMI shielding. Likewise, there is little information on the corrosion resistance or general durability of such electroless coatings. The purpose of this paper is to show research results for various electroless nickels, electroless coppers and composite coatings, both for EMI shielding and for corrosion resistance. This information may help clarify some of the areas of uncertainty regarding the useability of POP for EMI/RFI shielding.

Why is plating on plastics a good choice for EMI/RFI shielding? One reason is that it will form a continuous film of uniform thickness over the whole surface of the part. This is very important in shielding because thin spots or scratches or uncoated areas would allow EMI radiation to leak out of the enclosure. Pure electroless coatings would seem to be the method of choice for these applications, rather than the traditional electroless followed by electrolytic coatings. The reason for this is that the electrolytic coatings often contribute to burn-off or thin spots in the low current density areas or at the contact points and give other problems. The work reported here has been done solely with pure electroless coatings of various kinds.

Some of the shielding possibilities include electroless copper, electroless nickel/phosphorus, electroless nickel/boron, electroless copper coated with immersion tin, electroless copper coated with a chromate or with an organic protective layer, and composites of electroless nickel and electroless copper. The coatings that we will discuss here are limited mainly to electroless copper, electroless nickel of various kinds, and composites of electroless nickel and electroless copper.

All test results reported here for EMI attenuation were obtained by the use of the transfer impedance method on special test panels. A series of test panels was prepared and analyzed for shielding efficiency as prepared. A subset of these panels was placed in salt-spray testing for 72 hours and then the panels were removed and again tested for RFI shielding efficiency. Another subset was placed in humidity testing for 336 hours and again at the conclusion of the test, the panels were tested for RFI shielding. Let's begin with the consideration of the RFI shielding efficiencies for various coatings. (Slide #1.) This slide shows the shielding efficiency in decibels upon the left versus the frequency in MHz or millions of cycles per second on the bottom. Frequency range covers that basically regulated by the FCC which is <.1 MHz to 1,000 MHz. This slide shows a series of test results for standard 7-8% nickel/phosphorus electroless coatings. Both sides of the test plaque were coated. The bottom line, number 1, corresponds to 7 mircoinches per side or 14 microinches total. As you can see, the shielding efficiency is very low, basically only suitable for electrostatic discharge applications. This had been expected from the very low conductivity of this thin film. Line number 2 shows a large jump up from about 15 to almost 40 decibels of shielding efficiency with a doubling of the electroless nickel thickness to 28 microinches or 14 microinches per side. Evidentally the thinner coating was not truly continuous because the resistivity of the coating dropped dramatically with the doubling of the thickness. Shielding efficiency is now basically minimal for many applications. Line 3 shows how the electroless nickel shielding efficiency increases when it is about doubled again to 48 microinches or 24 microinches per side, and finally line 4 shows another doubling of thickness to 94 microinches or 47 microinches per side. As you can see, there is a progressive increase in shielding efficiency with increasing thickness of electroless nickel.

Next (slide #2) shows the results for different types of electroless nickels. The top line shows the curve for 3% nickel phosphorus, with 32 microinches total thickness. This, having a higher conductivity than the nickel/boron, shows a higher shielding efficiency. The second line from the top shows 3% nickel/boron, 32 microinches total thicknesses. As you can

see, the nickel boron has slightly higher shielding efficiency than 6-7% phosphorus electroless nickel, which would be expected due to its higher conductivity. The third line down is for 6-7% nickel/phosphorus alloy, 28 microinches total thickness. The bottom curve shows 28 microinches of a 10-11% phosphorus high resistivity nickel/phosphorus coating. As you can see, the shielding efficiency is much lower than the rest. The basic general rule is that the higher the conductivity of the coating, the better the shielding efficiency.

This rule is borne out in the next slide, #3, which shows the effect of thicknesses for various pure electroless copper coatings. As you can see, a total thickness of 20 millionths of an inch of electroless copper has better shielding efficiency than 94 millionths of an inch of electroless nickel. As the thickness of the copper approximately doubles to 48 microinches and then again to 98 microinches, the shielding efficiency becomes very great. The shielding efficiences shown for the top line are greater than that required commercially for almost every device manufactured.

Slide #4 shows the effect of combining electroless copper and electroless nickel together for shielding applications. Three different coatings are incorporated in this figure. Line A is 7-8% nickel/phosphorus with a total thickness of 18 microinches (remember this is 9 microinches per side) over a total of 22 microinches of electroless copper. The second line, B, is 10-11% nickel/phosphorus, 18 microinches total, over 22 microinches of electroless copper. As you can see, the shielding efficiencies are essentially identical. The third slide shows 20 microinches of electroless copper total applied over 16 microinches of 7-8% nickel/phosphorus. Shielding efficiency is just slightly lower due to the lower copper thickness. What we have found is that the shielding efficiency of a composite coating, for all but the very thinnest layers of electroless copper, is dependent almost completely on the electroless copper. The electroless nickel used has almost no effect and I will go over this in a moment.

(Slide 5) Because the shielding efficiency is essentially independent of the electroless nickel's composition or thickness, it depends solely upon the electroless copper thickness. This slide shows the effect of different copper thicknesses versus shielding efficiency at the various frequencies. As you can see, electroless copper has excellent shielding efficiency at low frequencies and much better shielding efficiency at high frequencies. This is very important for several reasons actually. One of which is that most of the competitive methods such as nickel paints, copper paints, conductive plastics, and so forth would not even be shown in the graph because their shielding efficiencies at all wavelengths are at the low end or below the low end of that recorded here.

The second is that the FCC regulates different frequencies of radiation in different ways. Up through the 30 MHz range, the FCC regulates what is called conductive EMI/RFI. This is the radiation which escapes along power cords, through connectors and so forth. From 30 MHz to 1,000 MHz the FCC regulates transmitted EMI/RFI. This is the radiation which would escape through the plastic housing, through free space. It's very important that you have pore-free coating, a uniformly thick coating, and a high shielding efficiency, especially in the 30-1,000 MHz range. As you can see, electroless copper is outstanding in this frequency range.

(Slide #6) A little earlier I said that the composite of electroless nickel and electroless copper gets its shielding efficiency almost exclusively from the electroless copper. This is true because of the nature of the measurements that we make. Decibels of shielding efficiency is not a linear function as might be infered from the graph, but is a logrithmic function. Thus, there is a very large difference in actual shielding efficiency for each arithmatic difference of ten in dB of shielding efficiency. This slide shows the equation. If you do the calculations, you will see that if you take an electroless copper layer, which has 65 decibels of shielding efficiency, and overcoat with a layer of electroless nickel which by itself has 40 decibels of shielding efficiency, the total shielding efficiency of the coating is only 65.01 decibels. In other words, the 25 decibels difference in shielding efficiency between nickel and copper corresponds to a factor of several hundred difference in actual total shielding efficiency.

As we've seen, the relative shielding efficiency is different for electroless coppers and electroless nickels. Slide 7 shows relative conductivities of various metals based on copper being 1.0. On this same scale silver would rate 1.08 as it is more conductive than copper. On an equal thickness basis it would be a better shielding material. Electroless nickel is much less conductive than electroless copper. These conductivity figures are a very reliable guide to relative shielding efficensies of different coatings.

It is not only important to have a very good radio frequency interference shielding material on your plastic enclosure. It's also very important that this shielding material hold up over long periods of time. For example, if the coating would flake off or blister, there is a possibility that it could interfere with the electrical apparatus inside the case, perhaps short out some of the devices or circuits. Likewise, if you had a coating of RF shielding material only on one side of the plastics and part of it came off, you would now have a radio frequency leakage area. One of the advantages

of plating on plastics for RF shielding is that both sides of the part are plated. This provides a double protection against accidental scratches or blisters of any kind. Furthermore, the outside of most cabinets is painted for decorative reasons. This forms an additional layer of protection for the thin electroless layer.

The Underwriters Laboratory tests focus only on the adherence of any RF shielding coating to the substrate. Slide #8 shows the test methods employed by Underwriters Lab to qualify the coatings. As you can see, a modified thermocycle, a humidity, and an aging test are the test methods used.

In addition to mechanical adhesion though, there are some less obvious problems involved in RF shielding, one of which is the oxidation or degradation of the coating itself with time. There are two reasons for this being of grave importance. Oxidation may not seem too important if the part is painted, but not all of each part can be painted. All enclosures are made in two or more sections. The mating surfaces of each enclosure must be in electrical contact with each other. If these surfaces oxidize or degrade and form low conductivity or non-conductive paths, we now have what is known as a slot antenna. It is an interesting characteristic of radio frequency waves, that the amount of leakage through an aperture depends very little on the surface area of the hole but very strongly on the longest dimension of any such hole. Thus, a scratch one inch long will leak just about the same amount of radiation as a hole 1 inch in diameter. Likewise, if the whole perimeter of a box becomes non-conductive through oxidation of copper at the mating surfaces, then the whole box will radiate a very large amount of radiation.

One problem with using pure electroless copper is that copper is a very active metal and it oxidizes and breaks down fairly rapidly. We have run a series of tests to investigate the behavior of electroless copper and electroless nickel by themselves, along with combinations of nickel and copper in both salt-spray and humidity. Slide #9 shows the appearance of some of our duplicate series of test panels after 72 hours of salt-spray. Now it must be recognized that salt-spray is a very extreme test for a thin coating of 10-50 millionths of an inch. However, there is some applicability because perspiration and handling will deposit salt and cause coatings to degrade over time. Salt-spray can also be used as a rough guide to rank coatings.

Slide #9 shows the following:

Top row: electroless nickels

6-7% P 10-11% P 3% P 3% B

Second row: electroless coppers

As Is Anti-Tarnish Chromate

Third row: composites of nickel over copper

Cu + 6-7% P Cu + 10-11% P Cu + 3% P Cu + 3% B

Bottom row: composites of 6-7% nickel over copper

Cu + Ni + anti-tarnish Cu + Ni + chromate

10-11% P shows the least corrosion; 6-7% P panels are dark but not severely corroded. 3% P shows patches of corrosion with nickel salts and a few blisters. 3% B is very dark with small patchy areas of nickel eaten completely away.

All of the electroless copper coatings are badly corroded and pitted. Niether the anti-tarnish organic material nor the chromate gives any significant protection.

The composite coatings fared best. Large salt-spray performance differences are seen with the composites versus the plain electroless nickels. Niether the 6-7% phosphorus nor the 10-11% phosphorus nickels show any pitting. The high phosphorus coating is almost unchanged. The lower phosphorus coating has tarnished but has no pitting or green salts.

The 3% phosphorus panel shows erosion of the nickel in patches. The underlying copper, even though exposed, remains bright and shiny. This low phosphorus coating is more electrochemically active than the copper and is functioning as a sacrificial coating.

The 3% boron panel shows much green salt bleed thru from pores in the coating. Most of the panel is light in color and only slightly tarnished. The green salts are coming from the underlying copper. Here the Ni/B alloy is more noble than the copper and is accelerating, not retarding, corrosion at pits.

Slide #10 shows the shielding efficiency of electroless nickel on ABS after salt-spray exposure. This particular graph contrasts the results of a 6-7% phosphorus electroless nickel panel, total thickness 32 microinches versus the same panel after 72 hours salt-spray. You can see that the shielding efficiency has dropped in the low frequency range from about 40 decibels to about 30 decibels and in the higher frequency range, the difference increases to approximately 25 decibels. The actual loss in shielding efficiency by the electroless nickel is not too severe though. Again, this is very dependent

on the type of electroless nickel used. Higher phosphorus electroless nickels show less loss in shielding ability, and 3% phosphorus nickels show greater losses.

Slide #11 shows the results for electroless copper. There is much less difference after salt-spray exposure for the low frequency end, a difference of only about 8 decibels. However, by the time we get into the region of interest to the FCC for radiated RFI (>30 MHz), the difference becomes enormous, approximately 45 decibels. These figures illustrate again that electroless nickel is a fair coating by itself but not nearly as good as electroless copper. Unfortunately, electroless copper is very susceptible to corrosion and would not be suitable by itself in any application where a corrosive atmosphere would be expected to occur.

It is fortunate then that a composite of coating of electroless nickel on top of electroless copper offers the advantages of both coatings without any disadvantages. (Slide #12) This coating shows the same high shielding efficiency of electroless copper combined with the relatively good salt-spray resistance of electroless nickel. Again, the corrosion resistance of the electroless nickel coating over electroless copper varies with the type of electroless nickel, as I explained in my earlier slides. The slide here shows 6-8% phosphorus electroless nickel over standard electroless copper. As you can see, there is very little difference in shielding efficiency after salt-spray. What little difference there is is only in the high frequency and most of the differences can be related to experimental error. One thing that must be kept in mind is that even if the electroless nickel was almost completely corroded away, as long as the electroless copper layer was essentially untouched, there would be no difference in shielding efficiency. You must remember the figure I showed earlier on how the electroless copper layer itself dominates the shielding efficiency of this system.

Slide #13 shows the differences in the shielding efficiency of electroless nickel after 72 hours salt-spray at various frequency ranges. I have converted the decibels' difference into an arithmatic percentage drop based on the initial shielding efficiency. You can see that the drop in efficiency is anywhere from 90 to 99.75% based on the original shielding ability of the electroless nickel. You must recall, though, that this shielding efficiency, even after the drop, is still better than a number of competitive methods.

Slide #14 shows similar results for electroless copper. Here the efficiency drop is from 87% at low frequencies to 99.998% of the original value at higher frequencies. Again note that even at the higher frequencies, despite the percentage

decrease, the total shielding efficiency is still about equivalent to that of straight electroless nickel before salt-spray. One thing that operates very much in the favor of plated plastics in a test such as this is that most corrosion that takes place is on the upper-most portion of the test plaque. The lower-most portion of the test plaque is only slightly corroded and contributes the majority of the RF protection. These tests were run this way because this is indicative of what would happen in a real life situation - the outside of a cabinet containing electronics would be most exposed to corrosion.

Slide #15 shows the numerical differences for electroless nickel over electroless copper after salt-spray. Here the difference at the stated radio frequency intervals is only 2-3 decibels which is actually within experimental error. This difference translates into a 37-50% drop in actual shielding efficiency over the initial value. As you can see again, you must remember that the decibels of shielding efficiency is a logarithmic term.

Further data and discussions will cover the results for humidity testing.

The conclusions of this work are:

1. Plating on plastics is a very good method for RFI shielding applications.

2. Electroless copper is a much better shield than electroless nickel.

3. Electroless nickel offers better corrosion and oxidation resistance.

4. A composite coating of electroless nickel over electroless copper optimizes both RFI shielding efficiency and durability.

Acknowledgements

I want to thank all the people without whose help this project would have been impossible. This includes Carmine Nargi, Helen Craye, Jim Bongo, Juan Hajdu, and many others.

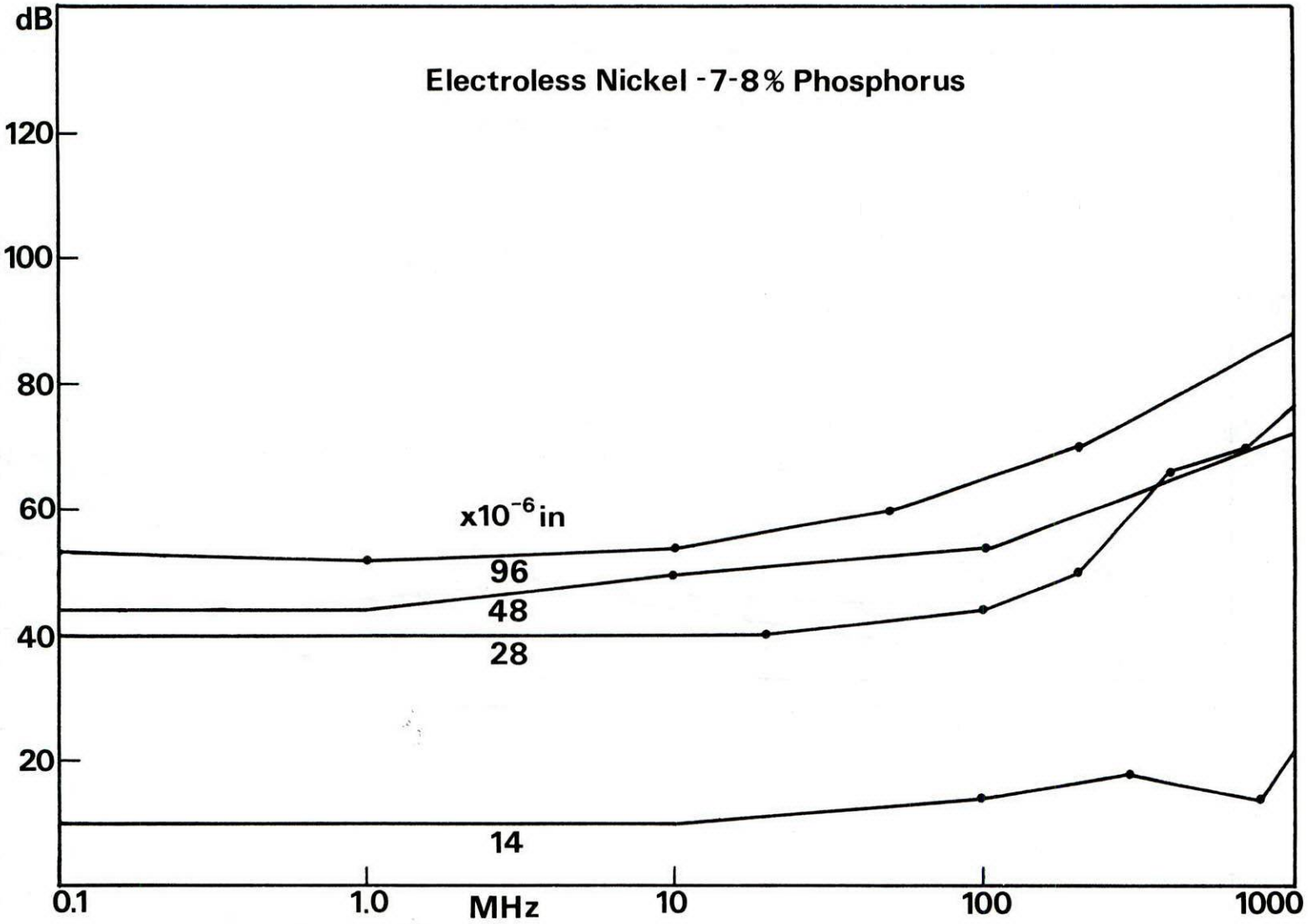

Fig. 1 Variation of Shielding Efficiency with Electroless Nickel Thickness

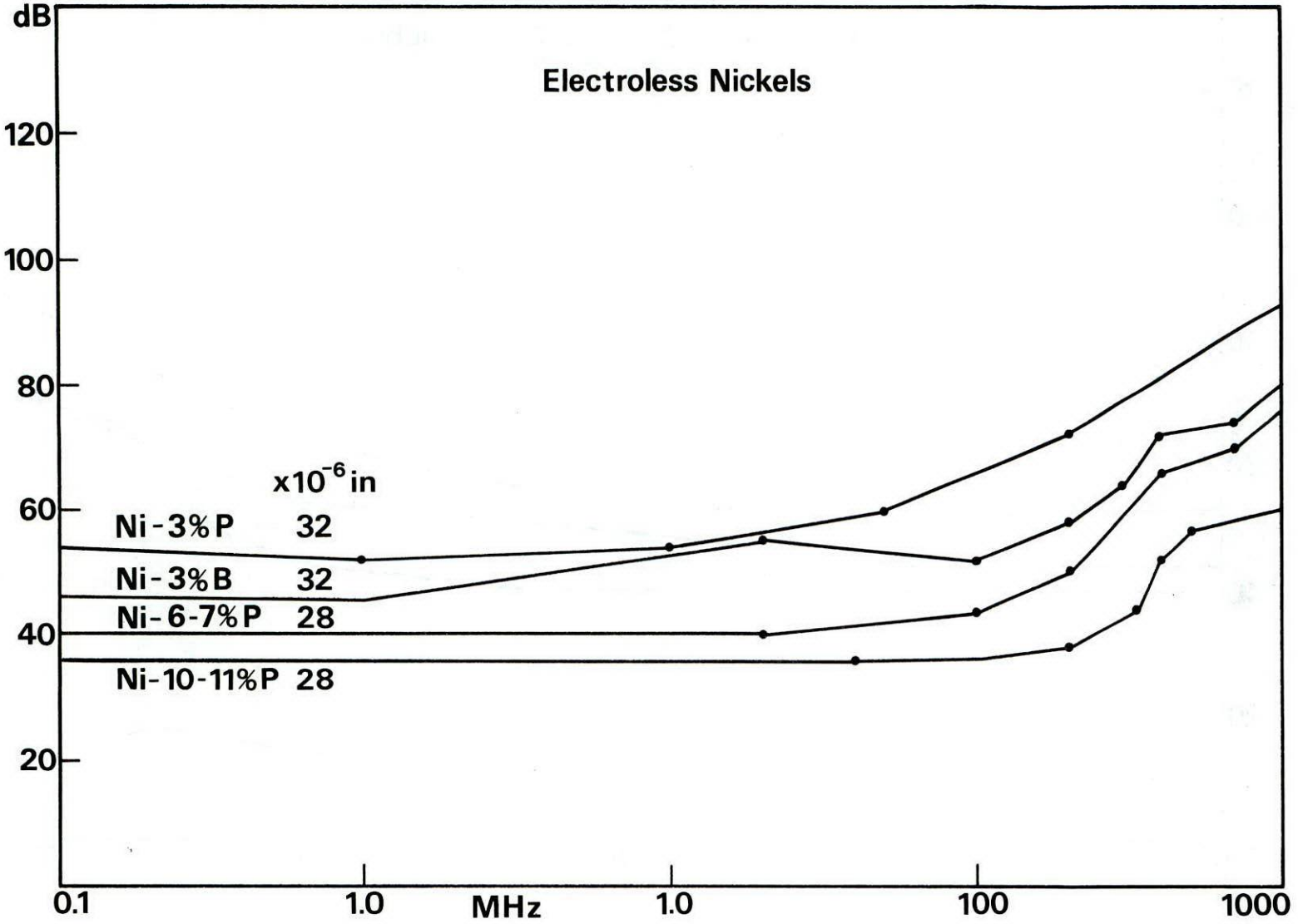

Fig. 2 Shielding Efficiency of Electroless Nickel Deposits

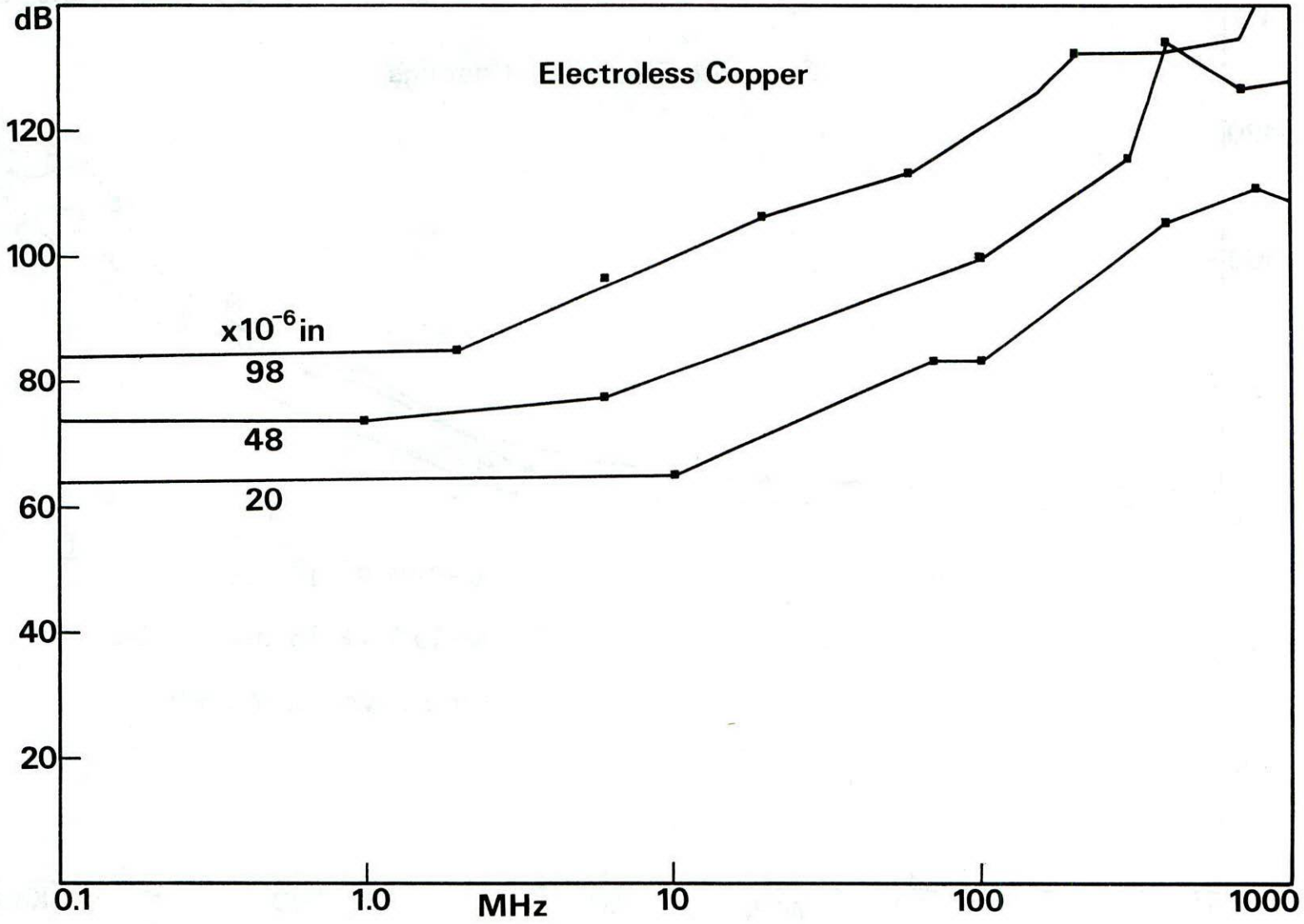

Fig. 3 Variation of Shielding Efficiency of Electroless Copper

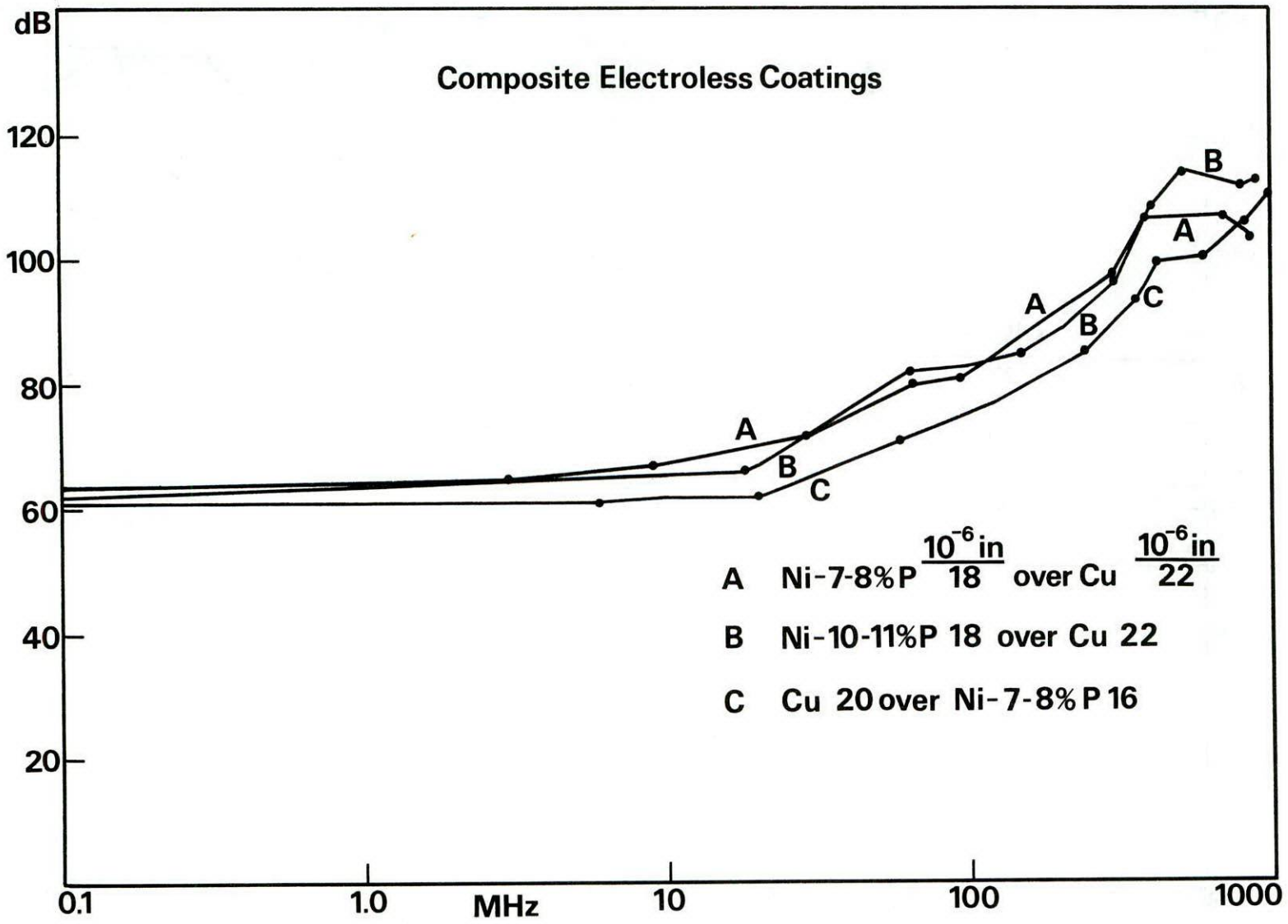

Fig. 4 Shielding Efficiency of Composite Electroless Coatings

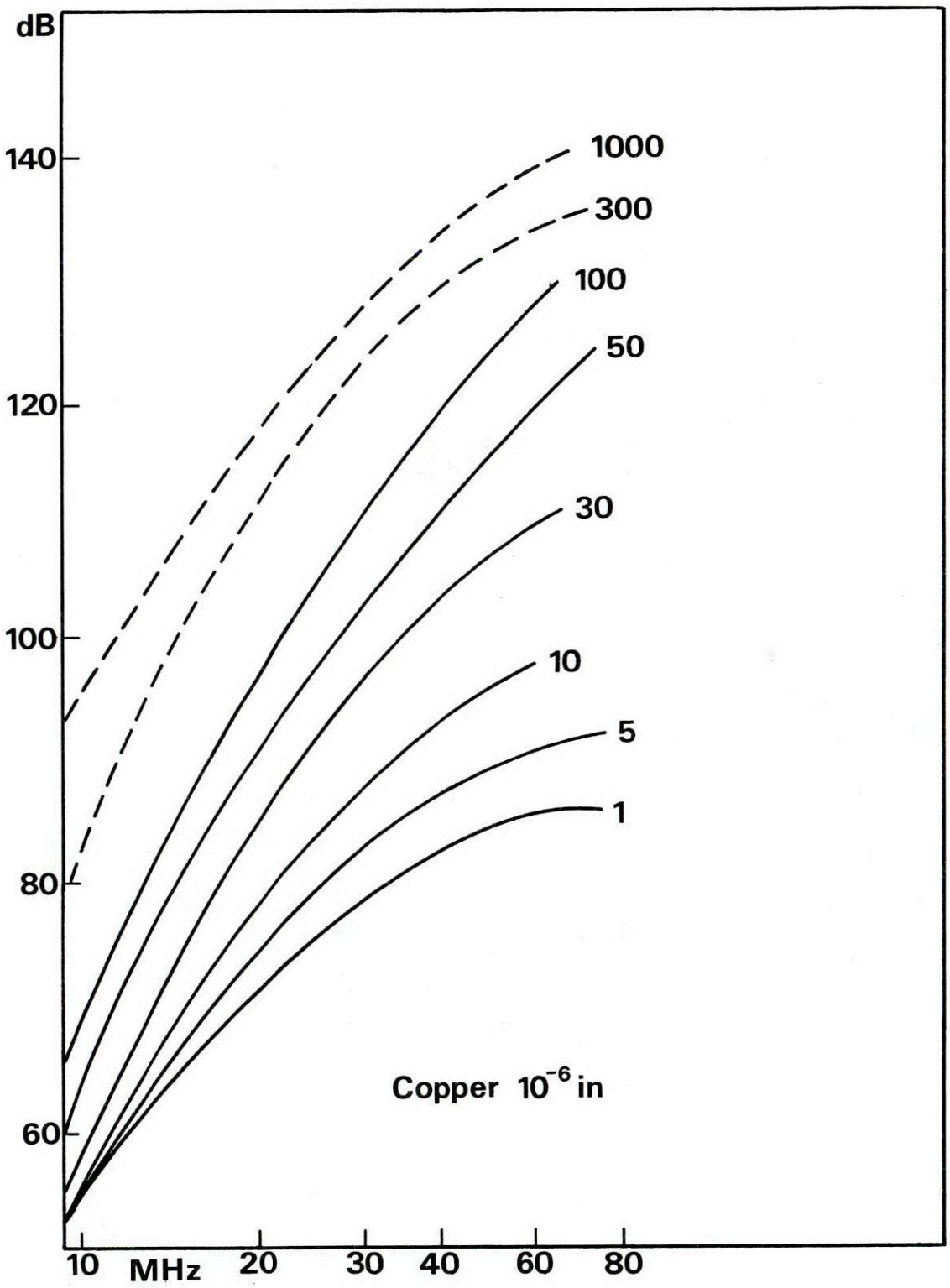

Fig. 5 Variation of Shielding Efficiency with Copper Thickness

FIGURE 6

$$dB = 10 \log \left(\frac{R_1}{R_2}\right)$$

If 65 dB electroless copper and
40 dB electroless nickel are combined,
the total shielding is 65.01 dB.

FIGURE 7

Relative Conductivity

Copper	1.0
Nickel	0.22
1% B/Ni	0.10
2.1% P/Ni	0.057
7% P/Ni	0.024

FIGURE 8

UL TESTS - RFI

ADHESION/CROSS HATCH

1. AS IS
2. HEAT AGED 85°C. 56 DAYS
3. HUMIDITY 90-95% RH 56 DAYS
4. THERMAL CYCLE 3X

R.T. - -29°C. - RT

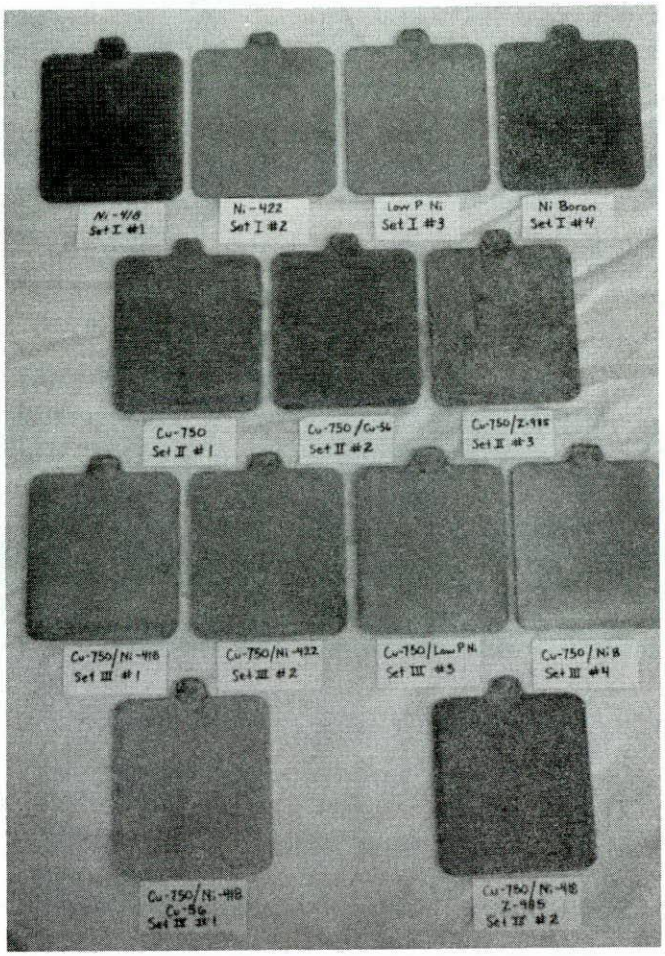

FIGURE 9

Salt-Spray Test Panels after 72 hours Exposure

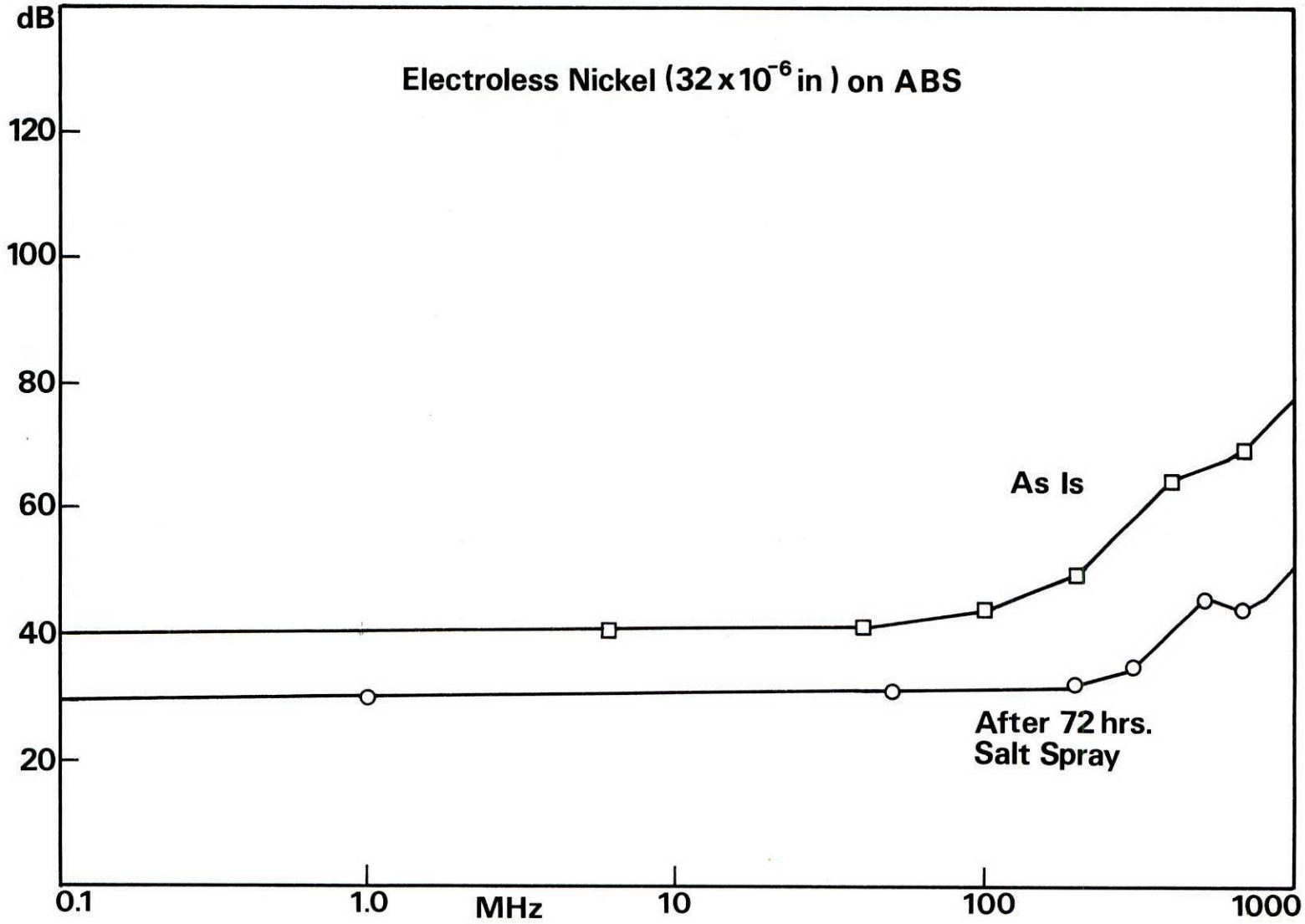

Fig. 10 Shielding Efficiency of Electroless Nickel after 72 hours Salt Spray Exposure

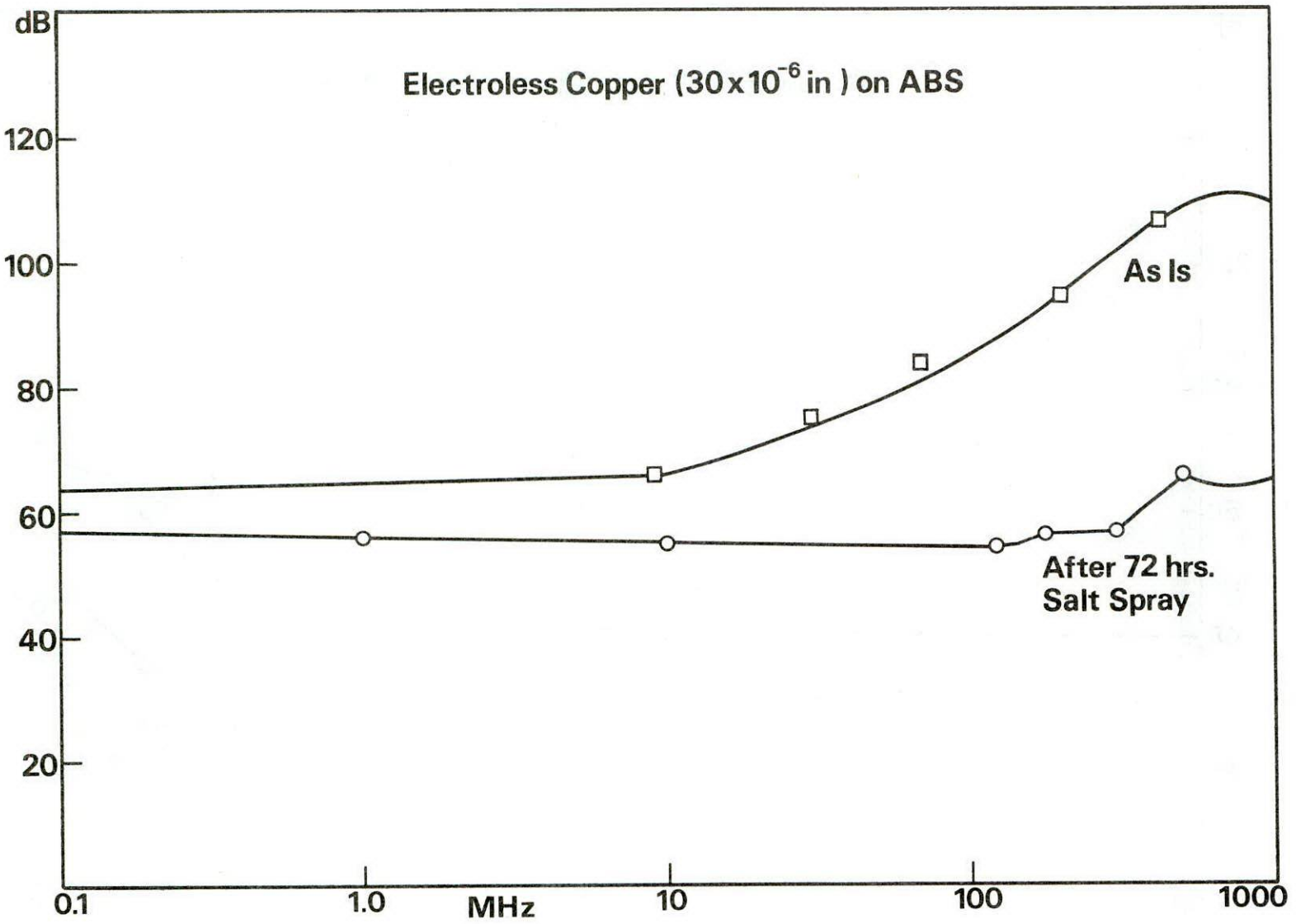

Fig. 11 Shielding Efficiency of Electroless Copper

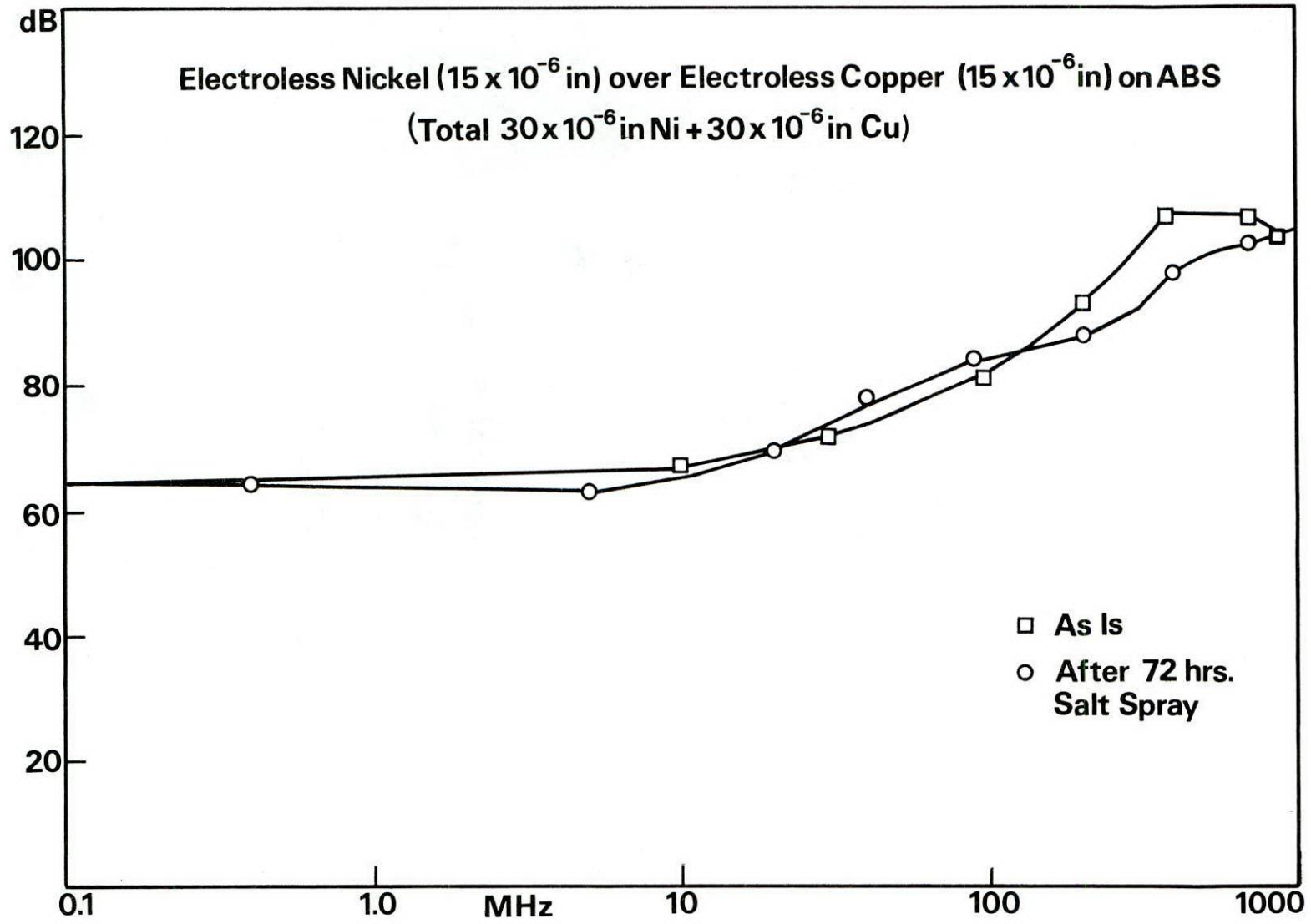

Fig. 12 Shielding Efficiency over Electroless Copper after 72 hours Salt Spray Exposure

FIGURE 13

Electroless Nickel

After 72 hrs Salt Spray

MHz	dB Difference	% Drop
1	-10	-90
10	-10	-90
100	-13	-95
800	-26	-99.75

FIGURE 14

Electroless Copper

After 72 hrs Salt Spray

MHz	dB Difference	% Drop
1	-9	-87.4
10	-11	-93
100	-33	-99.95
800	-47	-99.998

FIGURE 15

Electroless Nickel over Electroless Copper

After 72 hrs Salt Spray

MHz	dB Difference	% Drop
1	2	-37
10	2	-37
100	2	-37
800	3	-50

H-3

Electroless Plating Session H

Using Computer Technology in Electroless Nickel

Phillip D. Stapleton
Stapleton Company
Long Beach, CA

USING COMPUTER TECHNOLOGY IN ELECTROLESS NICKEL

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Abstract

Computers in the metal finishing industry can improve control of operations, automate repetitive operations, and provide for an orderly systematic growth. An application like operating an electroless nickel process can serve as an example of how a computer could be incorporated into metal finishing. This article covers the formulation of an electroless nickel data base, use of auto-analyzer on electroless nickel solutions, and overall design of system.

Computers are playing an ever-increasing role in improving the efficiency of metal finishing operations. Computers are also in the midst of a quantum transformation which will carry through into the 21st century. A typical piece of hardware like the 1.2 megabyte double-density floppy disc has been replaced by a 5 megabyte hard disc, which in turn will be replaced by a 50 megabyte and a 500 megabyte disc within five years. Other new technologies include Virtural Operating Systems (a type of unrestricted memory addressing) and light-powered computers. These advances will bring many new applications for computers and will force many of us to be directly involved in using these tools if we are to remain competitive within our respective fields.

The major reasons for using a computer in the plating industry and improve the efficiency are:

1. Improve control of operations
2. Automate repetitive operations
3. Provide for orderly systematic growth

We will discuss each of these reasons in reverse order.

Whenever a computer system is contemplated, several critical steps in organization are required. These steps involve describing the information required, all the input data necessary to compute the results, and how each item relates to one another. To accomplish this organization of each task, large flow charts may be developed which can trace how bits of information are processed. Using item list and flow charts, you will be able to visualize how you are processing information and how a computer might do it.

An example of this process can be seen in developing a program to monitor an electroless nickel process. In an electroless nickel process there are several factors and bits of information which are available and would be nice to know. If these were placed on a chart, they might look like Figure 1.

As all this information is assimilated into the computer system, reports may be generated which will provide management with the tools to operate efficiently. As you can see, a manually kept record would be awesome with 200 lots in process, while a mini-computer system would have no problem keeping up.

The important factor at this point is to understand that before you get a computer you must have a very complete definition of exactly what you need. Failure to identify a particular bit of information may cause thousands of dollars in software changes.

Another important consideration when organizing a system is how the reports are going to be used. In our operation we generate several monthly summary reports (Product Sales Analysis by Lot, etc...) which are important when the need arises to analyze some events. We seldom use these reports, however, because of the great amount of detailed information they include and limited requirements. This information will be stored in the computer data base in the future and seldom printed but available for query. In this example from Figure 1, the dates and times in and out would never need to be printed unless a rime study was undertaken.

To collect this information by manual means and compile it would be impossible, but with the use of data cap terminal or card reader it can all be automatic. To review all of this information would also be impossible, but yet the need does arise from time to time to analyze it. A sort and query program can be used to analyse large amounts of information quickly and provide the record of the event in question.

As you consider each task and what information is to be displayed and printed, logical CRT screens must be designed. With the use of sort and search software, information may be located and printed at will, providing for instantaneous review of any combination of data items. In addition, statistics on correlation of events can be made.

To establish these types of file systems (data bases), careful evaluation must be made of the software and hardware vendors you use. There are currently hundreds of data base systems available, many designed specifically for manufacturing and service industries.

By accomplishing these activities of organizing and evaluating the flow of information and capabilities of package software, a long-range plan can be proposed. This plan will provide you with the means to produce orderly systematic growth.

The second reason for using a computer is to automate repetitive operations. Some examples in a plating shop would include hoist control, inspection, billing, statements, quotations, analysis, automatic feed and word processing.

All of these functions can be integrated into most multi-terminal real time operating systems providing simultaneous processing of all functions.

If we continue the example of operating an electroless nickel system with a slight futuristic view, several interesting situations can develop. In this example, a host computer for a specific process is available which will coordinate user laboratory samples and user on-line solution analyses. The entire system uses phone and express mail communication. The system could provide electronic mail ordering and trouble shooting from the host computer as well as the standard business applications desired by most departments. All of the hardware exists today to accomplish building this system and will be available from several suppliers within a few years.

One feature which is unique to the metal finishing industry is the user on-line solution analyzer. This device which is available from several instrument companies provides for the separation and quantification of specific ions within the process. (See Figure 2) The Electroless Nickel Analyzer is able to analyze for the following:

Process pH
Process temperature
Nickel ion Ni++, Ni+++
Phosphorus PO2, PO3, PO4

Additives
- Brighteners
- Stabilizers
- Stress Reducers

Organic Solution Matrix

Anions Cl, NO3, NO2, SO4, SO2...

Trace elements Fe, Cd, Cu, Co, Cr, Pb, Sb...

As this information is produced at the users on-line analyzer, the coating alloy and solution performance can be tracked.

This continuous flow of information will be saved in the electroless nickel data base to be used later to generate certification, testing reports, and cost information. A general view of the hardware for such a system is shown in Figure 3.

This type of hardware system would depend on user samples being sent to the supplier labs and detailed analysis being coordinated with the user on-line analysis. With this situation, the system would be self-standardizing and maintenance would be kept to a minimum.

An additional feature of this computer system would be the ability of the purchaser or user of the coating to use the computer data base to assist in designing their parts by modeling corrosion performance and engineering properties. These could then be used to automatically adjust solution

operation to provide the specific properties desired and verify when the job is completed and what those properties should be. Additional testing by the supplier would then be used at periodic intervals to verify the accuracy of the on-line analyzer and modeling software. The information which is generated at the plating facility would be secured through several means, significantly reducing the chance to intercept valuable proprietary information by unauthorized persons.

These types of repetitive computer functions would relieve chemists and production people to be more creative and give them time to manage their departments far more effectively.

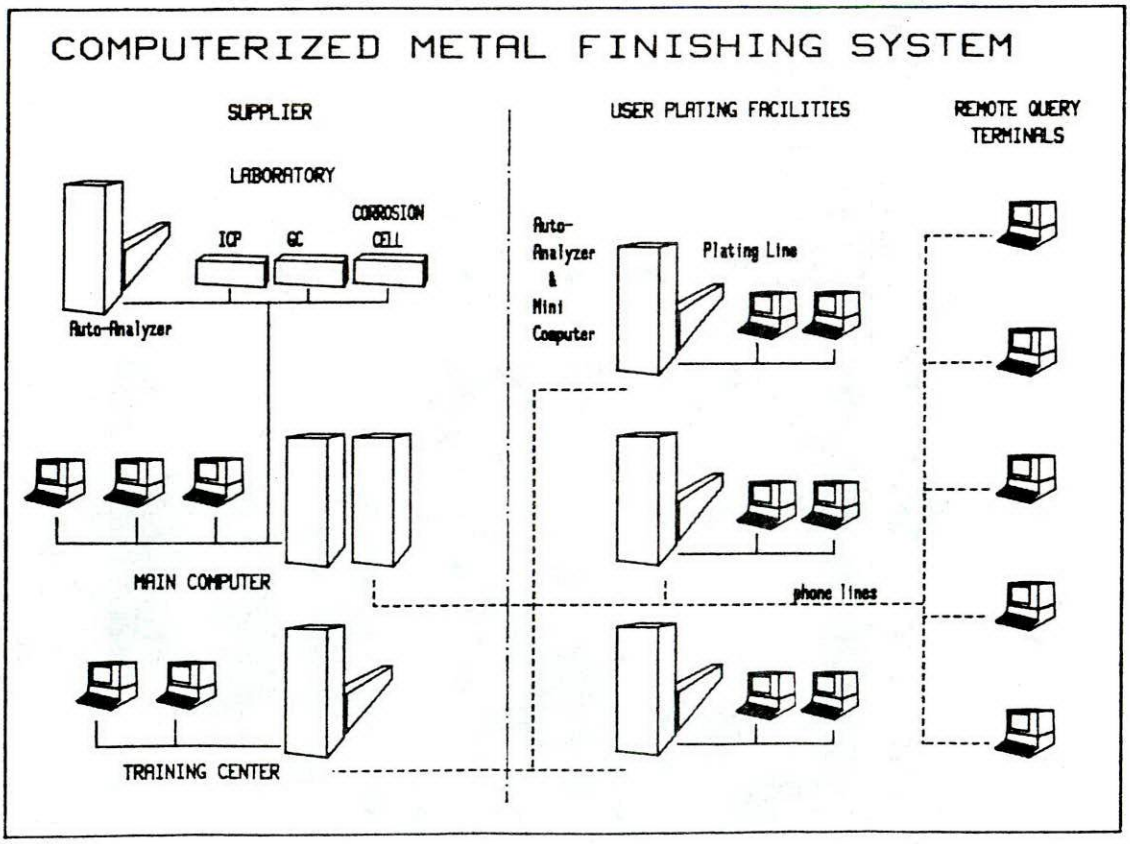
The third reason for computerization is to provide for the control of the operations. We have covered the organization and hardware and now come to the results of these efforts. For a manager to realize this phase, a tremendous effort will have had to be exercised in understanding the operation, flow of information, organization of software and hardware, training of operators, recovery of errors, and security. Each activity must be addressed and re-evaluated in order for the whole system to come together and the control of the particular operation be sound. Because Because this task is so large, it must be broken down into partitions which are manageable, and confidence must be developed each step of the way until the final goal is realized.

What is in store for the future in an information explosion. The ability of managers and technical persons to acquire, control, and disseminate this information will be critical to their success. What we have proposed here is being accomplished, and some are well on their way to using these powerful tools to make their operation run more efficiently and prepare for the future.

If you have throught about getting started and using a computer in your application, a suggestion would be to read as much as you can and talk to others who are doing what you want to do. Don't be a pioneer unless you are confident of success and remember that most applications have software which has already been written and may need little or no modification for your operation.

In this article we have attempted to point out some of the steps and goals necessary to address using computers in the metal finishing industry. The number of application possibilities are endless and care must be exercised to do those applications which will bring a savings and produce a benefit to your facility.

The management of an ever-increasing amount of detailed information will make the operation of metal finishing processes complicated. We trust that these thoughts and concepts will be of help in designing and planning your computer system.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REMOTE QUERY TERMINALS
LABORATORY
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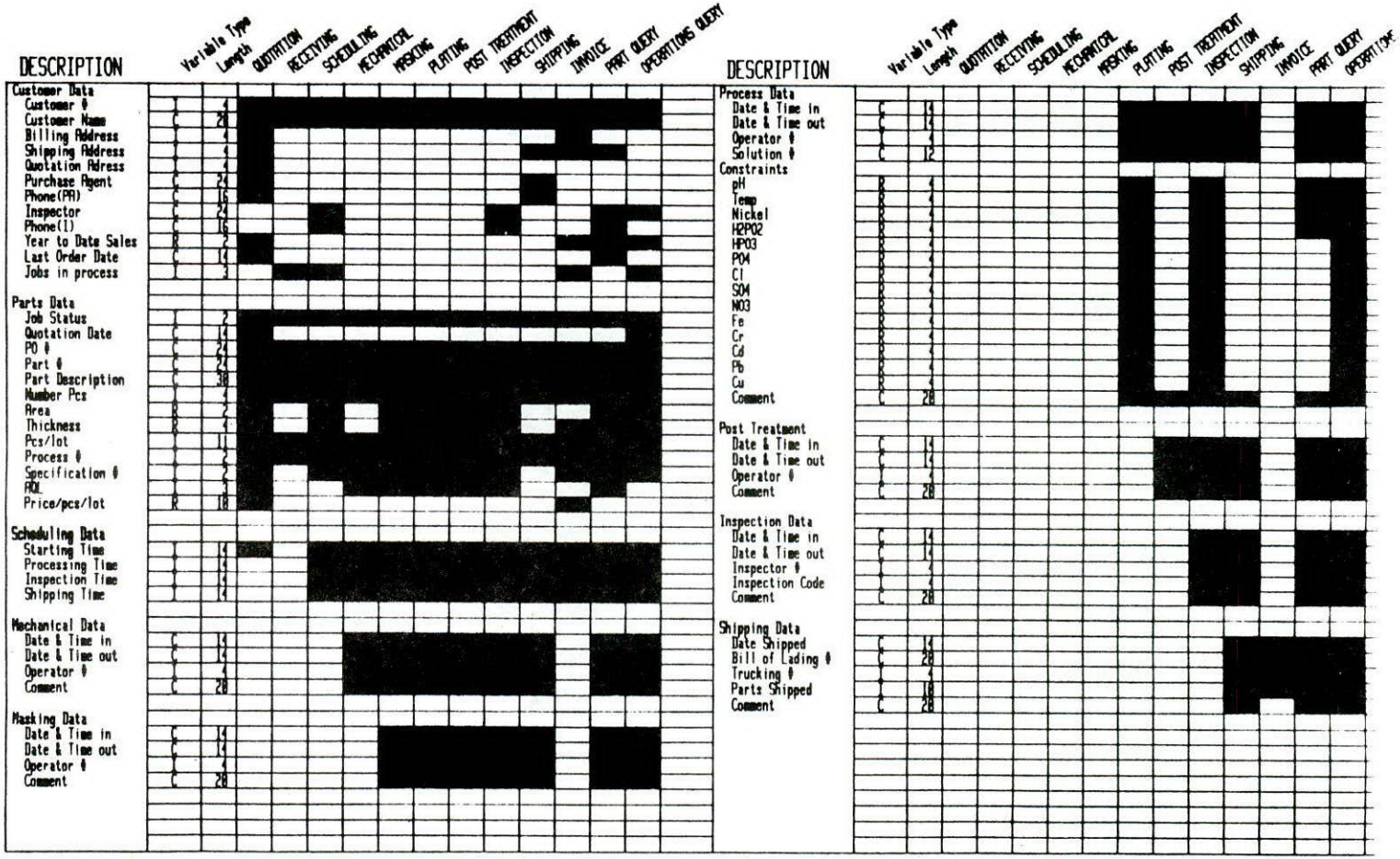
GC
CORROSION CELL
Auto-Analyzer
Auto-Analyzer & Mini Computer
Plating Line
MAIN COMPUTER
phone lines
TRAINING CENTER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OPERATIONS QUERY
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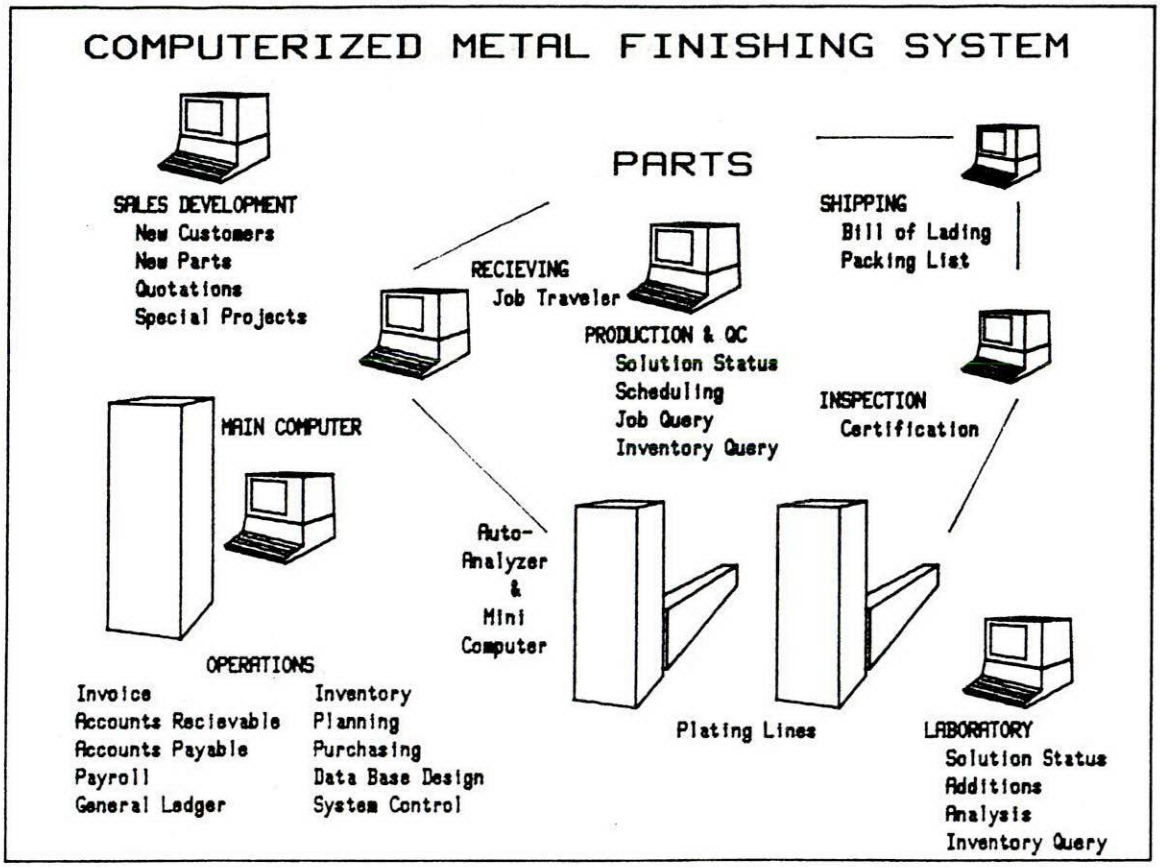
COMPUTERIZED METAL FINISHING SYSTEM
PARTS
SALES DEVELOPMENT
New Customers
New Parts
Quotations
Special Projects
RECIEVING
Job Traveler
SHIPPING
Bill of Lading
Packing List
PRODUCTION & QC
Solution Status
Scheduling
Job Query
Inventory Query
INSPECTION
Certification
MAIN COMPUTER
Auto-
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Accounts Payable
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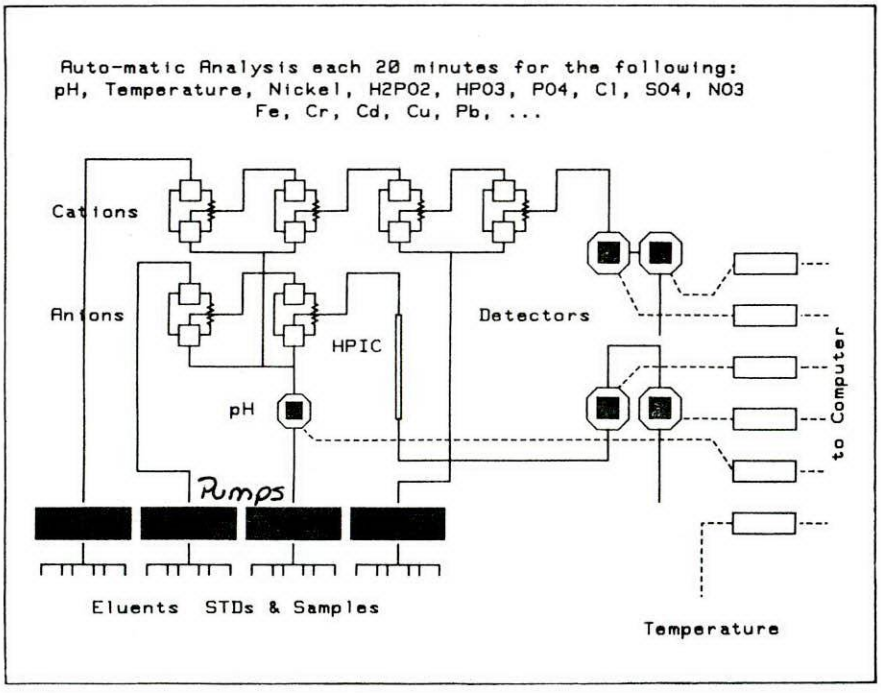
Auto-matic Analysis each 20 minutes for the following:
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Fe, Cr, Cd, Cu, Pb, ...
Cations
Anions
HPIC
pH
Pumps
Detectors
to Computer
Eluents STDs & Samples
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Electroless Plating
Session H

Electroless Gold

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ELECTROLESS GOLD

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Abstract

This paper describes a new non-cyanide electroless gold solution which is capable of depositing 3-4 microinches per minute of 24 karat gold on electroless nickel plated surfaces and 2-3 microinches per minute on immersion gold plated surfaces. The solution is superbly stable over very long periods of time, even at 200°F. Physical characteristics and kinetics are discussed, but not the chemical composition.

Introduction

Aside from some old formulations (1) which were called electroless while they were actually immersion baths, there have been, indeed, no real autocatalytic gold plating processes developed except two formulations (2, 3) developed by Sel-Rex and Engelhard Industries, respectively. Like most electroless processes, these two suffer from instability and slowness, at operating temperatures typically ranging from 180°-200°F. Both formulations referred to (2, 3) are also cyanide based and use powerful reducing agents or reducing complexes. The so-called "high build" gold composition (2) builds only about 40 microinches per hour and the autocatalytic gold builds up to about 72 microinches per hour on Kovar substrates and even less on other metallic substrates. Similar results are obtained with the Engelhard process also (3). The process developed by this author deposits up to 300 microinches per hour on electroless nickel plated substrates and up to 150 microinches per hour on immersion gold plated substrates.

Experimental

After preliminary experiments showed that this particular bath is, indeed, electroless and after a definite bath composition was established, experiments were carried out to arrive at some usable parameters such as operating temperature range, concentration, pH and rates of deposition. It was found early that direct plating on copper and brass substrates could not be done from this bath. Thus all panels were plated with either electrolytic sulfamate nickel or electroless (hypophosphite) nickel or immersion gold.

2" X 1" panels of cadmium copper, phosphor bronze and 70-30 brass were prepared. All panels were degreased and cleaned in alkaline cleaner and neutralized with 20% sulfuric acid

before further treatments. In each category above, three different sets were prepared.

One die set was plated with sulfamate nickel (100-150 mins.), electroless nickel (100-150 mins.) and immersion gold (10 mins.). Panels in each such set were then coated with the new electroless gold for intervals of 5, 10, 20, 30 and 60 minutes. Each such experiment was carried out at 160°F and 180°F as typical operating temperatures.

Thickness Measurement

Thicknesses were measured by cross-section, Betascope and weight gain. To obtain the weight gain in milligrams, each panel was thoroughly dried to constant weight after the substrate plating (Ni or gold) and weighed after electroless plating after thorough drying to constant weight.

Results

A. Rate of Deposition

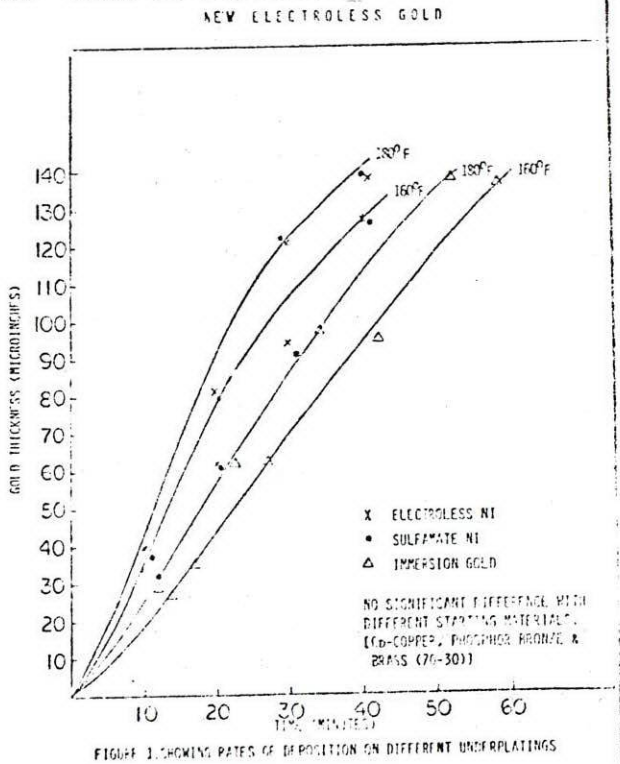

FIGURE 1 SHOWING RATES OF DEPOSITION ON DIFFERENT UNDERPLATINGS

Figure 1 shows a plot of thicknesses against time in minutes for each temperature, for each different substrate plated at the two different temperatures 160°F and 180°F. No elaborate studies were made at different pH values as there was no marked difference in pH value used (6-6.5). The figure shows clearly that the process is a true autocatalytic process with the rate leveling out exponentially with long times. It can be seen that the rate is close to an average of 4 microinches per minute on nickel plated panels and 2-3 microinches on immersion gold plated panels at 160°F and higher at 180°F.

B. Quality of Deposit

The thicknesses estimated from weight gain agreed almost exactly with those actually measured, thus showing that the deposits were of pure gold. EDAX analysis of the deposits also showed no evidence of contamination. The color was characteristic of pure gold and all deposits were smooth and bright, although no brightening agents are added to the bath.

The hardness of the gold on all panels was an average of 140 Knoop.

C. Adhesion

Adhesion checks were made by bending each panel through 180° and bending back 180°. Adhesion was found to be perfect on those panels where gold was deposited on electroless nickel and immersion gold. There was no adhesion on gold deposited on electroplated nickel.

D. Stability of Bath

There was no evidence of gold separating from the bath at boiling after 3-4 hours. There was no evidence of gold depositing on the walls of

the container (glass beaker or polypropylene). However, metallic particles such as nickel or gold introduced into the bath produced a slow build up on such nuclei.

E. Other Substrates

Unpassivated stainless steel, Kovar, metallized plastics and ceramics could all be plated without difficulty.

Discussion

The results of the experiments show clearly that an extremely efficient and practical autocatalytic gold process has been developed. The pH is near neutral. No filtration is necessary. Since the composition of the bath cannot be revealed, no discussion of the reduction mechanism can be given, suffice it to say that the system is not based on any known cyanide complexes. The system is patentable.

Conclusion

A highly stable, high speed and novel autocatalytic process has been developed. Its applications range from plating of electronic contacts of different shapes to plating of microelectronic circuits, including metallized ceramics. At the present time there is no method comparable available.

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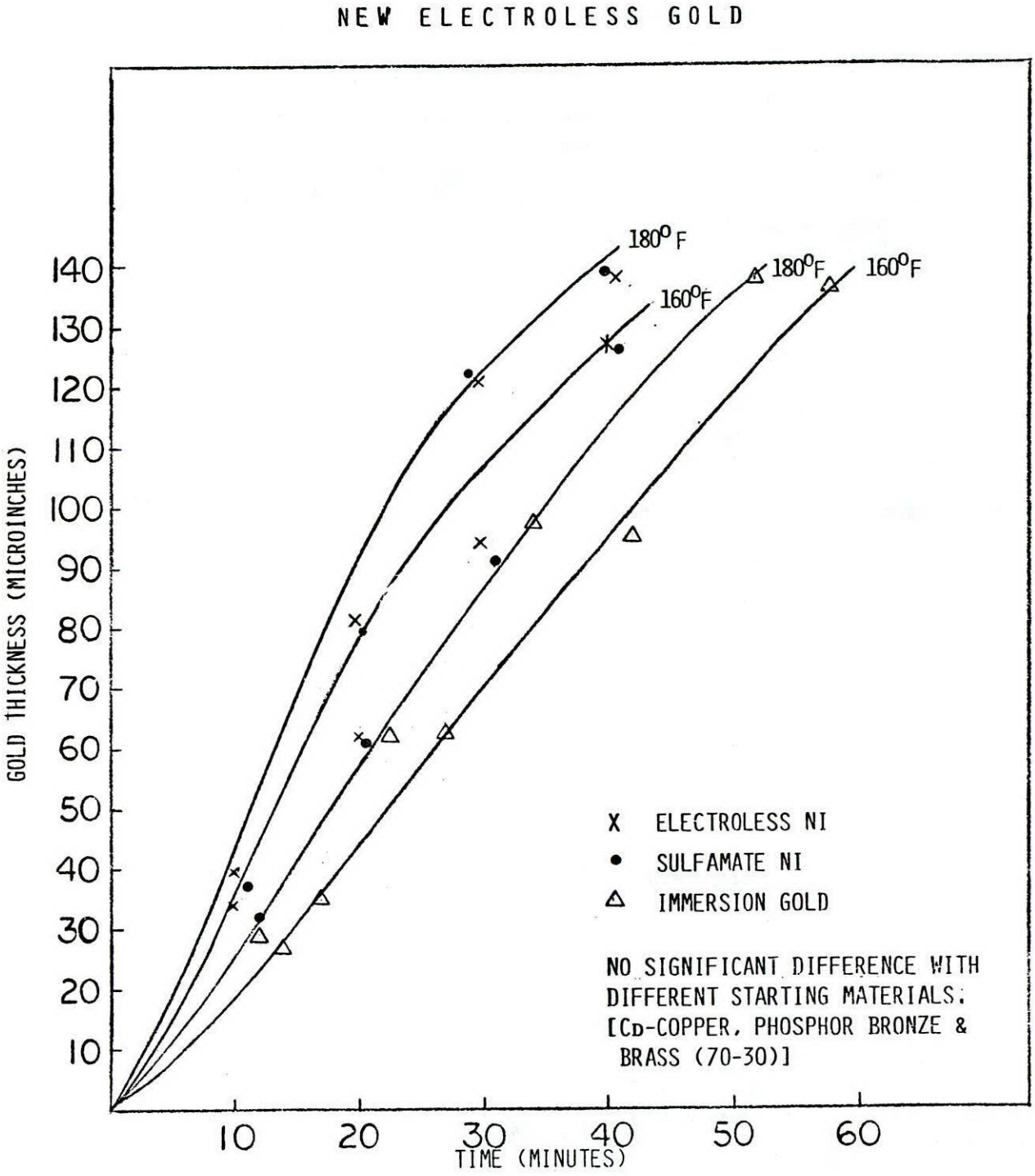

FIGURE 1. SHOWING RATES OF DEPOSITION ON DIFFERENT UNDERPLATINGS

H-5

Electroless Plating
Session H

Electroless Nickel for Stress Corrosion Protection in Power and Petrochemical Plants

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ELECTROLESS NICKEL FOR STRESS CORROSION PROTECTION IN POWER AND PETROCHEMICAL PLANTS

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INTRODUCTION

Usually electroless nickel is considered to be a wear and corrosion resistant coating (1). In most cases, studies in improving the corrosion behavior of materials coated with electroless nickel are aimed at improving the corrosion resistance of the coating considered in and of itself, or at reducing the porosity and defects of the coating upon a given base material. Though correct and valid in and of itself, this philosophy tends, nevertheless, to consider electroless nickel coating as being similar to chromium or ceramic coatings, with fewer air and water pollution problems and without the difficulties in current distribution or the need to grind the coated surfaces.

In effect, electroless nickel has been used as a substitute for hard chromium plating in numerous applications and represents an "ideal" coating whenever the corrosion problem has to do not so much with protecting the plant construction material as to avoiding contamination of the process fluids with corrosion products from the plant itself. This concept, however, does not take full advantage of the real possibilities of electroless nickel in corrosion prevention in plants; in fact, electroless nickel presents the following unique characteristics, with respect to all other types of coatings:

a) Its amorphous or microcrystalline structure, which produces a corrosion and metallurgical behaviour that is significantly different from that of crystalline metals.
b) Good chemical inertia without, however, the excessive brittleness of chromium, ceramic or other coatings.
c) High levels of phosphorus which, in the "corroded" form, i.e. when oxidized to phosphate, is a traditional corrosion inhibitor.
d) The uniformity of the coating and the possibility of applying it "in loco" even on structures of large dimensions and often when coating was not included in the initial design (2).

In addition, one should also consider the general lack of confidence which corrosion specialists have in coatings which can nullify the protective action or even increase the corrosion effect when there are defects, even incidental ones, in the coating itself. It would thus seem extremely useful to investigate the corrosion behaviour of the coated material-defect taken as a whole, in a given aggressive environment.

Localized corrosion, such as stress corrosion (SC), and hydrogen embrittlement (HE), as the result of a corrosive process, have recently become very important, due to the damage that they casue (3). Traditional coatings are ineffective in resolving the problem and can sometimes even be damaging; so they are prohibited by various specification (4). In power plants, there seems

to be difficulty in selecting the materials for heat exchanger structures, mainly because of the "latent" initiation and propagation of localized corrosion. In the case of condensers which operate with river water, some of the most widely used materials are single-phase aluminium brasses; these alloys, however, are susceptible to SC even in water that is not contaminated with ammoniacal substances (5,6). The SC is tied to the alloy chemical composition, particularly to the phosphorus and arsenic content (5); however, an excessive decrease in these elements would lead to dezincification of aluminium brasses. As a result, it is often necessary to resort to more costly materials, such as cupro-nickel or stainless steels which are not, however, immune to localized corrosion (7). Coatings have not been traditionally used in condensers, though this is a sector that would offer extensive applications in the event that one (or more) coatings were discovered which would not decrease thermal conductivity and which, even when incidental defects are present, would allow SC phenomena on brasses to be avoided or at least reduced, thus eliminating the need to use much more expensive materials (8).

In the petrochemical industry, the need to extract oil and natural gas under increasingly more difficult conditions requires the use of high strength steels capable of withstanding the high pressures that are involved (for example, in pipes and joints for deep drilling) (9). The possibility of using high strength steels is limited by the fact that they are susceptible to environmental fracture, the insurgence of which is intensified by the presence of hydrogen sulfide (10). The latter is a typical poison in the recombination of atomic hydrogen, which thus tends to be absorbed by the alloy (causing delayed fractures) or to be absorbed at the crack tips (causing hydrogen assisted SC cracking). Quenched and tempered low-medium alloy steels are one of the types used in this field, though they are susceptible to frequent environmental fractures; use of high alloy steels is of no avail either (9). Traditional metal coatings are usually damaging to the base metal, even when the coating itself is not defective; coatings are often prohibited as, for example, in the NACE specification (4). In the event that particular types of coatings are found (even very expensive ones) which can eliminate or at least reduce the incidence of failures (causing damage in the range of millions of dollar/failure), this would be another field in which such coatings would enjoy widespread use and development.

The aim of this research has been to study Ni-P electroless coatings, of lamellar or collumnar morphologies, applied to aluminium brass or Cr-Ni low alloy high strength steel, from acid or alkaline baths. A Watts type galvanic nickel was selected as a comparison coating. Accelerated SC tests were conducted in appropriate solutions simulating the aggressive environments of a power plant (for brass) and of drilling rigs (for structural steel).

2. EXPERIMENTAL

2.1 Nickel baths

The nickel baths were of the following compositions :

a) Electroless baths. 0.1 M $NiCl_2$, 0.3 M H_3PO_2, 0.2 M citric acid:
   1) - pH 4.3 with NaOH, 1 ppm $PbNO_3$, T = 90°C;
   2) - pH 4.3 with NaOH, 1 ppm MBTA, T = 90°C;
   3) - pH 9.5 with NH_4OH, 1.5 ppm $PbNO_3$, T = 80°C;
   4) - pH 9.5 with NaOH, 1.5 ppm MBTA, T = 80°C.

b) Watts bath. 1.3 M $NiSO_4$, 0.2 M $NiCl_2$, 40 g/l H_3BO_3, pH = 4.0, T = 50°C, 5 A/dm^2.

Reagent grade chemicals and distilled water were used to make all of the solutions.

2.2 Single-phase aluminium brass

The test specimens were 20 mm wide brass rings cut from a 1" heat exchanger tube, in the as-received condition, and of the following chemical composition (Wt %): Cu = 76.00; Pb = 0.002; Al = 2.03 ; Ni < 0.005; Fe = 0.005; Mn < 0.005; Sn < 0.005 ; As = 0.027 ; P = 0.001; Zn = rem.

Therings were diametrically drilled and C - cut longitudinally, according to ASTM G 38-73 specification (11). They then underwent one of the following surface treatments:
- Solvent cleaning (a);
- Wet grinding to grade 1000 SiC paper (b);
- Coating in : bath 1, 3 µm(c) and 20 µm(c'); bath 2, 3 µm(d); bath 3, 3 µm(e); bath 4, 3 µm(f); Watts bath, 4 µm(g) and 15 µm(g').

Before plating, the specimens were cathodically cleaned at 5 A/dm^2 and 60°C in the following solution: 30 g/l Na_2CO_3, 10 g/l EDTA, 10 g/l Na gluconate. The specimens were rinsed and then dipped in a cold 10% H_2SO_4 solution. This was followed by rinsings in distilled water twice. The electroless plating was initiated by suspending the specimens in the electroless bath via an iron wire.

After the surface treatment, the C specimens were bent by tightening a steel bolt centered on the ring diameter so that the brass aluminium yield strength was exceeded in the most strained areas . Phenolic material was used to insulate the specimen from the bolt and, when the tightening was conducted, the bolt was covered with epoxy resin and taped with polytetrafluorethylene. The specimens were bent 1% (with respect to the diameter) in a first series of tests, and 10% in a second series.

For the accelerated SC tests, the following solution was used : 0.1 M Na_2SO_4, 0.05 M $CuSO_4$, 0.005 Cl^-, pH = 3.0, as suggested by (4), to simulate the environment inside an occluded cell (crevice) developed on aluminium brass condensers and other heat exchangers using chloride polluted river water as the cooling medium. The bent specimens were simply immersed in the test solution maintained at 25 ± 0.1°C. In the first series of tests, a time of 144 h was taken, with a surface/volume ratio of 1 cm^2/10 cm^3, and the test solution was changed every 48 h; in the second series of tests, times of 144 h and 312 h were taken, with a surface/volume ratio of 1 cm^2/100 cm^3. At the end of each test, the specimens were diametrically cut and microscopically examined.

2.3 High strength steel

The structural steel (type AISI 4137 H) was of the following composition (Wt%) : C = 0.40; Mn = 0.095; Si = 0.37; P = 0.017; S = 0.016; Cr = 0.99; Ni = 0.16; Mo = 0.18.

The smooth cylindrical tensile specimens (3 mm in diameter) were longitudinally cut from a hot forget casing joint which was mill heat treated by oil quenching from 850°C and tempering at 600°C. Under these conditions, the steel has

the following metallurgical characteristics :
Y.S. = 975 MPa; U.T.S. = 1050 MPa; Elongation = 15%; Reduction of area = 57%; KV = 90 (J/cm^2); HRc = 33; Grain size = 5-8 ASTM.

The specimens underwent one of the following surface treatmens :

- Solvent cleaning (a);
- Coating in : bath 1, 13 µm(b); bath 2, 18 µm(c); bath 3, 13 µm(d); bath 4, 18 µm(e); Watts bath, 40 µm(f).

Before coating, the samples were anodically cleaned at 5 A/dm^2 and 95°C for 1 min in the following solution: 20 g/l NaOH, 20 g/l Na_2CO_3, 20 g/l Na gluconate. After rinsing, the specimens were anodically etched for 20 s at 25 A/dm^2 in a cold 70% H_2SO_4 solution and quickly rinsed in distilled water, no heat treatment was conducted after plating.

For the accelerated SC tests, the following solution was used, as proposed by NACE (4), at room temperature: 5% NaCl, 0.5% CH_3COOH, initial pH = 2.8, H_2S(bubbling).
The tests consisted of placing the unstressed specimens in the aggressive solution and after 30 min stressing and keeping them under a constant tensile load. Measurements were taken of the failure time corresponding to the various applied stress. When no failure occurred, the tests were stopped at 1000 h.

3. RESULTS AND DISCUSSION

3.1 Single-phase aluminium brass

In the first series of tests, the brass, in condition (a), did not reveal any considerable formation of corrosion products; however, the surfase generally appeared to be corroded and cracked with mixed morphologies of cracks (trans- and intergranular) more than 200 µm deep (Fig. 1). The brass, in condition (b), showed considerable copper displacement from the solution and cracks whose depth did not differ significantly from those found in the previous case (Fig. 1).

Regardless of the type of bath (1, 2, 3 or 4), the specimens, coated with electroless nickel, presented considerable copper displacement from the solution, but despite this, no SC phenomena were noted (Fig. 2). The coatings appeared corroded, with the same morphologies already identified in sodium chloride in our previous work (Fig. 2) (12).

The specimens plated with galvanic nickel maintain their original shine; the coating does not display overall corrosion attack, but rather, pitting corrosion can be seen (Fig. 3). In the pits, there is a strong intergranular attack with the SC crack formation; the latter are present even under the unpitted coating (Fig. 3).

Potentiodynamic measurements were conducted on the unstrained specimens in a solution analogous to the one used in SC tests, but with sodium ions being substituted for copper ions (Fig. 4). The anodic behaviour was analogous for all four types of electroless nickel coatings; in particular, in free corsorion ,electroless coatings were anodic with respect to the brass (contrary to the cathodic behaviour displayed by galvanic nickel coatings).

The second series of SC tests was conducted on specimens coated with electroless nickel and bent so as to crack the coating and thus expose the base

material as well to the aggressive environment. No SC was ever observed even in correspondence with coating lacerations; these lacerations were often filled by the copper displaced from the solution (Fig. 5). After 312 h, the coating of 3 μm was almost completely "destroyed"; nevertheless, no SC was observed so long as traces of the deposit still remained upon the surface (Fig. 5).

Once the coating had completely disappeared after 312 h, SC began in a manner analogous to uncoated specimens. Coatings that were initially of a greater thickness continued their protective action even after 312 h, despite the non-uniform overall corrosion attack (Fig. 6).

On the basis of the above observations, it would thus seem that SC phenomena in single-phase aluminium brasses are due to crack tip preferential dissolution. The protective action of electroless nickel coatings, which are anodic with respect to the base brass, appear to be that they dissolve preferentially, though not in a uniform manner. Their protective ability (at least as far as thin coatings are concerned) does not seem to be tied to any defects nor to the type of coating bath (either acid or alkaline), but to their slow corrosion rate.

The behaviour of galvanic nickel seems to be the opposite of that of electroless nickel. It is, in fact, cathodic with respect to the base brass; it seems to be susceptible to pitting corrosion, with a stimulation of intergranular attack in the pits; SC phenomena do not appear to be inhibited, not even beneath unpitted coatings.

3.2 High strength steel

The results of SC testing on high strength steel are summarized in Fig.7. Uncoated specimens presented very low failure times and a very low threshold stress level - if it existed. The specimen surfaces appeared corroded and when the applied stress was greater than 30% of the yield strength, gas evolution was visible on the surface (Fig. 8). The fracture appears to be macroscopically brittle; there is, in fact, no necking (Fig. 8). Cracks parallel to the applied stress (= secondary cracks) were observed particularly on the collapsed fracture surface (Fig. 8); no other perpendicular cracks were found. The fracture appeared to be microscopically brittle (Fig. 8).

All of the above leads us to presume that, on the one hand, self-stressing had occurred, as a result of the joint metallurgical history (hot forging, heat treatment); and, on the other hand, that the fracture did not occur because of a crack propagated from the surface towards the inside of the metal (as is typical of stress sulfide cracking), but rather, because of a crack originated and propagated within the specimen, as a result of embrittlement due to the hydrogen absorbed and produced in the corrosive process of the specimen surface (typical of delayed fracture).

Galvanic nickel coatings, due to their lack of macroscopic defects, extend failure time and greatly increase the threshold stress level, without however modifying the form of the applied stress-failure time curve. The fracture appears to be macroscopically and microscopically brittle, but less so than the previous case; the number of secondary cracks seems to be greatly increased (Fig. 9).

Nickel coating obviously modifies the kinetics of hydrogen evolution, which is complementary to the dissolution process; it also alters the stationary

surface conditions between atomic and molecular hydrogen as well as the diffusion kinetics of atomic hydrogen. It can thus be hypothesized that galvanic coatings do not modify the phenomenon of delayed steel failure, but reduce the amount of hydrogen absorption, with a subsequent increase in failure time and in threshold stress, and the maintaining of a certain ductility in the base material.

Electroless nickel coatings from bath 4 seems to have the effect of strongly increasing failure times when stress is highest, without however increasing the threshold stress; they also seem to modify the slope of the applied stress-failure time curve (Fig. 7). Observation of the specimens reveals that the coating has numerous spallings, also as a result of minimal deformations corresponding to a stress level which is 7% of the steel yield strength. Along with these spallings, there is preferential corrosion of the base steel, with the formation of V grooves which degenerate into cracks (Fig. 10). The fracture appears to be macroscopically brittle; furthermore, both secondary cracks and cracks perpendicular to the applied stress appear on the specimen surface (Fig. 10). The fracture reveals corroded areas alongside clearly ductile areas (Fig. 10).

In the case of electroless nickel coatings from bath 3, no failure occurred until 1000 h and until the steel had been stressed to 70% of the yield strength (Fig. 7). The fracture, obtained on the sample stressed at 90% of the steel yield strength, reveals a very small corroded area within a macroscopically brittle area without coating disjoining (Fig. 11); alongside the latter area, there was a macroscopically ductile area with numerous secondary cracks and coating disjoining. Both the macroscopically brittle and ductile areas were microscopically ductile (Fig. 11). In the case of electroless nickel coatings from bath 2 the fracture appear to be analogous to the previous one, but without coating disjoining (Fig. 12).

On specimens coated in the electroless nickel bath - 1, failure did not occur until the steel had been stressed to 90% of its yield strength and until 1000 h. After this time the specimens, subjected in air to a tensile test, reveals a macro and microscopically ductile fracture (Fig. 13).

It can thus be hypothesized that, in the case of specimens coated with electroless nickel from baths 2, 3 and 4, the fracture occurs because of SC or rather, because of a crack (corresponding to coating spalling) advancing, mainly by dissolution, and reducing the resistant section until the specimens collapse. The dissolution process thus appears to be preferentially localized at the crack tip, while the complementary cathodic process of hydrogen evolution appears to be localized on the nickel coating. The latter seems to have very little permeability towards the hydrogen itself. During steel plastic deformation, stress distribution, leading to secondary cracks, seems to also depend upon the coating mechanical behavior.

In one series of test, the specimens were placed in an N_2 deaerated testing solution in which hydrogen sulfide bubbling was begun after 15 min; no stress was applied for 30 min. Then the stress was raised to the yield strength within one hour and maintained at the level until failure. Throughout the test, measurements were taken of the specimen potential (with respect to a saturated colomel reference electrode(connected to the testing solution via a long, double-septum bridge). The results are reported in Fig. 14 and refer to NHE, having assumed E_{SCE} = 240 mV vs NHE.

From Fig. 14, it can be seen that :

- all of the coatings are cathodic with respect to the steel; the galvanic nickel takes on a potential close to the reversible one of hydrogen evolution, while the electroless nickel from baths 1, 2 and 3 is more noble than the latter.
- hydrogen sulfide bubbling mades the coatings become more noble;
- for coatings from baths 1, 2 and Watts, spalling (indicated by the potential lowering) occurs, in these relatively high loading rate, only when the yield strength is reached; for coatings from bath 3, spalling occurs a little earlier.

The fact that the electroless coatings from baths 1, 2 and 3 are more noble than the reversible hydrogen evolution potential, and that they are sufficiently ductile to withstand the static deformation, corresponding to 90% of the steel yield strength for bath 1 and 70% for baths 2 and 3, implies that there is practically no corrosion nor hydrogen evolution, thus explaining the failure lack after 1000 h.

In a final series of tests on specimens coated from baths 1, 2 and 3 and Watts, the following were conducted: Vickers indentations (diagonal of 50 μm), Rockwell indentations (diameter of 200 μm), and diametrical removal of the coating up to 1 mm in width. The coated specimens were then stressed in the aggressive environment to the same level as their threshold stress (Fig. 7); no failure occurred after 500 h.

It can, therefore be asserted that cathodic coating not only reduce the overall corrosion, but also exert a type of "anodic protection" on the steel exposed areas, thus reducing (if not actually impeding) hydrogen evolution on the latter. In addition, particularly for large potential differences and in the presence of small defects, galvanic coupling can contribute to crack tip blunting, by locally stimulating the dissolution process on the base material (Fig. 15), and can thus lead to a stress intensity factor less than the threshold value.

Thus, even in a high-defect situation, cathodic coatings not only do not lead to an increase in SC, but also continue to exert their protective action (though with less effectiveness). In addition, coating defects can easily be identified by potential measurements.

4. CONCLUSIONS

The scepticism and diffidence of corrosion specialists with regard to the application of metallic coatings whenever localized corrosion problems occur, do not always seem justified, despite the fact that it is not always easy to select coatings which are not damaging.

In the case of single-phase aluminium brasses, operating in chloride-contaminated river water (typical of power plants), the SC problems can be reduced by using electroless Ni-P coatings that are anodic with respect to the brass, and thus provide effective cathodic protection. Conversely, galvanic nickel coatings, which are cathodic with respect to the brass, lead to an SC intensification.

In the case of high strength structural steel (type AISI 4137 H), which is used in deep oil and natural gas drilling, the problems of failure (delayed or due to sulfide stress corrosion) can be reduced by ductile nickel coatings

that are cathodic with respect to the steel and which provide a type of effective "anodic protection". Better yet are non-brittle electroless Ni-P coatings that are not only cathodic with respect to the steel, but also more noble than the reversible hydrogen potential and provide the nullification of hydrogen evolution.

It would thus seem that numerous new fields of applications can be found for electroless nickel if, on the one hand, more in-depth knowledge is acquired about corrosion phenomena, and on the other hand, electrochemical-corrosion controls are added to the usual ones now conducted on coatings.

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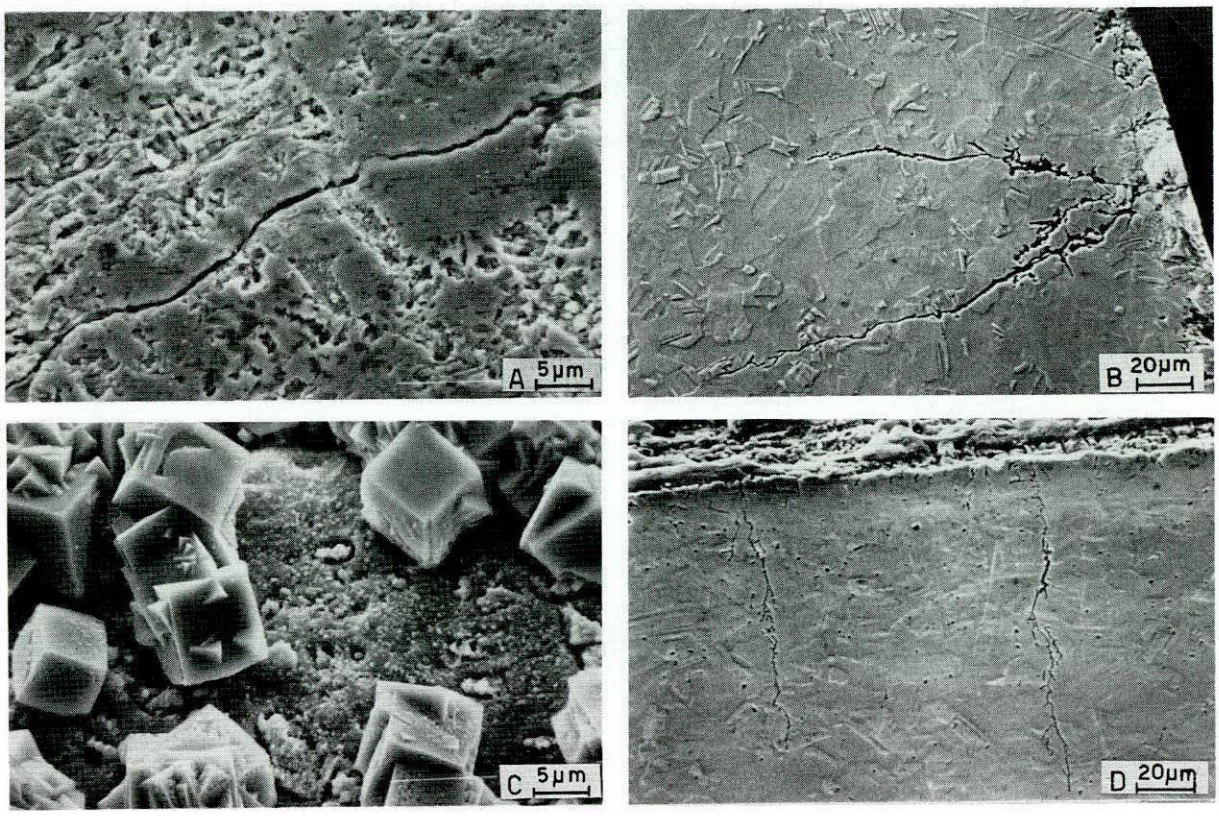

Fig. 1 - Corrosion morphologies of aluminium brass after 144 h SC testing time. As received (A), (B), wet grinding (C), (D) conditions.

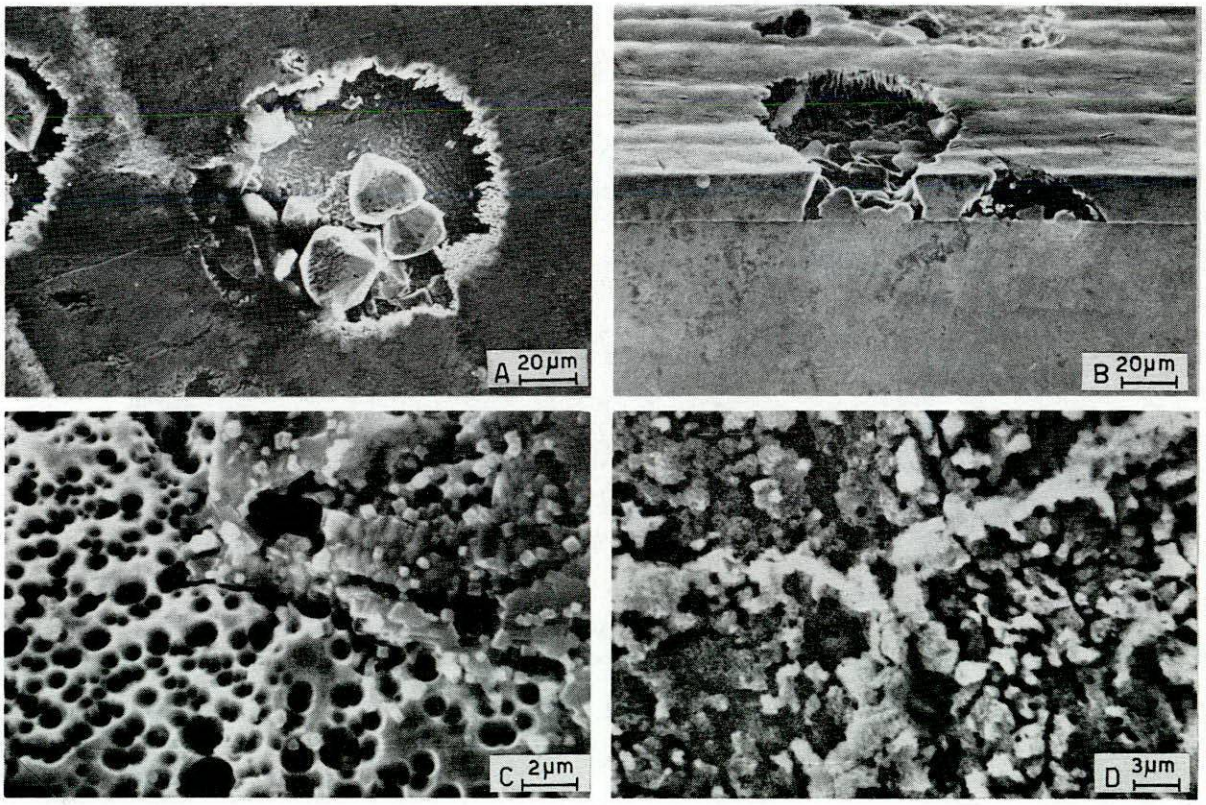

Fig. 2 - Corrosion morphologies of electroless nickel coated aluminium brass after 144 h SC testing time. Bath type 1, 20 µm, (A) (B); Bath type 1, 3 µm, (C); Bath type 2, 3 µm, (D).

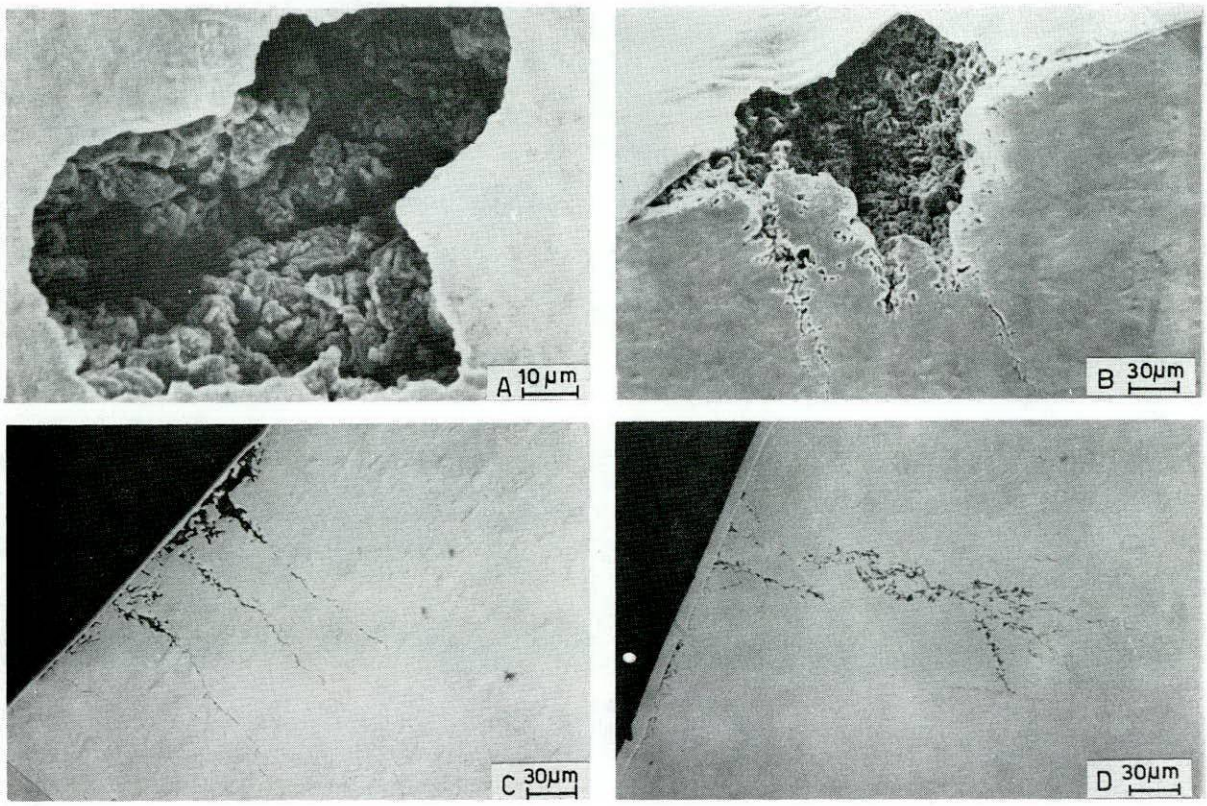

Fig. 3 - Corrosion morphologies of Watts nickel coated aluminium brass after 144 h SC testing time. 4 µm (A), (B), (C); 15 µm, (D).

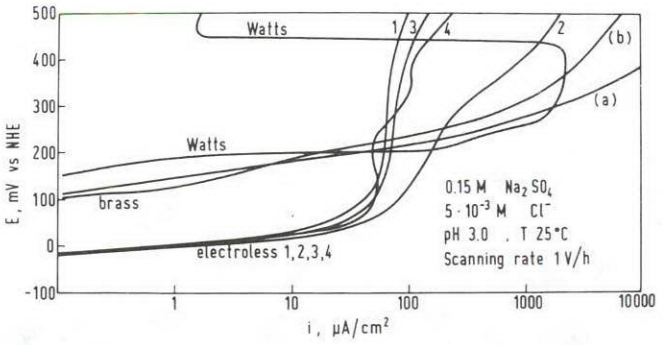

Fig. 4 - Anodic potentiodynamic curves of uncoated and coated aluminium brass in the unstrained condition.

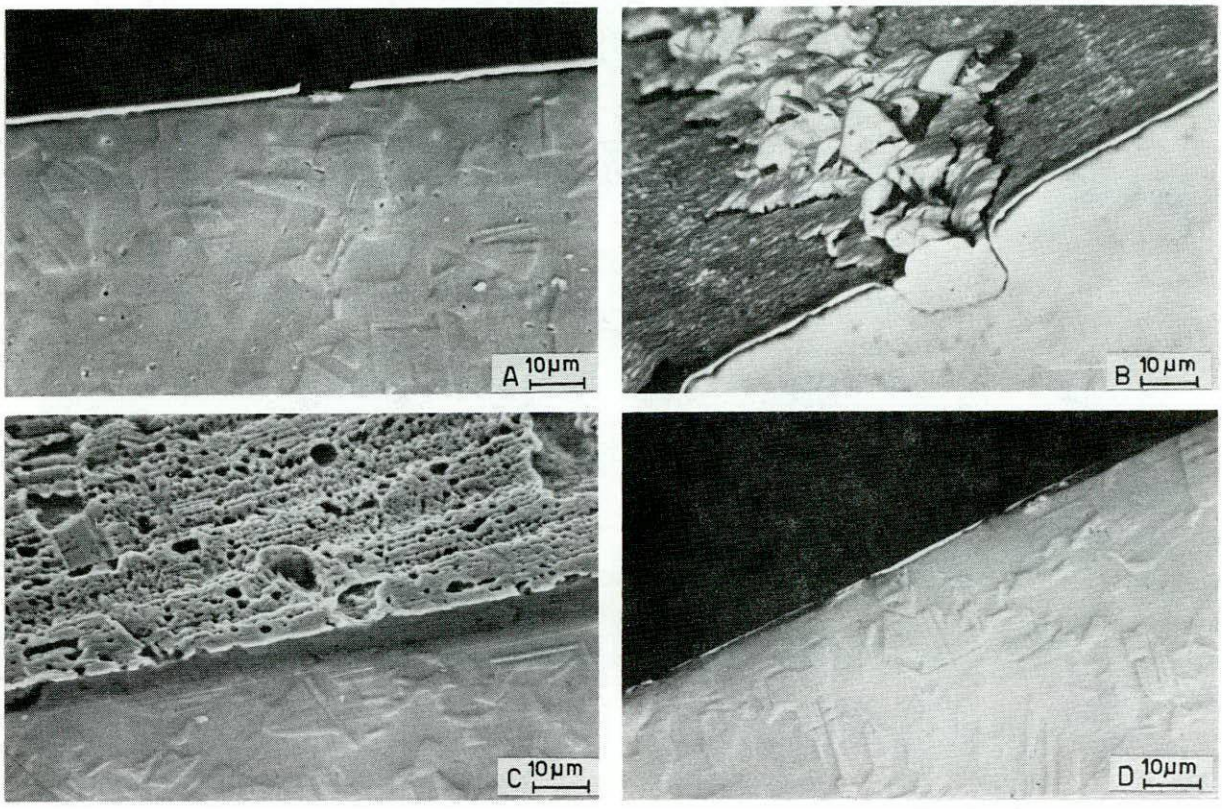

Fig. 5 - Corrosion morphologies of electroless nickel coated aluminium brass (C - specimens bent 10% with respect to the diamter). Bath type 2 (A), and Bath type 4, (B), 144 h SC testing time; Bath type 2, 312 h SC testing time (C) (D).

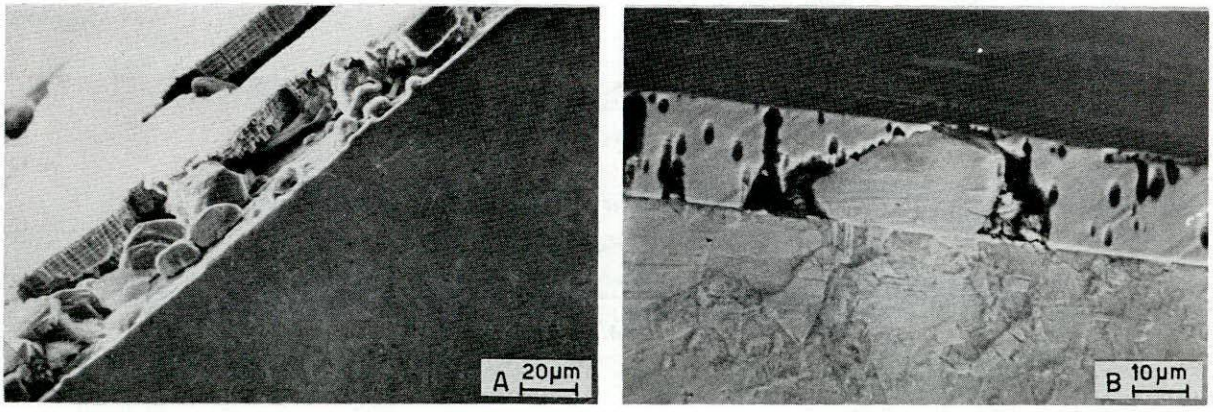

Fig. 6 - Corrosion morphologies of electroless nickel coated aluminium brass. Bath type 1, 20 µm, 312 h SC testing time.

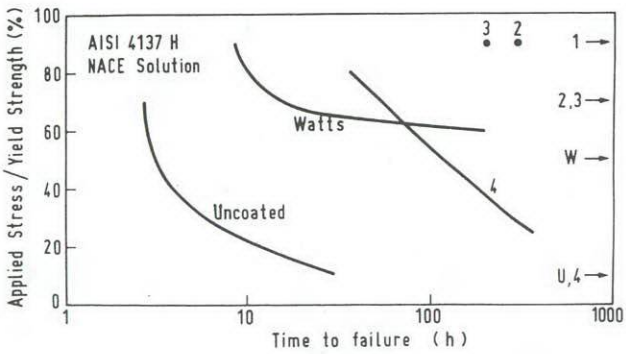

Fig. 7 - Applied stress-failure time curves for uncoated and coated high strength steel.

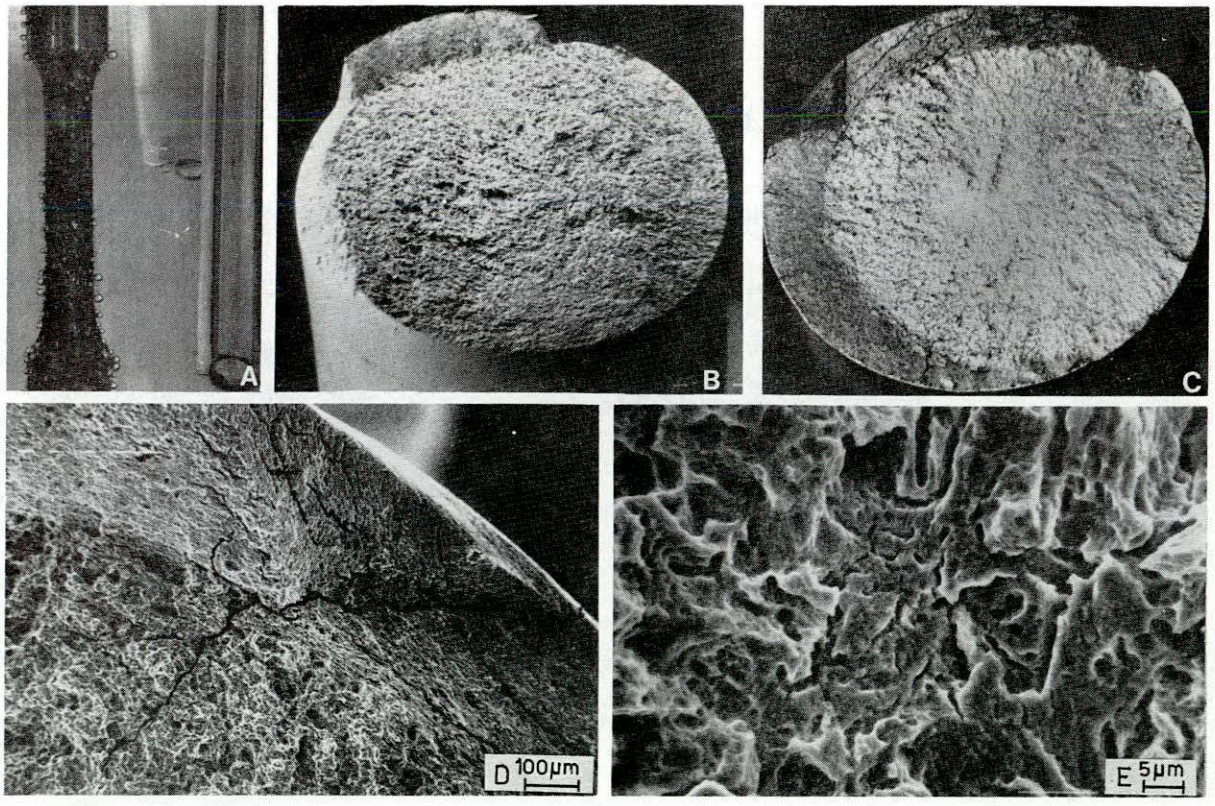

Fig. 8 - Fracture morphologies of high strength steel loaded in NACE solution at: 15% (B), (E); 70% (C), (D), of yield strength.

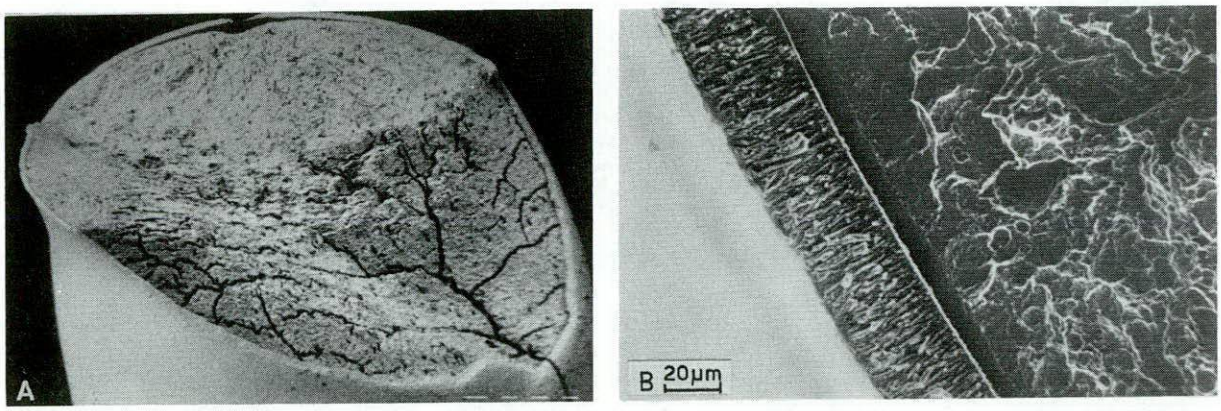

Fig. 9 - Fracture morphologies of Watts nickel coated high strength steel loaded in NACE solution at 90% of yield strength.

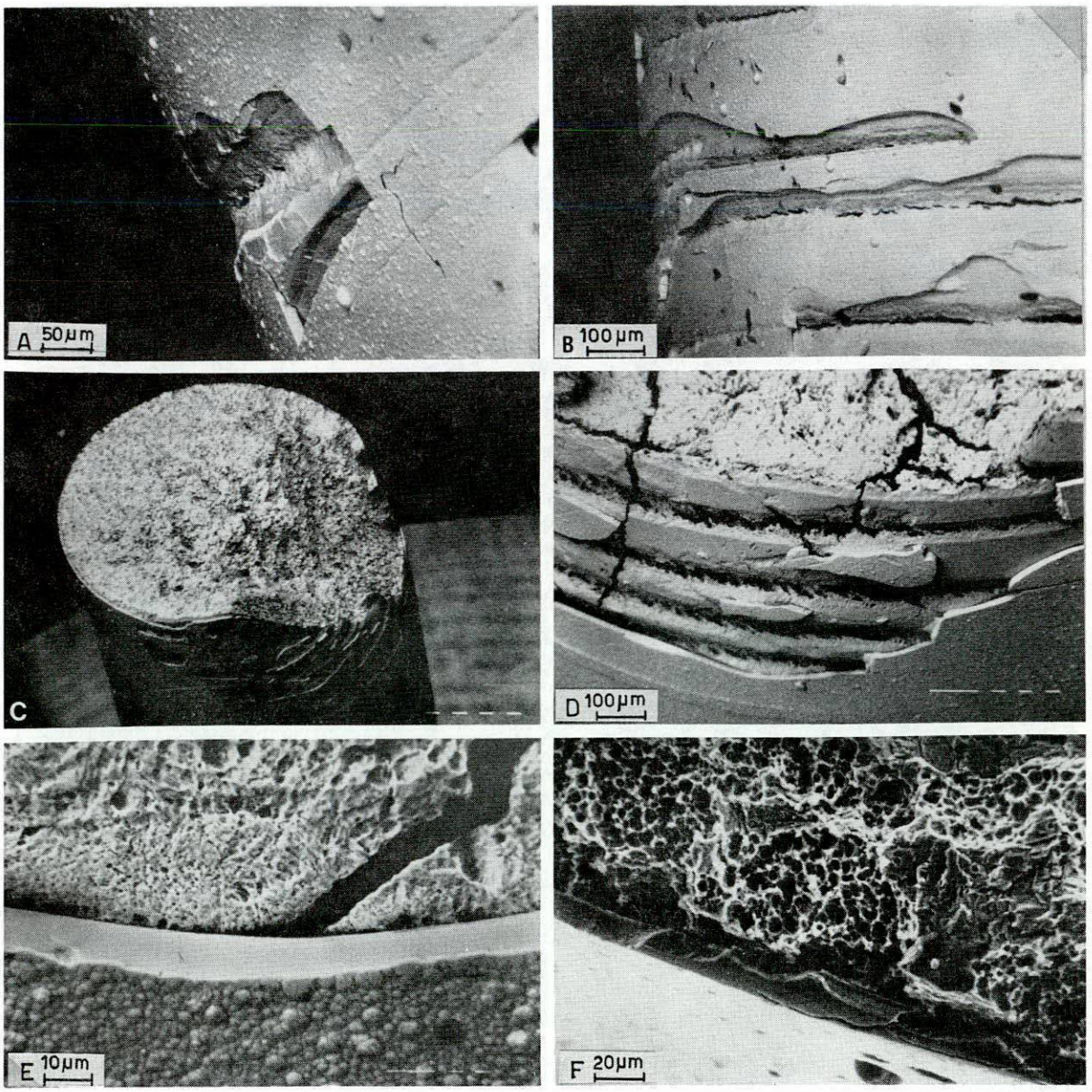

Fig. 10 - Fracture morphologies of high strength steel electroless nickel coated from bath 4 and loaded in NACE solution at : 70%, (A), (B), (D), (E); 50% (C) (F) of yield strength.

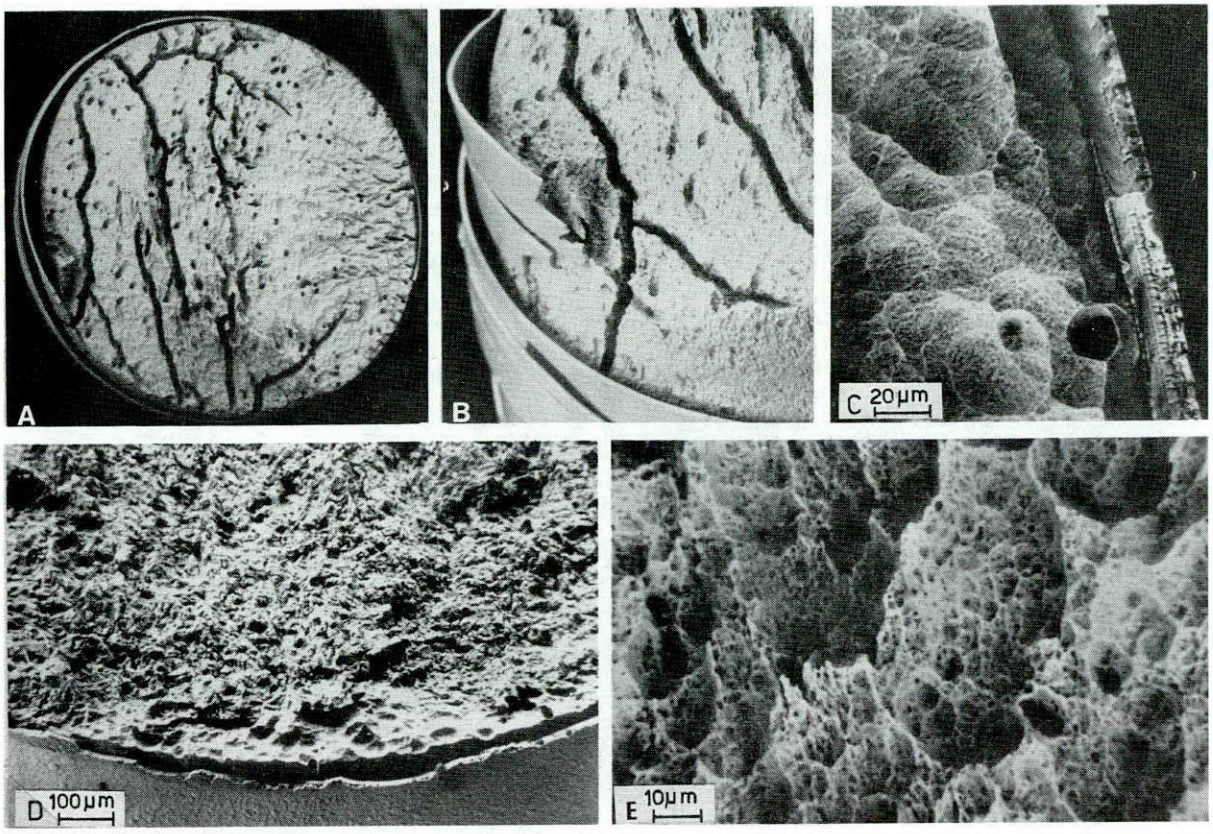

Fig. 11- Fracture morphologies of high strength steel electroless nickel coated from bath 3 and laoded in NACE solutions at 90% of yield strength.

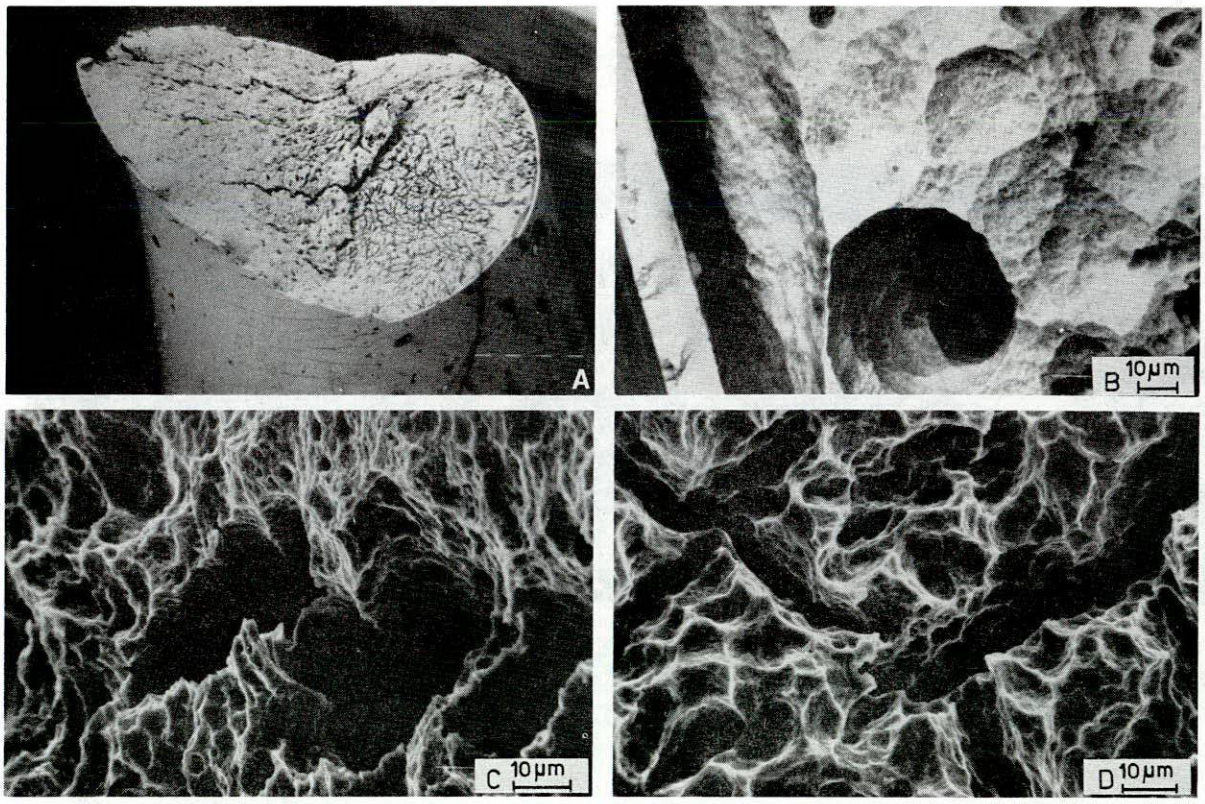

Fig. 12 - Fracture morphologies of high strength steel electroless nickel coated from bath 2 and loaded in NACE solutions at 90% of yield strength.

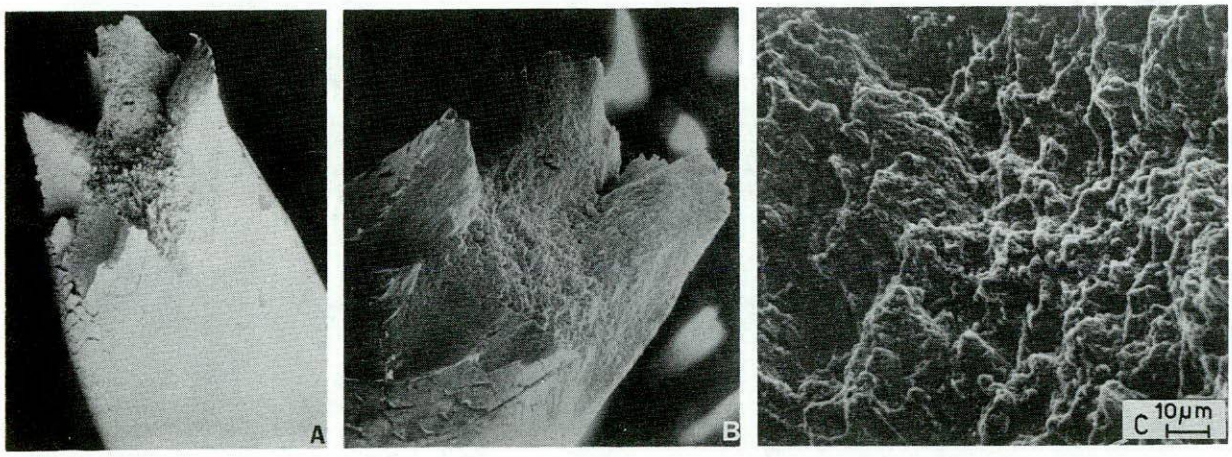

Fig. 13 - Fracture morphologies of high strength steel electroless nickel coated from bath 1, loaded for 1000 h at 90% of yield strength in NACE solution and then tensile tested in air up to ultimate tensile strength.

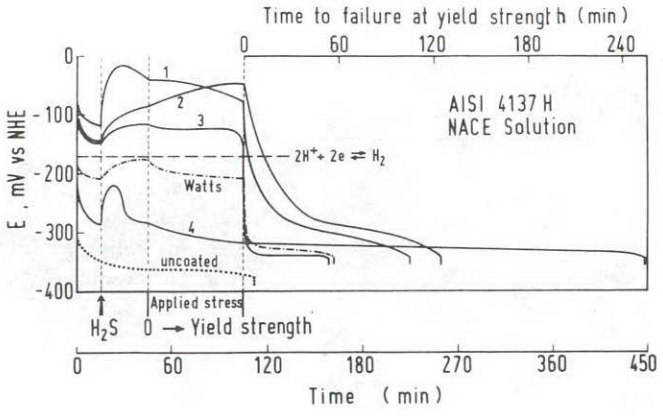

Fig. 14 - Free corrosion potential vs time of uncoated and coated high strength steel.

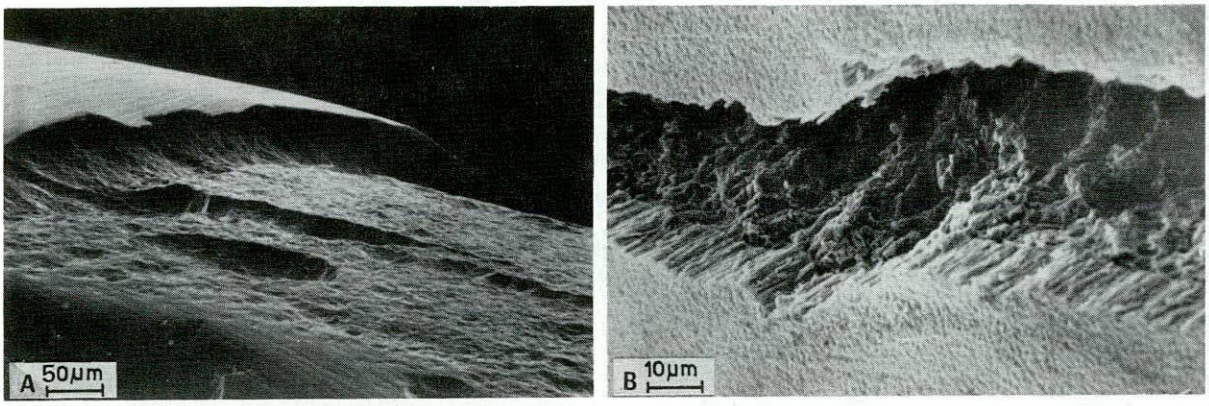

Fig. 15 - Corrosion morphologies of high strength steel Watts nikel coated and loaded at 50% (A) and 100% (B) of yield strength. Mechanical coating removal (A) and crack (B) like defects.

H-6

Electroless Plating
Session H

Diverse Applications for Electroless Tin

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Hatfield, PA

Diverse Applications for Electroless Tin

by Jack Fellman
CuTech, Inc., Hatfield, PA

Introduction

Electroless, electrolytic and immersion deposits of tin and its alloys enjoy one common feature in respect to the electronics industry. Functionality. Tin is plated for what it does, not for what it looks like. The scope of this discussion is to present some "old" and "new" applications for electroless tin plating. All of these applications presently involve the use of tin or tin-lead, the difference being the method of applying the metals. These differences will become apparent with each application.

Applications

- Print/Etch

High reliability single-sided boards are being produced for the telecommunications industry by the print/etch process. Requirements for these boards include: solderability, surface electrical properties (dielectric constant) and appearance. Specific utility of these boards is for cable TV boxes and microwave broadcasting equipment.

Process flow for print/etch boards is shown in Figure I.

a. Single-sided copper-clad laminate with 2-ounce foil is the typical starting material.
b. A positive image is screened on the board and the remainder of the ink developed away, leaving exposed copper to be etched.
c. Undesired copper is etched away with either an alkaline ammonia solution or an acid solution, such as persulfate or hydrogen peroxide in sulfuric acid.
d. The etch resist is stripped leaving the circuit pattern remaining on the board.
e. The circuitry is selectively plated with electroless tin to a thickness capable of being reflowed.
f. Boards are reflowed in a hot oil pot at 255°-260°C (490°-500°F) or in an infrared fusing machine. Both reflow processes require a suitable flux.

Conventional technology for producing this type of board is to apply tin-lead by dipping in a molten solder pot and air-leveling or oil-leveling the solder. Another alternative is to use a negative image and electroplate tin-lead as an etch resist and reflow as the final step.

- Flexible Circuits

Light-weight, portable electronic devices such as calculators and watches use flexible circuits in their assemblies. They are produced with the same electrical sensitivity as rigid boards, but on a lighter laminate.

Process flow for flexible circuits is shown in Figure II, which is basically the same as that shown for rigid print/etch boards.

Applications exist where through-holes are punched and plated, as for double-sided rigid boards, followed by pattern plating copper and electroless tin. The final solderable coating is the same for either product, reflowed electroless tin.

- Boards With Solder Mask Over Bare Copper (SMOBC)

a. Etch Resist

Electroplated tin and tin-lead deposits have been used almost exclusively as etch resists for protecting copper circuitry while copper foil is etched away. The deposits are subsequently reflowed as the final solderable coating. In the past two years, board requirements have specified the use of solder mask as a conformal organic coating to protect the circuitry while the product is in use. With the demand for finer lines and spaces, bridging of the solder between two close lines during assembly and wave-soldering has become a problem, since it creates an electrical short. To avoid this, a demand for "no-flow" boards, SMOBC, has become common in the industry. For this type of product, the etch resist is a temporary coating and must be removed after etching.

Typical applications for SMOBC boards are for commercial uses such as computers.

Process flow for SMOBC boards is shown in Figure III. The bare copper board is produced after stripping the tin etch resist. Solder is applied as the final coating on pads and in holes by selective coating with a hot air leveling machine.

b. Solderable Coating Over Copper

Equipment for hot air leveling of solder is expensive to purchase and maintain. A comparable product can be produced by selectively plating with electroless tin, after solder mask has been applied, and reflowing in either hot oil or an infrared machine. The process flow for this modification is shown in Figure IV. In comparision to Figure III, it differs only with the final two steps of electroless tin plating and reflow.

Electroless Tin Process

Electroless tin plating is referred to as a process since it requires surface preparation and activation prior to plating. The precise steps are shown in Figure V.

a. Micro-etch

A brief immersion of the panels in a micro-etch solution is required to roughen the copper surface for good plating. Typical solutions for this function are ammonium or sodium persulfate in sulfuric acid, or hydrogen peroxide in sulfuric acid.

b. Activate

A proprietary copper activator solution is used to assist in the initiation of electroless tin plating. It is formulated around a strong acid and contains organic materials that trigger the electroless plating reaction.

c. Electroless Tin Bath

A proprietary plating solution is used to produce heavy, functional deposits of tin. The bath is mildly acidic, but non-halogenated, and contains tin salts and other components necessary to plate tin. It is operated at 49°C (120°F) with solution agitation and filtration.

Although the bath is electroless in its plating mechanism, it does not suffer from the instability typical of electroless copper and nickel baths. It may be operated indefinitely with proper maintenance and replenishment by a powder product, which allows for a very low cost of operation.

FIGURE I

PROCESS FLOW

Print/Etch Boards With Reflowed Electroless Tin



FIGURE II

PROCESS FLOW

Flexible Circuits With Reflowed Electroless Tin

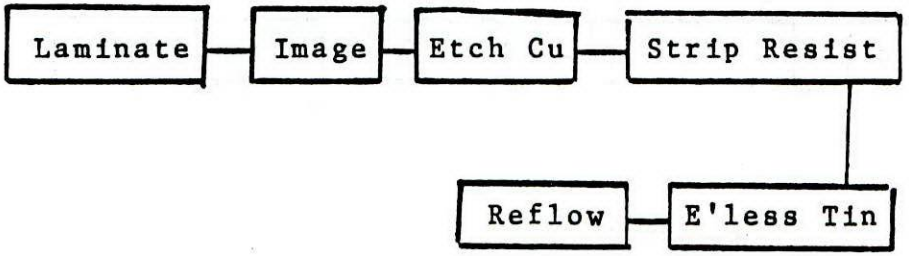


FIGURE III

PROCESS FLOW

SMOBC Boards With Electroless Tin As Etch Resist

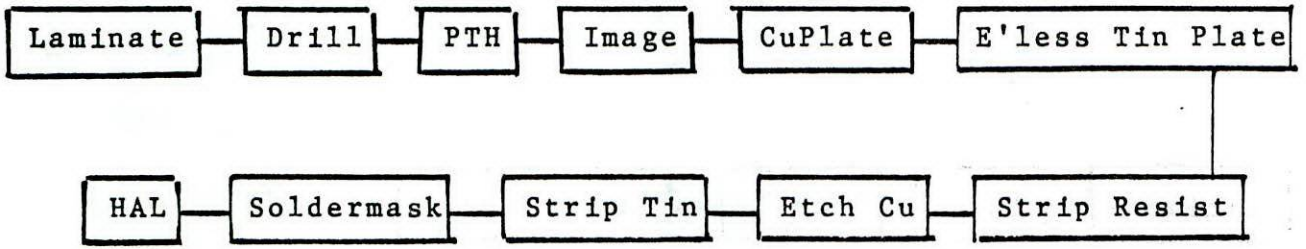


FIGURE IV

PROCESS FLOW

SMOBC Boards With Electroless Tin As Etch Resist
And
Final Solderable Coating

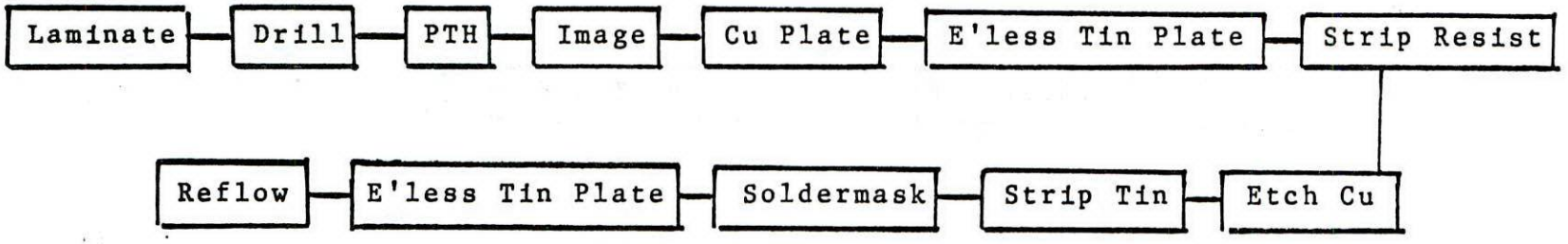
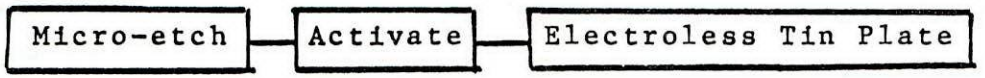


FIGURE V

PROCESS FLOW

ELECTROLESS TIN PROCESS



I-1

General Interest Session I

The Role of Boric Acid in Dilute Chromic Acid Plating Baths

James P. Hoare
General Motors Corp., Research Labs.
Warren, MI

ON THE ROLE OF BORIC ACID IN DILUTE CHROMIC ACID PLATING BATHS

by

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ABSTRACT

It has been found that deposits of metallic chromium may be plated on Pt cathodes from chromic acid with boric acid additions. From steady-state polarization studies of Pt microelectrodes in boric acid-catalyzed chromic acid, it was concluded that boric acid in aqueous solution can imitate the behavior of HSO_4^- in sulfate-catalyzed chromic acid solution. Consequently, the $B(OH)_4^-$ ion can complex with the polychromate ions through hydrogen bonding to act both as a blocking agent and as a catalyst. Since the number of dischargeable complexes with $B(OH)_4^-$ ions is very low (pK = 9), the efficiency of boric acid-catalyzed baths are much less than sulfate-catalyzed baths.

INTRODUCTION

It has been reported (1-3) that the optimum concentration for the deposition of Cr from dilute baths ranged between 25-50 g CrO_3/L catalyzed by H_2SO_4 with a CrO_3/HSO_4^- ratio of 100/1. However, Konishi and Tadagoshi (1) reported that the brightness range became narrower as the concentration of CrO_3 was reduced from the normal concentration of 250 g/L to the dilute, 50 g/L. LaBoda found (4) for high speed Cr plating that the brightness range could be increased in the dilute plating bath by adding boric acid to the bath. In the concentrated CrO_3 solutions, boric acid additions seemed to have little or no effect.

In nickel plating baths, boric acid is added as a buffer (5); but since solutions of strong acids such as chromic acid are inherently well buffered, the role of boric acid in chromium plating must be quite different. To shed light on the role of boric acid in dilute chromium plating baths, a basic study of this system was carried out using steady-state galvanostatic and potentiostatic polarization techniques.

EXPERIMENTAL

Platinum was chosen as the basis metal not only because Pt is well behaved in chromic acid solutions, but also because its electrochemical behavior in general is understood (6). The test electrodes were in the form of small beads (~0.04 cm^2 in area) melted at the end of Pt (99.99% pure) wires in an oxygen torch. After sealing the beads to the Teflon spaghetti covering the Pt lead wires, three test electrodes were sealed in a Teflon cell filled with the solution of interest. The details of the preparation of the electrode and cell, and the assembly of the system have been presented in earlier reports (7,8).

Runs were made in 0.25 M chromic acid to which either sulfuric or boric acid were added. To minimize mass transfer effects the solutions were stirred with purified N_2-gas bubbling at a rate of about 200 cm^3/min. Once the rest potential of Pt in the N_2-saturated chromic acid became virtually steady, the polarization curves were obtained on the Pt cathode as described earlier (7), with a saturated calomel electrode (SCE) as a reference electrode. All measurements were obtained at ambient temperature (23 ± 1°C).

At the end of the run, the cell was opened and the test electrode removed, washed in distilled water, and air dried. The coating on the Pt bead was analyzed with Auger electron spectroscopy (AES), and with argon sputtering, a depth profile of the concentration of the elements of interest was made in the surface deposit.

RESULTS AND DISCUSSION

In Fig. 1, the steady-state galvanostatic polarization curve is plotted for a Pt cathode in uncatalyzed 0.25 M chromic acid (circles). After the run, examination of the bead showed a darkening of the surface and the AES indicated that large amounts of oxygen (about 40 atomic percent, a/o) were associated with the Cr to a depth of 50 Å. Such a deposit may be considered as a smut of chromic oxides.

The plot for a Pt cathode in 0.25 M chromic acid catalyzed by 0.0025 M H_2SO_4 is indicated by the squares in Fig. 1. In this case, the bead was bright and AES analysis indicated that a thin layer of metallic Cr was deposited on the Pt surface (oxygen was about 4 to 5 a/o).

Finally, the curve for 0.25 M chromic acid catalyzed by 0.08 M H_3BO_3 is denoted by the triangles in Fig. 1. Although the bead was bright, the AES analysis detected a thin metallic layer of chromium with a high oxygen content (20-30 a/o).

The open circuit potential is a local cell potential determined by the oxidation of Pt

$$Pt + H_2O \rightarrow Pt\text{-}O + 2H^+ + 2e \qquad (1)$$

at anodic sites and the reduction of Cr VI ($HCr_3O_{10}^-$) (3,4) to Cr III (Cr^{+3} ions)

$$HCr_3O_{10}^- + 12H^+ + 6e \rightarrow 2Cr^{+3} + HCrO_4^- + 6H_2O \qquad (2)$$

at cathodic sites on the equipotential Pt surface (9). The overall local cell reaction is as follows.

$$3Pt + HCr_3O_{10}^- + 6H^+ \rightarrow 3Pt\text{-}O + 2Cr^{+3} + HCrO_4^- + 3H_2O \qquad (3)$$

The cathodic polarization of this local cell (10) produces the first linear section of the curves in Fig. 1 at low current densities.

At higher current densities, the potential falls below the reversible potential of the anodic process, Eq. 1 (~0.8 V) and the local cell ceases to exist. In this region the current is consumed in the reduction of Cr VI to Cr III, Eq. 2, and generates the second linear segment of the curves in Fig. 1. With the application of still higher current densities, Eq. 2 can no longer support the demanded current, and the potential falls at a limiting current to values where some other cathodic process can take place. This process, of course, is the reduction of H^+ ions with the evolution of H_2 gas in the third linear region of Fig. 1. The slope of this curve is about 0.03 which is consistent with the reported value (11) of the Tafel slope for hydrogen overvoltage on Pt. At the highest current densities, there follows a region where metallic Cr may be deposited if the conditions are proper.

Plotted in Fig. 2 are the steady-state potentiostatic polarization curves obtained on Pt in the same solutions studied in Fig. 1. As in Fig. 1, these curves consist of three linear regions separated by limiting current areas with the same interpretation. At the high current densities, however, one observes that the catalyzed curves double back on themselves which may be described as a negative resistance region. This behavior occurs because area changes take place when a deposit is laid down on the electrode surface. Under these conditions, the true area is greater than the apparent area, and as a result, the true current density is less than the apparent.

In Fig. 2, the uncatalyzed chromic acid curve does not exhibit a negative resistance region at high current densities in agreement with the observation from AES analysis that a metallic Cr deposit did not plate out on the Pt surface. As expected the sulfate-catalyzed curve does have a negative resistance region at high current densities betraying the presence of the metallic Cr layer detected by AES. Somewhat more surprising is the presence of a metallic Cr layer found by AES on Pt cathodized in boric acid-catalyzed chromic acid and shown by the negative resistance region in Fig. 2 (triangles).

Recently, Wu (12) observed that thin deposits of bright Cr could be deposited from CrO_3 solutions catalyzed by boric acid. He used high boric acid concentrations, 30 g/L or 0.48 M. In every case, the Cr layer was covered with a brown stain or film which could be removed by treatment with dilute acids. Wallace (13) also observed a similar behavior during the conventional plating of Cr from dilute sulfate-catalyzed CrO_3 (50 g/L) solutions.

To check on the ability of boric acid to catalyze the reduction of chromic acid to metallic Cr, steel panels (6.5 x 9.5 cm) were degreased, cleaned and plated in a Hull cell filled with a boric acid-catalyzed chromic acid solution (50 g/L CrO_3; 5 g/L H_3BO_3) at 10 A for 5 min at 45°C. In each case a brown film was obtained on the panel. A 1 cm wide strip was cut from each panel at the high current density end. The brown film formed on these panels was removed with cheesecloth and pumice since acids did not seem to remove the film as reported by Wu (12). Possibly the difference may have been that we dried our panels before stripping whereas he stripped the film while it was still hydrated. Then 1 cm square samples with and without the brown stain removed were analyzed by AES and XPS (x-ray photoelectron spectroscopy).

The brown film could not be examined with AES because of the extreme electronic charge built up on the insulating film. Consequently, only the film-free samples were analyzed with AES. On the samples, a film of Cr metal was detected under the brown film. Using positive ion sputtering and sputter rate of 1000 Å/min (calibrated with an SiO_2 film), the thickness of the Cr deposit was determined as 170 nm with an oxygen content of 18 a/o.

From XPS analysis, the brown film could be investigated. It was determined from binding energy measurements that the Cr in the film is in the Cr III state. Because of the very high oxygen content of the film (63 a/o), it is reasonable to assume that the brown stain is a layer of Cr_2O_3. Boron at a concentration of about 1 a/o was detected in the film.

According to the model of Cr deposition from chromic acid set forth in the literature (7,8), the Cr in a plating solution exists predominantly as the trichromate ion, $HCr_3O_{10}^-$. The added catalyzing agent must act not only as a catalyst but also as a blocking agent by forming complexes through hydrogen bonding with the trichromate. By consecutive electron transfer steps and reaction with H^+ ions, the proper complex can be reduced to $Cr(OH)_2^-$ which is in equilibrium with $Cr{=}O + H_2O$. The CrO can complex with a HSO_4^-

ion to form a chromous-oxy-bisulfate complex which can be specifically adsorbed on the cathode surface. From this complex, metallic Cr can be deposited and HSO_4^- ion split off (HSO_4^- acts as a true catalyst).

If boric acid behaves as a catalytic agent for the reduction of chromic acid to metallic Cr, it must imitate the behavior of sulfuric acid (HSO_4^- ion). It is known (14) that boric acid in water can hydrolyze to a tetrahydroxide ion with a pK of 9.00.

$$H_3BO_3 + H_2O \rightleftarrows B(OH)_4^- + H^+ \qquad (4)$$

The $B(OH)_4^-$ may then hydrogen bond with the double bonded oxygens on the trichromate ion to form a complex with one end blocked so that the opposite end may be reduced as described before (7,8). In the role of a catalyst, $B(OH)_4^-$ ions may hydrogen bond with the CrO formed during the reduction process to make the chromous-oxy-borontetrahydroxide complex from which metallic Cr may be deposited. Since the concentration of the tetrahydroxide ions should be small (large pK and strong acid environment), the number of proper complexes (8) for discharge would be much less than with HSO_4^- ions. From this viewpoint, one would expect that the rate of Cr deposition from the boric acid-catalyzed solution would be much less than for the bisulfate-catalyzed case. This expectation, of course, is realized in the very thin deposits obtained with H_3BO_3 as a catalyst.

It was observed (2) that a yellow adherent film was formed on steel tube cathodes in sulfate-catalyzed, dilute, chromic acid solution at very high rates for bright Cr deposition. This observation was accounted for by the codeposition of hydrated chromium oxide species from the bisulfate complexes. Since the rate of Cr deposition from H_3BO_3-catalyzed chromic acid is so low, brown films of hydrated chromium oxide are deposited even at the lowest current densities for which metallic Cr may be plated. As long as these stains remain hydrated, they may be removed with standing in the chromic acid. Once such films are dehydrated for analysis with AES or XPS, the brown or yellow film is converted to an insulating layer of Cr_2O_3 which is resistant to attack by strong acids. Some evidence for the concept of the codeposition of the chromous-oxy-borontetrahydroxide complex along with its discharge to metallic Cr and $B(OH)_4^-$ ion (true catalytic action) is the detection of boron in the brown film with XPS.

It is concluded from these studies, that boric acid added to dilute chromic acid solutions acts as a blocking agent to form the proper complex through hydrogen bonding for reduction of Cr VI to chromous hydroxide, and as a catalyst by bonding to the chromous hydroxide to make the chromous-oxy-borontetrahydroxide complex from which metallic Cr is deposited. Since the pK for the $B(OH)_4^-$ ion reaction is large, the concentration of proper complexes with trichromate ion is expected to be small in such an acid environment. Consequently, the rate of deposition of Cr from an H_3BO_3-catalyzed chromic acid bath is low and the deposit is accompanied by a brownish stain or film of hydrated chromium oxides.

ACKNOWLEDGEMENTS

The author is indebted to J. D. Thomas, assistant department head, M. A. LaBoda and O. J. Klingenmaier of the Electrochemistry Department of GMR for many stimulating discussions and to D. Radovic for carrying out the Hull cell measurements.

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FIGURE CAPTIONS

Fig. 1 Steady-state galvanostatic polarization curves obtained on a Pt cathode in N_2-stirred uncatalyzed chromic acid 0.25 M CrO_3 (circles), chromic acid catalyzed by 0.0025 M H_2SO_4 (squares) and chromic acid catalyzed by 0.08 M boric acid (triangles): open symbols denote increasing cd, and filled, decreasing. A line with a slope of 0.030 V/decade is drawn to show data are consistent with H_2 overvoltage on a Pt cathode.

Fig. 2 Steady-state potentiostatic polarization curves obtained on a Pt cathode in the same solutions as those in Fig. 1 with identical notation.

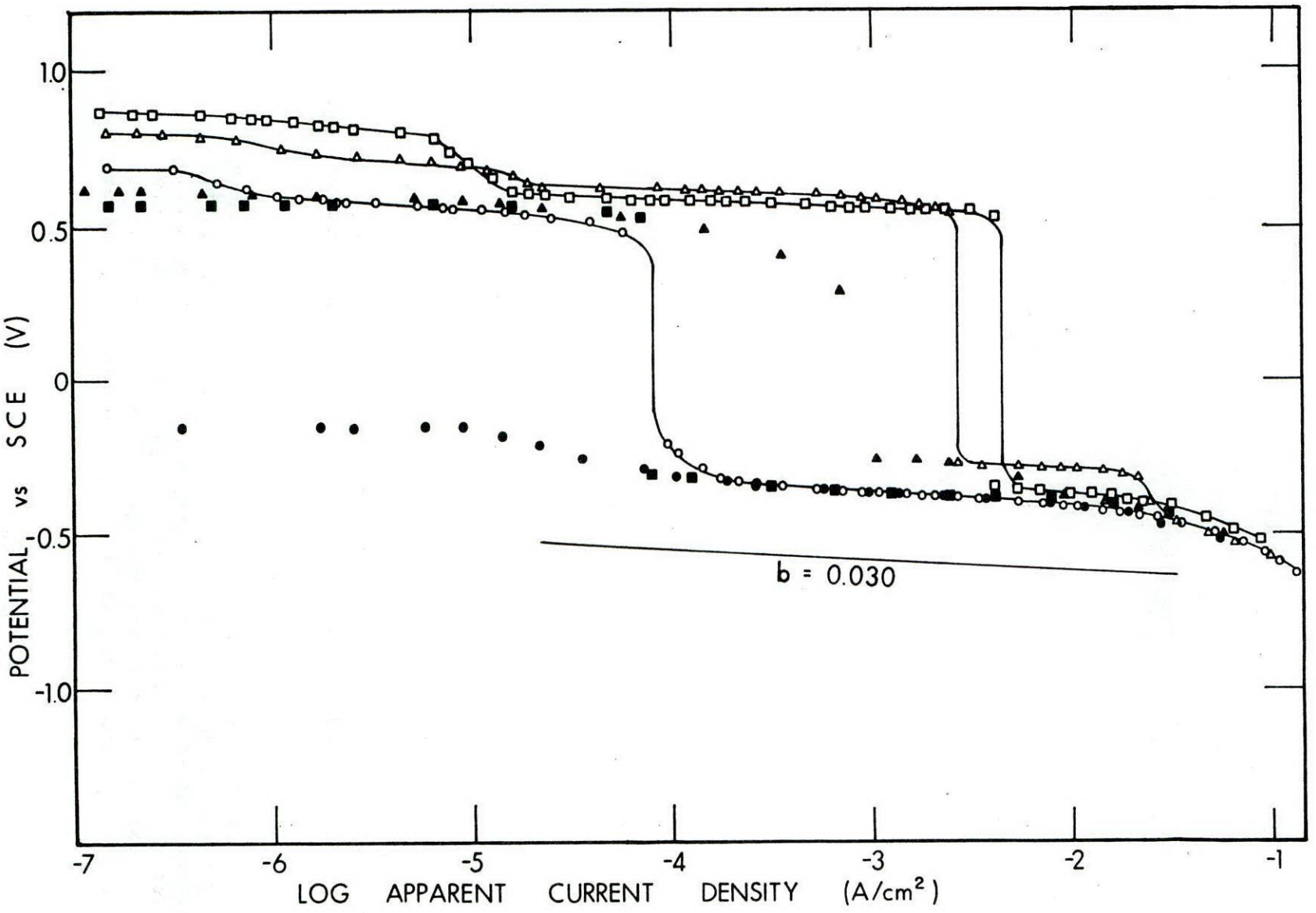
1.0
0.5
0
-0.5
-1.0
POTENTIAL vs SCE (V)
b = 0.030
-7
-6
-5
-4
-3
-2
-1
LOG APPARENT CURRENT DENSITY (A/cm²)

FIGURE 1

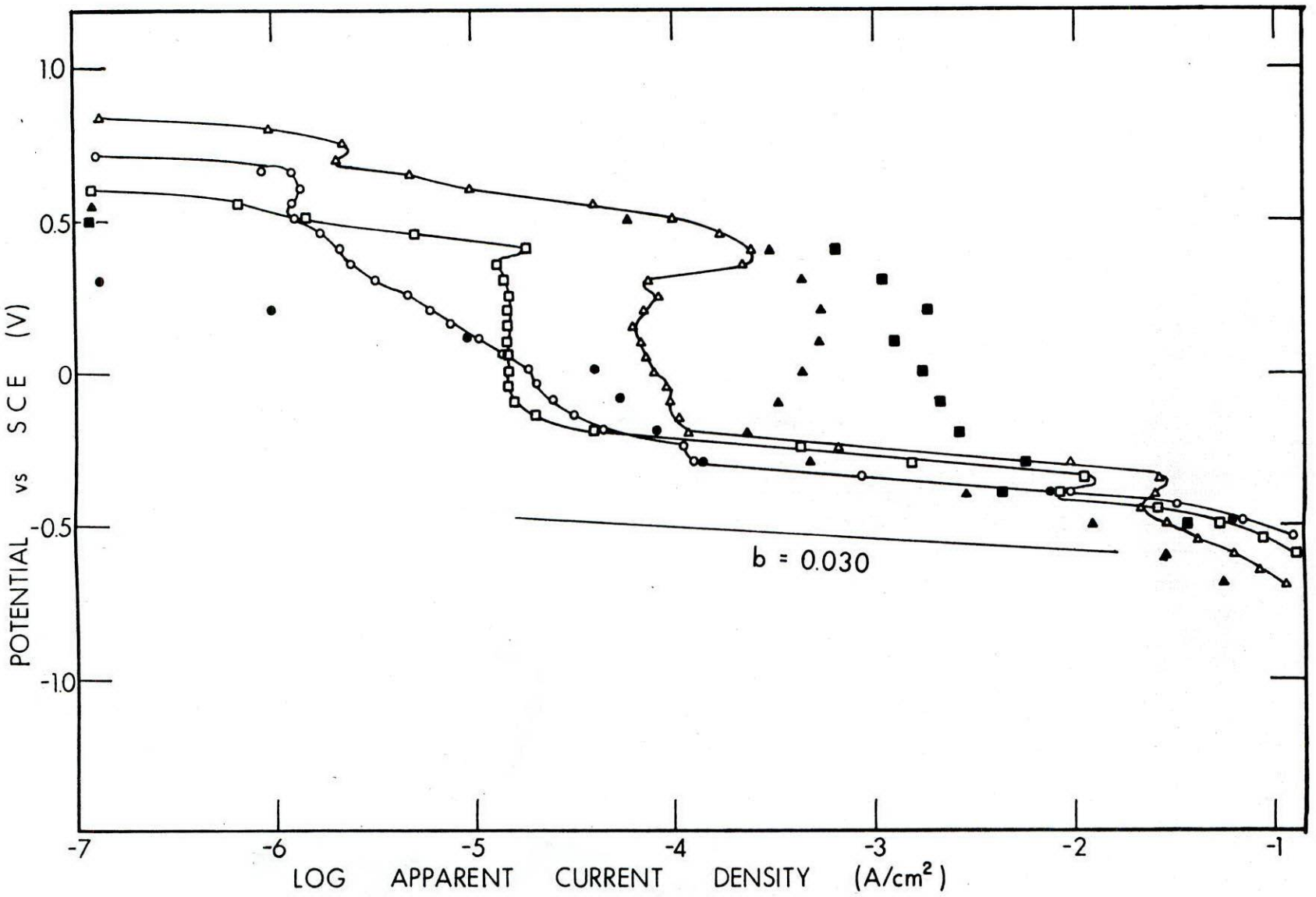
1.0
0.5
0
-0.5
-1.0
POTENTIAL vs SCE (V)
b = 0.030
-7
-6
-5
-4
-3
-2
-1
LOG APPARENT CURRENT DENSITY (A/cm²)

FIGURE 2

I-2

General Interest Session I

Cleaning, Descaling, Passivation, and Inspection of Stainless Steels

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CLEANING, DESCALING, PASSIVATION, AND INSPECTION OF STAINLESS STEELS

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Throughout the past decades, there has evolved numerous concepts and methods for achieving a passivated surface on the various stainless steel alloys. Depending on the industry served, the concepts have included: "stainless is stainless and doesn't require further processing", to "in order to achieve a uniform and corrosion resistant passivation, well-adhered-to processes and process controls are a basic requirement".

Who is right? Both concepts may be, depending on the industry served, alloy(s) assumed, and the hardware application. A sheet metal fabricator handling Condition A 300 Series alloys for kitchen exhaust hoods does have different passivation processing needs than a shop supplying finished 17-4PH castings for a Navy aircraft application. Suppliers of eating utensils and also medical supplies have yet different criteria that is not frequently addressed by industrial applications. With the diversity of needs and specifications (or lack of) to work to, just how does the plating shop effectively and consistently service the purchase orders for "passivation" and then follow up with a certification vouching for its proper completion? It is not unusual for Customer A to inspect parts for passivation uniformity, and Customer B to accept lots based solely on the certification paper.

With the continuing rise in operating costs and increasing needs/demands for yet higher quality hardware, the Flight Structures Division (FSD) of Western Gear Corporation, Jamestown, North Dakota, re-addressed our approach to traditional passivation processing and the subsequent inspection. Both in-house processing and outside purchased processing have since been affected. Three initial assumptions were made approximately four years ago. The first was to recognize the acknowledged replacement for Federal Specification QQ-P-35[1] and adapt the ASTM A 380[2] guidelines for cleaning, descaling, and passivation.

Secondly, a concerted effort was to be made to tailor the processing to our customers' needs in the most cost effective way to achieve consistently acceptable hardware, by inspection. The third goal was to participate with the ASTM committee work after accumulating experience in exercising the specification.

The remainder of this paper addresses common subtopics of passivation, presented in a question/answer format. They are questions frequently asked by our own people, vendors, and customer representatives. Being that in-depth discussions on given items may be appropriate to a group of readers, a list of references has been included at the end of this paper.

1. QQ-P-35 "Passivation Treatments for Corrosion Resisting Steel".
2. ASTM A 380 "Cleaning and Descaling Stainless Steel Parts, Equipment, and Systems".

1. What is meant by passivation/passivity?

   Passivity is a complex concept generally addressing oxide film theory and how it relates to given electrochemical conditions. The 10A to 50A invisible passive film allows the stainless steel alloys to assume a level of inertness to oxidizing environments. Stability of these films depends on their uniformity, metal surface pecularities, such as mechanically stressed area slip bands, carbide precipitates, and inclusions. Externally imposed variables would include exposure to a reducing condition, i.e., chlorides which increase surface activity and ultimately destroy the protective oxide film.

2. In general terms, how is the state of passivation attained?

   Passivation of a metal surface requires that the entire bare metal surface be contacted by an oxidizing medium. Should part of the surface be covered with an oxide or dirt, a passive film is not generated in those spots, and corrosion activity is accelerated, due to the active/passive gradients created.

3. What is generally meant by "passivation treatment"?

   This treatment consists of immersing cleaned and descaled stainless steel parts in a solution of nitric acid and dichromate salts, dissolving surface iron (contaminate and/or integral) and leaving an exposed and oxidized chromium rich surface.

   Descriptive words sometimes become too numerous, and then they still do not really cover the practicality of the processing. The key words in the description are "cleaned" and "descaled".

4. What is meant by cleaning?

   Cleaning frequently references two distinct stages of preparation. Precleaning includes the removal of grease, oils, paint, soil, grit, or other gross contamination that needs to be done prior to descaling or fabrication of weldments. Precleaning is accomplished by vapor degreasing, scrubbing with abrasive cleaners, solvent wipe down, high pressure stream, water jets, etc. Descaling follows the precleaning, and then comes final cleaning. Final cleaning is done immediately prior to immersing the hardware in the passivation solution to assure that all exposed metal surfaces are free of oils or other handling contaminants that inadvertently were collected after descaling. Vapor degreasing and alkaline cleaning are most frequently used for this operation. Electrolytic alkaline cleaning or acid electrocleaning (controlled electropolishing) can also be effectively used.

5. What is meant by descaling, and is it really necessary?

   Removal of all thermal oxides is needed, whether it be from heat treating, forging, or casting. Manhour allowances in many facilities for

"passivation processing" frequently overlooks the more labor intensive descaling procedures which may include one or more of the following:

- Mechanical Descaling - Sandblasting is the most common. Use of a 150 grit alumina produces a fairly uniform surface suitable for subsequent passivation, and it also adequately prepares surfaces that will ultimately be painted or coated with a dry film lubricant. Topography of a sandblasted surface is less desirable than a smooth surface because of its tendency to retain foreign residues and form micro bubbles that slow down the wetting action during passivation.

- Electrocleaning (alkaline) - Use of a reversible alkaline cleaner is very effective in removing heat treating scale. Unlike the sandblasting, there is no increased topography realized. Cyanide and non-cyanide containing baths are commercially available, as are the rectifiers having automatically timed reversing cycles.

- Electrocleaning (acid) - This could also be referred to as controlled electropolishing. Although not as effective for scale removal as the reversing alkaline bath, it does remove light scale (oxide discoloration), dissolves iron, and oxidizes the chromium. Almost sounds like passivation, doesn't it? It is a passivation procedure that takes approximately a 20 second cycle. There are additional controls required on the bath in order to assure that close tolerance dimensions are maintained. A metal removal rate of less than .00015" for a 20 second cycle at the Western Gear Corporation facility has proven to be acceptable for just about all of the machined hardware. Where tolerances are less than $\pm$ .0005", the electrocleaning is either not used, or the critical dimension may be masked. Also, electrocleaning should not be used on hardware requiring a coat of solid film lube.

  Electrocleaning is extended into electropolishing on many programs in order to obtain additional corrosion protection, visual effects, and/or surface finish requirements. In these cases, the metal removed may approach .001" per surface and, therefore, must be preplanned.

  Stainless steel investment castings are particularly well suited for electropolishing prior to machining. Refer to question 8.

- Acid Pickling - Acid pickling removes metal, but unlike electropolishing which liberates oxygen on the parts, the acid cleaning baths liberate hydrogen. Thus, a subsequent and timely post-bake is necessary for the pH, ferritic, and martensitic alloy grades. In the case of castings, the metallurgical

variables within the castings themselves will favor non-uniform metal removed rates. Although the acid etch method is effective and has been used cautiously for many years, we recommend its usage in the aircraft hardware industry to be limited to non-structural hardware.

6. Should passivation be accomplished with a given procedure?

Yes, as long as it is documented and produces a demonstrated uniform film consistently. The procedure itself will vary from company to company, but the determination of acceptance is measureable by inspection criteria.

For all prime contractors on government programs a "Corrosion Prevention and Control Plan" is a contractually required document to be completed before hardware delivery. The submitted plan is distributed among the affected hardware users for reviews and comments which ultimately must be responded to at a design review prior to hardware delivery. With product liability being a reality for all manufacturers, pursuing a well controlled processing capability is of interest.

7. What is realistic inspection criteria for uniformity of passivation?

With the exception of the 400 series alloys, the most realistic and cost effective procedure is to 100% check using a coppersulfate solution per ASTM A 380. The 100% check is completed by processing personnel. (A subsequent QC inspection is accomplished on a sample basis.) A bath is set up for total immersion of the parts following passivation rinse. This approach has some very positive features, as listed.

- It provides the processing personnel with continual guidance as to the effectiveness of the overall cleaning, descaling, and passivation process; and when copper deposits are realized, there is a positive and timely indication of a problem whether it is traceable to the baths, procedures, or material.

- When copper sulfate reacts with iron, an exchange reaction occurs on the steel surface during which the surface iron is displaced, allowing the copper to deposit. Thus, for a failed lot, the copper sulfate bath has inadvertently become an asset to re-passivation because of the prior reaction, and chances are very good that re-running the parts will result in a favorable inspection.

Other inspection criteria has been written into various documents, as listed.

- Sample Panel - A 300 series alloy test panel is referenced to be run with loads being passivated and acceptance based on humidity test of that panel. Obvious problems using this test procedure arise since the panel simply does not represent machined hardware, particularly structural pH series alloys, forgings, castings, or machined parts.

- Humidity Test - These tests do not provide timely results, and results are generally interpretive.

- Certification - I have found that some companies accept passivation processing based solely on a certification paper stating that a given procedure was completed. This is a cost effective alternative but not too reasonable for processing structural hardware carrying unwritten liability warranties, and contract agreements such as "Corrosion Prevention and Control Plans."

8. Are there apparent degrees of passivation that are peculiar to different alloys or products?

The wrought austenitic series is by far the most readily passivated. In fact, in many cases, the oxidizing that occurs in a normal atmosphere is sufficient to provide passivity. As chromium content drops or carbon increases to tie up the available chromium, the effective passivation is reduced, and the alloy is less corrosion resistant.

As can be concluded, the 400 series alloys really are not classical stainless alloy by the same criteria as a 300 series alloy. Application of 400 alloy series hardware is best made when all surfaces are highly polished and in a lubricated environment, such as bearings. In some applications other than household cutlery, the items may be cadmium plated.

Investment castings deserve special recognition, particularly the structural pH alloy type. Some processed lots will resist acceptance of passivation much more than others. This can be traceable to a carbon pickup which results from reactions between the molten metal and mold, or it can be due to cooling rates and formation of a delta iron. Much of the segregation can be eliminated or reduced if the casting has been through a homogenization high temperature heat treatment. At Western Gear Corporation, troublesome lots are experienced periodically and do require repetitive cleaning and a descaling cycle in order to attain a good surface.

9. What process controls are desirable?

Depending on the company QC organization and the customers served, a greater (or lesser) amount of paper controls exist. I will assume that adequate controls/inspection are available for the cleaning and descaling processes, and start with passivation.

- Passivation Bath - A relatively simple way to control the bath and assure its activity is by drawing a one gallon sample (for the Lab) each time the bath is renewed. Then, during the duration of bath use, the Lab sample bath becomes a reference referee should a problem arise. Problem parts are then run in the Lab sample. If they accept passivation, then the processor's bath is likely the cause. Should they fail, then there is a

material or procedural problem. No bath titration analysis is done at Western Gear, since the bath is frequently renewed and made up to the concentration called for in the in-house specification.

At one time, monitoring of the bath using the hydrometer methods was done. After some frustrating results with the "certified hydrometers", and an evaluation of these hydrometers for accuracy and spread, we learned that the reliability of reading was not satisfactory and generally misleading. At that time, the one gallon Lab sample approach was adopted.

As mentioned in item 7, the primary process control of the invisible film is the use of a 100% immersion of parts in the copper sulfate solution. This does not apply to the 400 series alloys and is used cautiously with the 303 free machining grades. Free machining grades contain non-metallic stringers which act as chip breakers. They also selectively protect surface iron from being removed during passivation.

10. Does the coppersulfate test work 100% of the time?

Not 100%, but just about. There is a nasty phenomenon that does occur on occasion, called pseudo passivation. In plain words, it means that the processor can indeed very conscientiously complete the entire passivation cycle, pass a coppersulfate test, ship your parts, and then the parts will fail miserably in your facility. No one has, to my understanding, really been able to document the explanation of why parts can be passivated, then after handling revert back to an active state. However, re-running of the parts does correct the situation, particularly if the parts are processed through an acid electroclean process.

Other observations and practices that reduce rework time of pseudo-passivated hardware include:

- Rinse water - use of warm D.I. is more favorable than cold tap water (in North Dakota). In some geographical areas, there may be chlorides in the tap water that cause deterioration of the passivation oxide layer during all passivation processes, including the final rinse.

- Follow the water rinse with an alcohol dip plus fan dry before immersing in the copper sulfate bath. A wet part having unstable passivation may not respond to the test.

11. Is the passivation processing costly?

Costs and delivery are important criteria for staying in business. As with any process, costs vary depending on labor rates, quantity, degree of automation, geometry, and requirements. ROM estimates of manhours can be offered and accepted as relative figures only (assume 100 piece lot).

	Manhours/Part
Cleaning	.002
Descaling	
Sandblasting	.010
Electroclean (alkaline)	.002
Electroclean (acid)	.002
Passivate/Inspect	.004

Standard total run times for many jobs is in the order of .01 manhours.

12. Is there an industry wide specification available that addresses cleaning, descaling, passivation, and inspection processes for stainless steel alloys?

    Yes. ASTM A 380 is now one of the available documents, starting with the '78 revision. Federal Decument QQ-P-35 had been and still is widely recognized. However, the Army (custodian) withdrew interest and formally accepted ASTM A 380 as its replacement document in 1980 (refer to addendum). The '78 revision of the ASTM document incorporated much of the QQ-P-35 information.

    ASTM A 380 addresses recommendations and precautions for cleaning and descaling the stainless steel alloys. From it, a suitable in-house document can be formatted. However, that still leaves the industries processors with innumerable individualized documents that might more suitably be addressed in a new revision of the ASTM document.

13. What can be done to facilitate changes, if desired, to the ASTM document?

    First, please review the referenced document. It addresses a wide range of industries and will likely generate a wide range of responses/impressions.

    Second, please document your impressions, ideas, and desires relative to use (or potential use) of the document in your facility.

    Third, please send your notes to the author of this paper. You are also welcome to make a telephone call.

14. Can the use of ASTM A 380 or a revision of it be a benefit to processors and their customers?

    The practices of passivation processing vary considerably as do the needs from industry to industry. As the requirements vary, so do costs, whether they be short term or related to product liability. Should a purchase order reference ASTM A 380 or other document that provides guidance and an initial understanding for processing, then it has assisted in vendor-customer communications and definition of cost.

REFERENCES

1) Peckner and Bernstein, Handbook of Stainless Steels, McGraw-Hill, 1977, (Chapters 16, 24, and 38). Discusses in-depth processing and theory.

2) Hall (ed.), Metal Finishing and Guide Book Directory, Metals and Plastics Publications, Inc., Hackensack, N.J. Published annually and received with subscription to Metal Finishing. Good for description of individual chemical.

3) Ugiansky, Payer (ed.), Stress Corrosion Cracking, The Slow Strain Rate Technique, ASTM, 1979 (pp. 312-313). Discusses SCC susceptibility of various stainless alloys.

4) NACE Task Group, Corrosion Problems Due to Carbon Pickup in Stainless Alloy Castings, NACE Headquarter, Houston, Texas, Publication No. 5A179. Discusses causes and cites examples.

5) Fontana and Greene, Corrosion Engineering, McGraw-Hill, New York, 1967 (predominently Chapter 5). However, numerous references throughout the book either directly or indirectly address passivity.

6) Faust, Electropolishing, Metal Finishing issues July 82, (pp. 21-25), August 1982 (pp. 59-63), September 1982 (pp. 89-93), Metals and Plastics Publications, Inc., Hackensack, N.J.

7) Federal Specification QQ-P-35 (1973) entitled, "Passivation Treatments for Corrosion Resisting Steel".

8) ASTM A 380 1978, entitled "Cleaning and Descaling Stainless Steel Parts, Equipment, and Systems".

In addition to the eight listed references, there are major company specifications and intercompany papers addressing passivity that are generally available to their vendors on request.

Addendum

ANSI/ASTM A 380-78
31 January 1980
USED INSTEAD OF
QQ-P-35B
5 April 1973

ACCEPTANCE NOTICE

The above non-Government Document was adopted on 31 January 1980 and is approved for use by the DoD. The indicated industry group has furnished the clearances required by existing regulations. Copies of the document are stocked by DoD Single Stock Point, Naval Publications and Forms Center, Philadelphia, PA 19120 for issue to DoD activities only. Contractors and industry groups must obtain copies from ASTM, 1916 Race Street, Philadelphia, PA 19103.

Title of Document: Cleaning and Descaling Stainless Steel Parts, Equipment, and Systems

Date of Specific Issue Adopted: 28 July 1978

Releasing Industry Group: American Society for Testing and Materials

Custodians:

Army -- MR
Navy -- SH
Air Force -- 11

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Army -- MR

Project No. MFFP-0195

Review interest:

Army -- GL, MI, AR
Air Force -- 11
DLA -- IS

User interest:

Army -- AV
Air Force -- 99

Area MFFP

The DoD has recently implemented a change in policy regarding the automatic distribution of adopted non-government documents and related acceptance notices. In the past, the acceptance notice was distributed automatically to DoD subscribers as an integral part of the adopted document. Neither the notice nor the adopted document were provided to anyone outside the DoD. Effective with this new policy, the acceptance notice is mailed to all subscribers including the private sector by automatic distribution at the time a non-government document is adopted by the DoD. The adopted non-government document, however, is no longer distributed automatically to the DoD users. The adopted document is normally available to DoD users from the NPFC within 60 days and may be obtained by using DD Form 1425. All other users must obtain the document from the releasing industry group indicated on the applicable acceptance notice.

I-3

General Interest Session I

Trivalent Chromium: A Commercially Viable Alternative

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TRIVALENT CHROMIUM: A COMMERCIALLY VIABLE ALTERNATIVE

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Abstract

A high performance, decorative trivalent chromium plating process with superior properties has been developed. The new process has been found to be dependable and more tolerant to metallic contamination than previous systems, based on development of a unique addition agent system. Production experience has proven that the new system can be readily adapted to existing equipment and plating cycles and that it provides improved productivity, quality, bath reliability and reproducibility of deposit appearance and properties. Deposits have an inherent microdiscontinuous surface, outstanding covering power, good color and hardness comparable to that of hexavalent chromium. In exterior applications, corrosion performance compares favorably with hexavalent systems. Numerous operational advantages demonstrate the utility of this new technology.

Introduction

Chromium deposition from electrolytes containing trivalent chromium salts has been in commercial use since the late 1970's. The benefits of trivalent chemistry are improved covering power, absence of high current density burning, low metal concentration, elimination of hexavalent chromium and improved performance; all of which lead to increased productivity and reduced cost of operation.

The commercialization of a trivalent chromium plating process was a long time in coming. Initial deposition of chromium from such electrolytes took place in the late 1800's.[1-3] Over the years, considerable research has gone into attempts to develop a practical trivalent chromium plating process.[4-21] Unfortunately, most of these processes exhibit inherent disadvantages, and fail to match the dependability of hexavalent chromium baths.

Problems encountered in attempting to develop a viable trivalent chromium plating process were largely due to the complex nature of the chemistry of chromium (III) in aqueous solutions. It was suggested that cations such as chromium (III) are strongly solvated.[22] They form aquo-complexes,[23] whose inner coordination sphere is so tightly bound that chromium cannot readily be released from the complex. In order to deposit chromium metal from trivalent chromium electrolytes, one must prevent the trivalent chromium ion from forming these very stable aquo-complexes.[24] The most feasible solution to this problem is to replace the water molecules surrounding the chromium ion by other complexing ligands. The new metal complex that is formed should be sufficiently stable to retain the chromium as part of the complex yet permit the chromium to be released during electrolysis and subsequently deposited on the cathode.

In the early 1970's various government agencies encouraged the metal finishing industry to curb the use of hexavalent chromium. Chromic acid has undesirable characteristics. It is toxic and corrosive to the skin causing ulcers; inhalation causes damage to the respiratory system, and it is a suspected carcinogen. In anticipation of further government regulations, a research program was initiated which results in development of the novel trivalent chromium process described in this paper.

Solution Composition

The plating solution composition is summarized in Table I. The bath contains conductivity salts, a buffer, catalyst, complexing ligand, trivalent chromium salts and a reducing agent.

The conductivity salt is a dry mix containing alkali metal and ammonium salts, (e.g., chlorides, fluoborates and sulfates) which improve the conductivity of the bath. These chemicals are lost by drag-out. The conducting salts also contain other chemicals which are essential to the proper function of the bath. These include boric acid and a reducer which controls the reaction at the anode.

The reducing agent limits the formation of hexavalent chromium during electrolysis where the use of insoluble anodes results in trivalent chromium being oxidized to hexavalent. The reducer is lost by drag-out.

The catalyst's main function is to improve chromium distribution on areas where air agitation is not very effective; it also reduces surface tension to minimize drag-out losses.

The role of the complexing ligand is to form the proper water soluble complex with the chromium ion allowing the metal to be readily deposited at the cathode. The complexing ligands, generally simple aliphatic carboxylic acids, together with the trivalent chromium, chlorides, sulfates and ammonia form the coordination complex from which chromium is deposited. The complexant is lost both by drag-out and through electrolysis.

Chromium is supplied to the bath in the form of trivalent salts such as, chromium sulfate ($Cr_2(SO_4)_3.XH_2O$) and/or chromic chloride ($CrCl_3.6H_2O$). The sulfate salt is generally preferred because of the cost factor.

The process solution is maintained by replenishment based on drag-out and/or electrolytic consumption. Electrolytic consumption exceeds drag-out loss for the complexant, chromium and catalyst and these are maintained by making additions on an ampere hour basis. Analysis for these materials provides the final control.

Operating Conditions

Operating parameters are summarized in Table II. The pH range of this bath is 2.8-3.5. An optimum pH range of 3.0-3.2 provides the most effective compromise between deposition rate and covering power. Below a pH

of 2.8 the covering power of the bath is reduced though plating speed is increased. At pH values about 3.5 one obtains improved coverage at the expense of plating speed. The pH has to be monitored instrumentally and maintained within the specified range by addition of ammonium hydroxide.

The optimum operating temperature range is 18°-30°C (64°-85°F). Covering power increases at the lower end of the temperature range, while higher temperatures will decrease the coverage and tend to produce nonuniform, dark chromium deposits. Operating the process continuously on a production basis, above 0.5 ampere per liter, may increase the temperature above the specified range and require cooling of the solution.

Cathode current densities of 10-21 A/dm^2 (100-200 A/ft^2) are generally employed. It was noted that plating at high current densities, i.e., up to 40 A/dm^2, does not produce burning. This lack of burning at high current densities is associated with a decrease in cathode efficiency with increasing current density.

Efficiencies of 11-14 percent have been obtained for this plating process, which is nearly identical to the values of 12-15 percent for hexavalent systems. The reason that efficiencies of both processes are so close is the fact that chromium metal is deposited from the trivalent state in both processes.[25] The deposition of chromium metal from trivalent chromium solutions was discussed earlier. The mechanism for the electrodeposition of metallic chromium from conventional chromic acid - sulfate plating systems takes the form of reduction of chromium (VI) by electron transfer to chromium (III). In the conventional hexavalent chromium plating process it is from this chromium (III) state that the deposition of chromium takes place. To protect the chromium (III) formed from reacting with water to form the very stable aquo-complex, $Cr(H_2O)_6^{+3}$, a chromic-dichromate complex is formed.[26]

Air agitation is utilized to insure uniform metal distribution. Agitation must cover the entire area under the cathode surface. Too little agitation may produce uneven metal distribution while too much may reduce coverage.

Equipment

Equipment for commercial operation of this process is summarized in Table III. Plating tanks must be of plastic or rubber lined. Lead-lined tanks cannot be used. Existing hexavalent chromium tanks having acceptable liners can be used only if they are thoroughly cleaned and leached to remove all traces of hexavalent chromium and lead.

High purity carbon (graphite) anodes equipped with a copper core are used, and connections should be made which are both mechanically and electrically sound. Bus bars must be protected from the plating solution to avoid contamination of the plating bath.

Plastic air lines, such as those designed for nickel processes, can be utilized to supply air agitation to the bath. A sufficient number of

lines should be installed to cover the anticipated cathode area.

Since the optimum temperature range is 18°-30°C (64°-86°F), some means of cooling is necessary for high volume, continuous production. Teflon coils or plate heat exchangers using cold water or refrigeration may be used. Cooling the solution below 15°C (60°F) should be avoided as crystallization of salts can occur restricting solution flow. In cold weather heating may be required to prevent precipitation of salts during idle periods.

To accommodate wide variations of anode and cathode areas, anode to cathode spacing, and other sources of voltage drops, rectifiers that provide 6-24 volt output have been found to be satisfactory. Trivalent solutions are less conductive than hexavalent chromium, and generally require higher voltages. Where possible, the anode to cathode distance may be decreased to offset the additional voltage required. Reducing the voltage will decrease the energy input and reduce the amount of cooling required.

Filtration of the trivalent chromium bath is recommended, especially to remove any precipitate formed from treatment of the bath for metallic contamination. Filters suitable for use with high chloride nickel solutions have been found to be satisfactory.

Ventilation is recommended as a standard operating procedure to remove any gases evolved.

Additional equipment, which may prove beneficial for process control includes; a pH meter, ampere-hour meter, hydrometer and stalagmometer.

Contamination and Purification

Trivalent chromium solutions are more sensitive to heavy metal contamination, such as, copper, iron, lead, nickel and zinc than hexavalent chromium, as shown in Table IV. These tolerance levels for heavy metal contamination are at optimum conditions, and in practice will generally be lower, since more than one contaminant normally will be present in the bath. However, production experience has indicated the process is more tolerant to nickel and iron contamination by a factor of 2 and 4 respectively compared to other commercial processes. The effect of these impurities in trivalent chromium deposits is to produce hazy-white to very dark, streaked thin deposits having poor coverage. Nickel contamination is due to improper rinsing between the nickel and chromium. This problem can generally be corrected by an efficient rinse cycle.

Lead contamination is the result of leaching of lead salts from liners previously used for hexavalent chromium baths. In spite of thorough cleaning, some lead and chromium salts can remain in the lining. Lead contamination can be removed by low current density electrolysis as well as by precipitation.

Copper, iron and zinc contamination results from dropped parts or attack

on unplated areas, as for example, blind holes and open tubing. Fortunately, these impurities can be removed either by precipitation and filtration or by low current density electrolysis. Good results can be obtained by electrolyzing at 1 to 3.2 A/dm^2 (10-30 A/ft^2) using nickel plated cathodes with high surface areas.

Frequency of bath purification will depend on the efficiency of the rinsing between nickel and chromium, type of work being plated, number of parts falling into the tank and plating time. Where nickel drag-in is an ongoing problem, and cannot be corrected because rinsing procedures cannot be improved, treatment of the bath on a routine basis may be necessary.

Use of a Controller material, which allows plating of acceptable chromium deposits from contaminated baths, and a cyanide free Precipitant for this process will be discussed under "Production Experience".

Physical Properties

The color of the chromium deposit plated from the process described in this paper, is close to that of hexavalent chromium. Figure I, compares two identical parts, one plated in a hexavalent bath and one plated in a trivalent chromium bath. Results show very little difference in color between the two. Figure II shows a variety of parts that have been plated in this trivalent chromium process and the excellent results that have been obtained.

Hardness measurements were made, using a Diamond Pyramid Indenter under a 100 gram load, on chromium deposits ranging in thickness from 58 μm to 74 μm (0.0023 to 0.0029 inches). The results summarized in Table V indicate that the new trivalent chromium system produces deposits which compare favorably with the hardness of hexavalent chromium deposits.

Deposits from this process, like those from other trivalent processes, are microporous up to 0.2-0.3 μm and microcracked above 0.6 μm. A cross-section view of a typical deposit is shown in Figure III. The photomicrograph shows the pores and cracks traversing the thickness of the chromium plate. The photomicrograph of a cross-section of a chromium plate from a chromic acid bath is compared in Figure IV. The chromic acid deposit shows many short, random pores which never come close to traversing the thickness of the chromium deposit.

Deposit Composition

A significant difference was found in the chromium deposit composition between trivalent and hexavalent chromium deposits as shown in Table VI. Differences in composition could certainly account for the variation, in such properties as color, stress and inherent microporosity/microcracking.

Corrosion Performance

Corrosion performance of these trivalent chromium deposits, which have a natural microporosity, was compared with both microporous and nonmicroporous hexavalent chromium systems. Comparison was made using duplex nickel-chromium as well as thin nickel (5-8 μm) chromium systems.

All deposits were plated on 10 x 17 cm (4 x 6 inch) steel panels. Identical bright nickel deposits were utilized on all test panels. Microporosity in the hexavalent chromium was induced by interposing a 1 to 2 μm nickel deposit containing fine, insoluble particles between the final bright nickel and hexavalent chromium deposits.

Duplex nickel-chromium panels were exposed to marine and industrial environments. The marine exposure was at Kure Beach, North Carolina at a site 240 m (800 ft.) from the ocean. The industrial site was a roof in Warren, Michigan, which has a moderately severe industrial environment. The thin nickel-chromium deposits were subjected to a neutral salt-spray test.[27] Test panels were rated according to a standard ASTM rating system.[28]

Table VII summarizes the corrosion performance data for duplex-nickel-chromium on steel. The corrosion performance of trivalent chromium deposits is equivalent to those of hexavalent chromium in the industrial environment, and significantly better than hexavalent chromium in the marine environment. Corrosion performance of microporous hexavalent chromium is only slightly better than trivalent chromium in both industrial and marine exposure.

Thin nickel - chromium (III) deposits appear to be more susceptible to corrosion than those obtained from hexavalent chromium, under the same conditions after six hours in neutral salt spray. As a result, it is necessary to use a suitable post-dip in order to enhance the corrosion resistance of these deposits.

Production Experience

The two key factors to consider when taking a new process from the research laboratory to a production situation are:

1. Will the process produce consistent results on a day to day basis under production conditions? Specifically, can the process stand up to around-the-clock operation with minimal technical control and no loss of production?

2. Will the process operation be cost effective? How is the cost of the finished product affected by the process?

The new trivalent chromium process has now operated in the field for over two years in a wide range of applications including steel stampings, wire goods, and tubular steel.

What lessons have been learned from field experience on the ability of the process to produce consistent results? Historically, trivalent chromium was considered a greater control problem than hexavalent chromium due to the number of additions required to maintain the process. Trivalent systems also have exhibited relatively low tolerance to metallic impurities when compared to hexavalent systems.

Production experience has shown that maintenance of bath constituents has not been a major problem. Laboratory facilities used to maintain the process have ranged from as little as a pH meter to fully equipped laboratories. A typical control program consists of the following:

1. Daily pH check
2. Weekly chromium analysis
3. Weekly conductive salt analysis
4. Weekly Hull Cell tests
5. Monthly metallic impurity check

Process control other than the impurity check, does not require special laboratory equipment or procedures. Laboratories presently equipped to maintain nickel and hexavalent chromium process solutions are adequate. Moreover, "in-tank" conditions are duplicated very closely by Hull Cell panel testing which can be used to predict the effect of additions to the trivalent process.

Field experience has also shown that the new trivalent process has an improved tolerance for the two major metallic impurities encountered in production, specifically nickel and iron. The major effect of these two impurities is black deposits in the high current density areas. Production experience has shown that 400 mg/L nickel and 1000 mg/L iron is trouble free and values even as high as 550 mg/L nickel and 2000 mg/L iron have been tolerated. Even with a highly tolerant process, impurity control is still important in order to maintain consistent production.

Two unique service tools were developed for use in the trivalent process to insure consistent production. The first material is the Controller - whose function is to surpress the formation of black deposits resulting from high nickel and iron levels. The Controller is added at the first sign of trouble and allows production to continue until the impurities can be removed as part of planned maintenance. The second service tool is designated as a Precipitator and its function, as the name implies, is to remove harmful nickel and iron impurities by precipitation and subsequently removing them by filtration. The unique features of the Precipitator are:

1. Use of the Precipitator in excess will not permanently damage the process due to breakdown of the chromium complex.

2. The Precipitator can be added directly to the process while in operation.

3. The metallic precipitate formed is very coarse, facilitating its easy removal thru a filter without excessive plugging and eliminating redeposition of powdery deposits on the plated work.

4. The precipitate requires no special waste treatment.

5. Unlike other precipitators, it is free of cyanide and its derivatives.

Consistent operation is but one factor in a successful process. For a new process to be practicable, it must be economical. The cost of installation and chemical maintenance must be offset by its operating characteristics.

When considering installation of a trivalent system, the present operating cycle must be considered in determining the number of stations available for use in the new process. A typical trivalent cycle is shown in Table VIII. Good rinsing between nickel and chromium is essential in order to prevent the carryover of nickel salts into the trivalent solution. A "dry-tank" is preferred ahead of the trivalent process to limit volume build-up in the trivalent chromium tank. Dilute chromium activating solutions used in many hexavalent chromium cycles are not necessary. For cycles using thin nickel or ferro-nickel deposits, or in operations processing tubular steel, a proprietary post-dip is required to remove any entrapped chloride ion and to passivate unplated or low current density areas where a thin underlying deposit may be porous.

The trivalent system has been introduced into existing hexavalent chromium plating cycles with little or no changes. Installation of the trivalent process requires that all hexavalent chromium salts be removed from existing tanks. In older installations, the use of drop-in tank liners may be more cost efficient than cleaning existing tanks. Cooling requirements will vary for individual installations. A trivalent process running in Michigan and applying less than 2 amperes per gallon current to the process tank has been operated satisfactorily using tap or well water for cooling, whereas a bath operated in the South with currents over 2 amperes per gallon definitely requires refrigeration. The key factor influencing the selection of a rectifier is to insure that the amperage available is high enough to take full advantage of its potential for increased productivity.

In analyzing the comparative cost of conventional and trivalent chromium processes, several factors must be considered. In terms of the cost of chemicals consumed, the hexavalent system is more economical to operate. Typical trivalent chromium chemical cost is 2-3 times the cost of hexavalent chromium. The cost differences are from drag-out based on the higher make-up cost per gallon of trivalent chromium. One important aspect of running trivalent chromium is to eliminate drag-out through the use of delay times over the trivalent tank and drag-out rinses.

Despite the increased chemical cost, the trivalent process is still more cost effective to operate due to its improved productivity. The following

features have been demonstrated under full production conditions:

1. The trivalent process has the unique ability to eliminate high current density burning and provide excellent low current density coverage, allowing more parts to be plated per rack. Increases in rack area up to 50% have been achieved in trivalent installations. In addition, current robbers, shields and, in many cases, auxiliary anodes have all been eliminated from racks.

2. Further economies in operation are achieved by drops in reject rates up to 50%. The trivalent process not only eliminates high current density burns and many chrome stains; it also does not produce the whitewash stains caused by electrical current interruption which plague many operations.

3. Labor cost savings are achieved by elimination of color buffing operations for chromium burns and whitewash. Use of trivalent chromium has allowed, in several operations, one and sometimes more employees per shift to be relieved from chrome buffing duty to pursue more productive work.

The cost of waste treatment for both trivalent and hexavalent chromium can vary widely, depending on existing equipment and local regulations. In many cases, it is possible to simply neutralize and precipitate the trivalent effluent in the existing facilities. The high cost of chemically reducing the hexavalent chromium, which can run as high as $1.25/pound of chromium, is completely eliminated.

Further cost savings are available through reduction of metallic sludges. Trivalent chromium contains 25 grams/Liter total chromium compared to 120-140 grams/Liter chromium in a standard hexavalent process. Given equal drag-out conditions, the weight of sludge to be disposed of from a trivalent chromium process is reduced by a factor of 5 or 6.

Elimination of hexavalent chromium itself is a major benefit of the trivalent process. Removal of dangerous chromic acid spray, elimination of storing and handling problems, as well as the elimination of hexavalent chrome bleed-out in racking areas are also important considerations.

Finally, the trivalent process, because of its excellent covering power, produces a quality chromium finish on parts which were previously run through nickel-only cycles because of chromium coverage problems. The process is particularly well adapted to completely cover holes and slots which, in the past, have been marginally acceptable. Complex wire displays, which were sent out for zinc plate to obtain a uniform appearance, are now nickel-chromium plated with complete coverage. In addition, the trivalent system is not sensitive to high nickel brightener levels.

Conclusion

A practical trivalent chromium process has been developed and subjected to over two years of field experience. The benefits of this process are significantly improved chromium coverage which allows more parts per rack, reduced reject rate, improved quality, reduced waste treatment cost and elimination of toxic chromic acid. These advantages result in a significant increase in productivity which, in turn, leads to reduced unit cost.

Corrosion performance, for exterior application, compares favorably with hexavalent systems, both in marine and industrial environments. For interior specifications using thin nickel deposits, a post-dip treatment is required for equivalent protection.

The future of trivalent chromium plating, as an alternative to the hexavalent process appears bright since a highly reliable process is now available which offers significant improvement in productivity in addition to a substantial reduction in environmental risk.

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TABLE I

SOLUTION COMPOSITION

MATERIAL	CONCENTRATION
Conductivity Salt	225 g/L (30 oz/gal)
Catalyst	1 mL/L (0.1% by volume)
Complexant	80 mL/L (8.0% by volume)
Chromium Metal	22 g/L (2.9 oz/gal)
Reducer	2 g/L (0.26 oz/gal)

TABLE II

OPERATING PARAMETERS

OPERATING CONDITIONS	RANGE
pH (Electrometric)	2.8-3.5
Temperature	18°-30°C (64°-86°F)
Cathode Current Density	10-21 A/dm^2 (100-200 A/ft^2)
Anode Current Density	5-10 A/dm^2 (50-100 A/ft^2)
Specific Gravity	1.2-1.3
Surface Tension	30-50 Dynes/Cm
Agitation	mild, uniform air

TABLE III

EQUIPMENT

Tanks	Plastic or Rubber lined
Anodes	Carbon (Graphite) Copper Core
Agitation	Air
Cooling/Heating	Required
Filter	Necessary to remove purification products
Rectifiers	6 - 24 Volts
Ventilation	For gas evolution

TABLE IV

METALLIC CONTAMINANTS

METAL	TOLERANCE UNDER OPTIMUM CONDITIONS
Copper	20 ppm
Iron	500 ppm
Lead	20 ppm
Nickel	200 ppm
Zinc	50 ppm

TABLE V

HARDNESS TRIVALENT VS. HEXAVALENT CHROMIUM

CHROMIUM DEPOSIT	HARDNESS DPH*
Trivalent	803-974
Hexavalent	800-1100

*Measurements were made using the diamond pyramid indenter under a 100 gram load

TABLE VI

DEPOSIT COMPOSITION

TRIVALENT VS. HEXAVALENT CHROMIUM

CHROMIUM DEPOSIT	CARBON WT %	OXYGEN WT %	CHROMIUM WT %
Hexavalent	0.0	0.4	99+
Trivalent	2.9	1.6	95+

TABLE VII

CORROSION RESULTS

DUPLEX NICKEL - CHROMIUM ON STEEL

SET	SEMI-BRIGHT NICKEL um	BRIGHT NICKEL um	CHROMIUM um	ASTM RATINGS INDUSTRIAL 5 MONTHS	ASTM RATINGS MARINE - KURE BEACH 6 MONTHS
1	18	7.5	0.25 - 1	9/8	7/6
2	18	7.5	0.25 - 1,2	10/8	10/10
3	18	7.5	0.25 - 3	9/9	9/7

1 - Hexavalent Chromium
2 - Microporous
3 - Trivalent Chromium

TABLE VIII

TYPICAL TRIVALENT CHROMIUM OPERATING CYCLE

NICKEL OR FERRO-NICKEL PLATE
NICKEL DRAG-OUT
COLD WATER RINSE
COLD WATER RINSE
DRY TANK
TRIVALENT CHROMIUM
DRAG-OUT TANK
COLD WATER RINSE
COLD WATER RINSE
POST-DIP
COLD WATER RINSE
HOT WATER RINSE

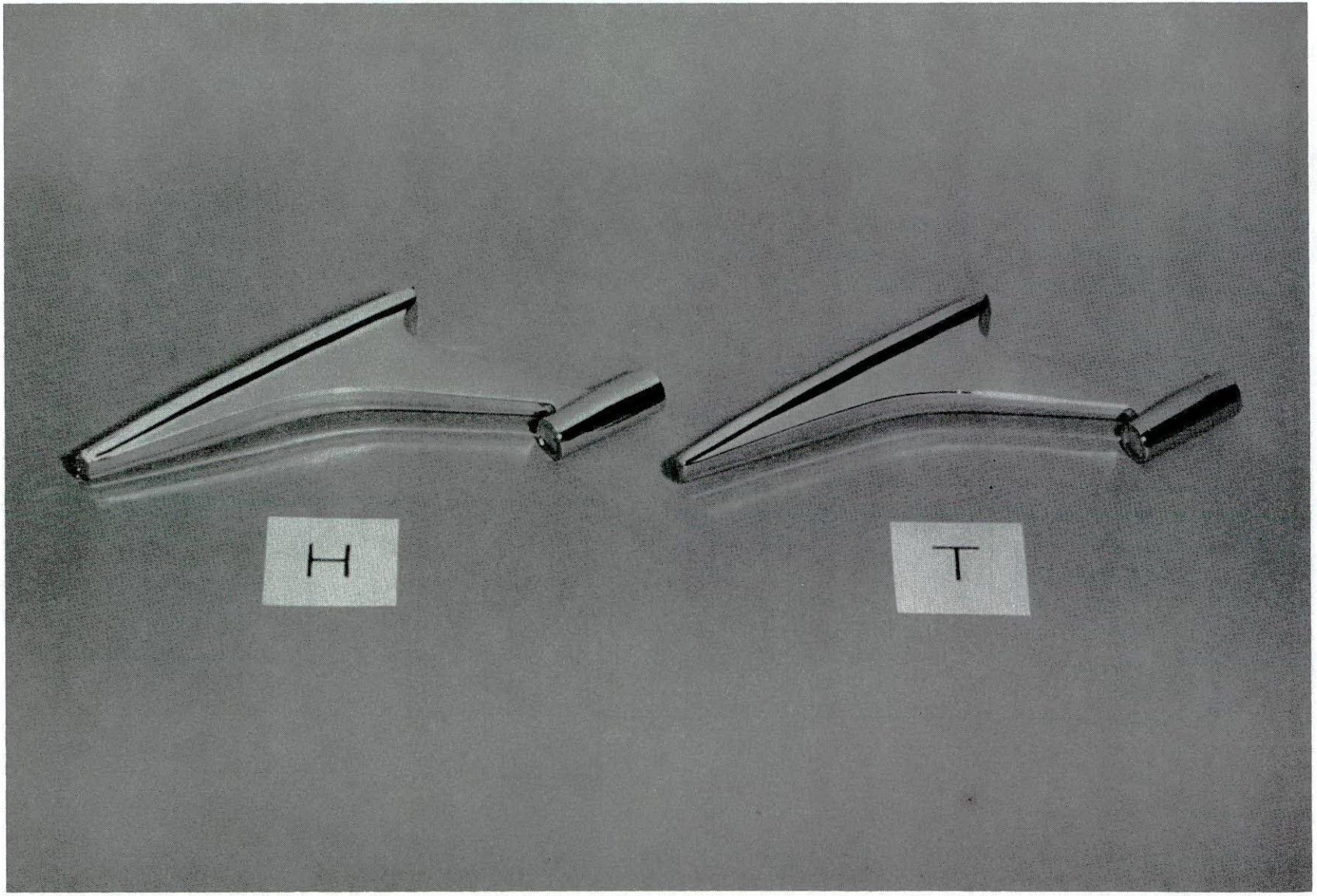

Fig. 1 Comparison of chromium deposits plated from hexavalent and trivalent solutions.

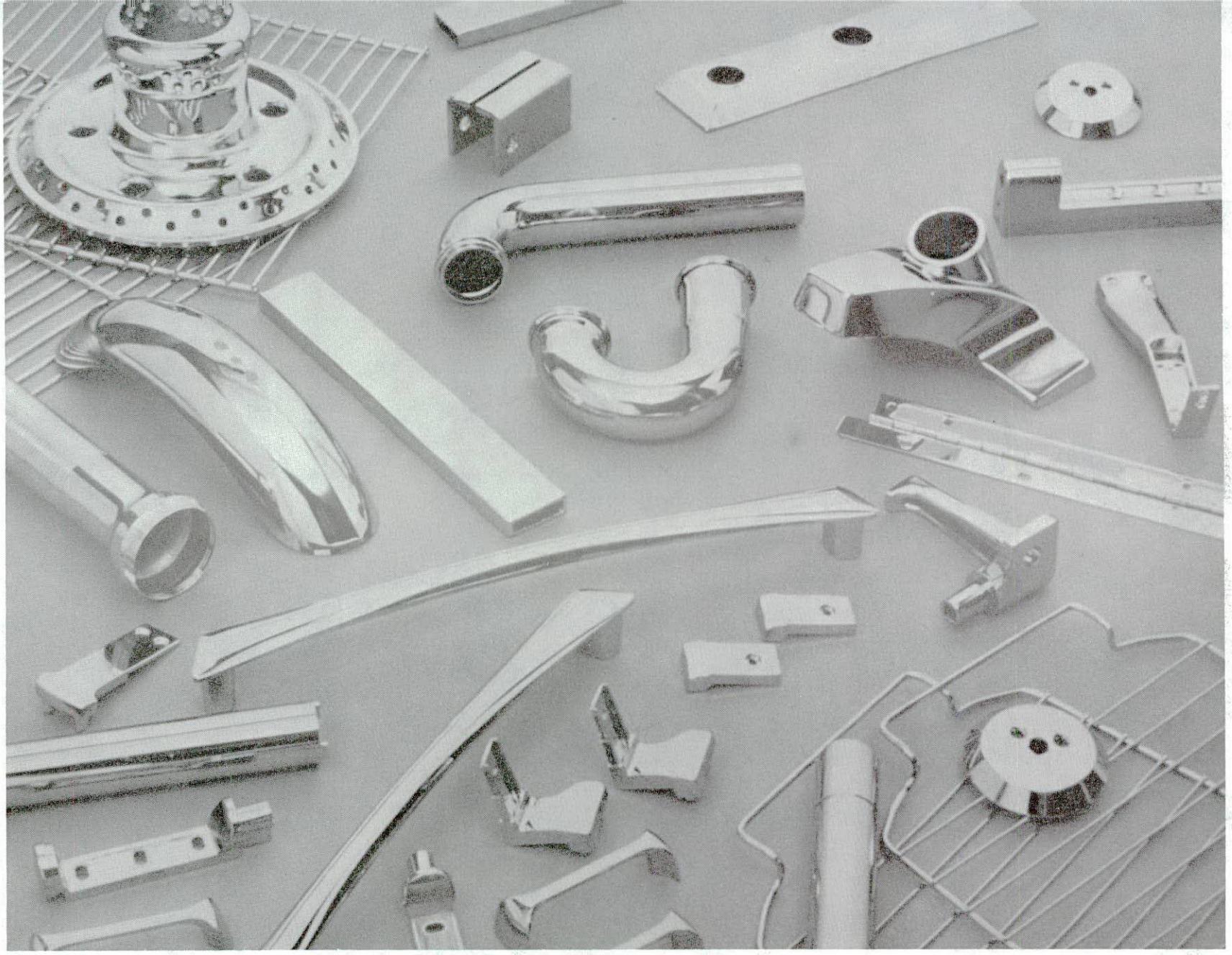

Fig. 2 Various parts which have been plated from trivalent chromium baths.

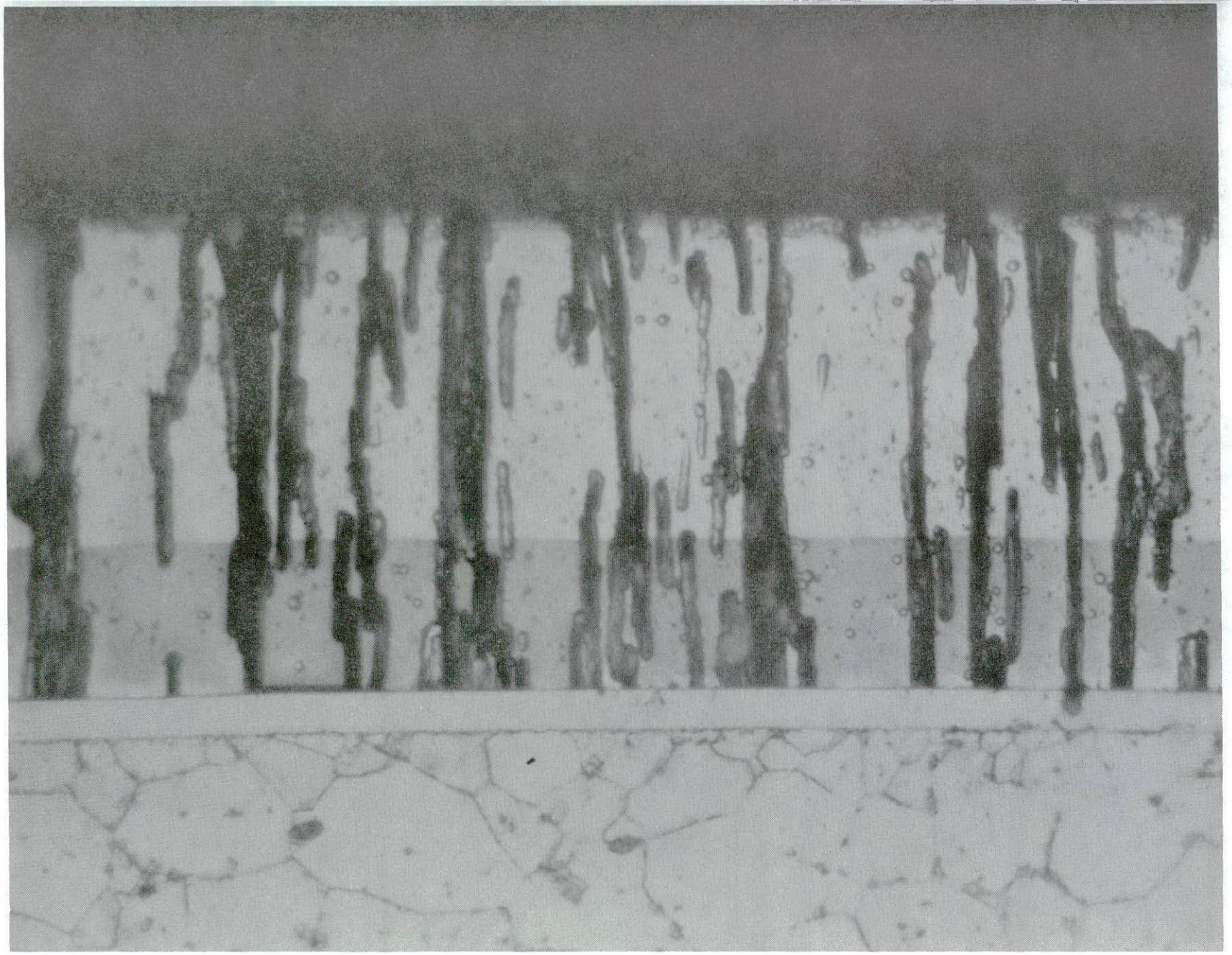

Fig. 3 Photomicrograph of 90 µm thick chromium deposited from a trivalent bath.

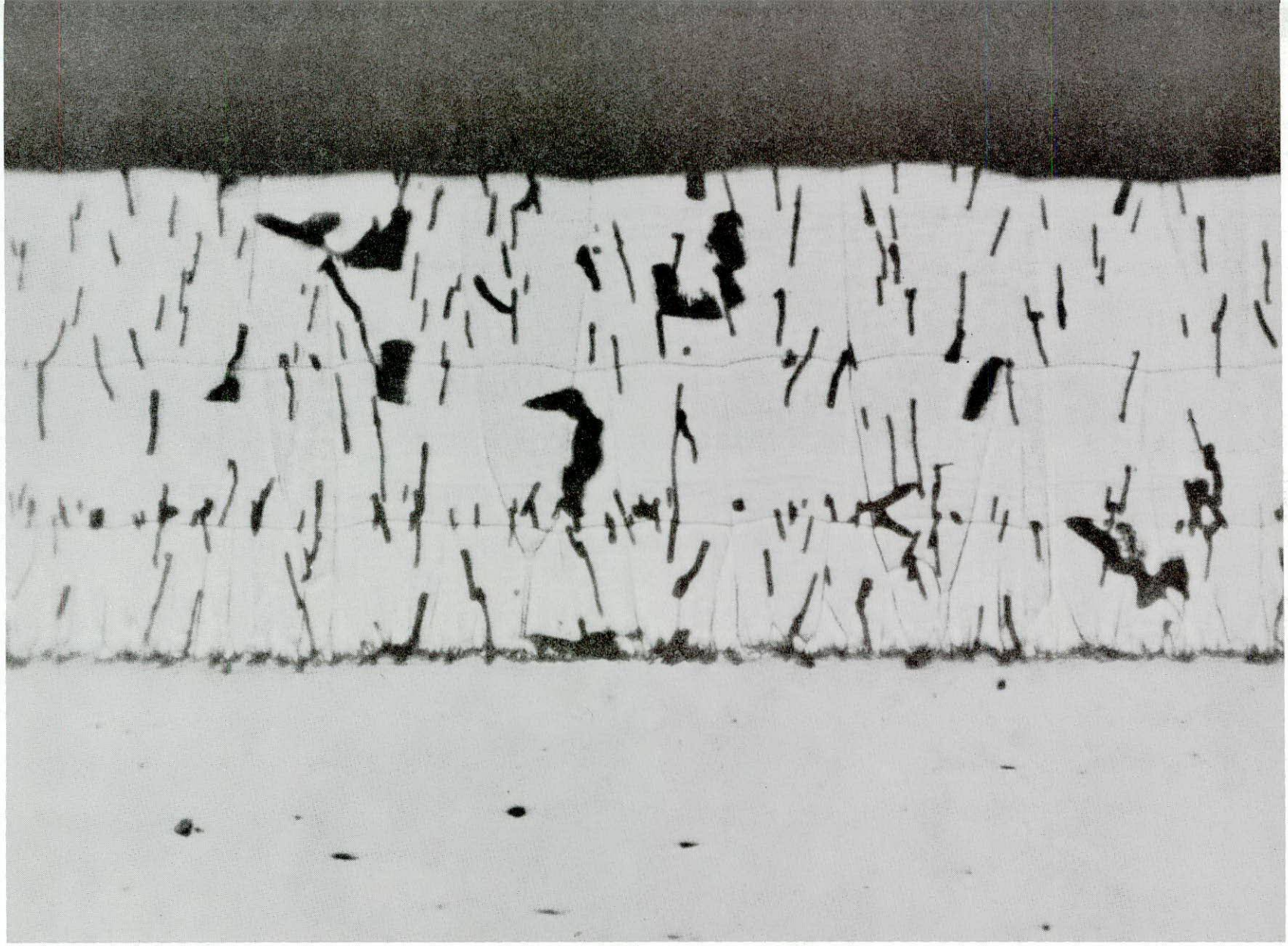

Fig. 4 Photomicrograph of 90 μm thick chromium deposited from a hexavalent bath.

I-4

General Interest Session I

Zinc/Graphite—A Potential Substitute for Anti-Galling Cadmium

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ZINC/GRAPHITE - A POTENTIAL SUBSTITUTE FOR ANTI-GALLING CADMIUM

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Introduction

A chronic problem which has plagued the automotive industry for years is a phenomenon known as "stick-slip" friction. It happens when coated fasteners such as phosphated and oiled or zinc plated nuts and bolts are tightened with power tools. As the name "stick-slip" implies, there may be a momentary tendency during tightening, for the coated fasteners to stick and then break loose or slip. The coefficient of friction and the integrity of the coating play a significant role in this "stick-slip" phenomenon.

As an example, let us consider a poorly phosphated batch of bolts used during mechanical assembly. If the power tool used to drive down the bolts is torque controlled it may shut down prematurely due to stick-slip. If this occurs, the mechanical assembly will be improperly secured and will require rework upon identification by an inspection system. This results in less assembly line productivity and higher costs. Even where the coating is electroplated zinc, the galling nature of the deposit can produce similar stick-slip problems.

For years cadmium electroplating has been used in applications where good lubricity, sacrificial corrosion protection and anti-galling properties were required. Recently the increasing cost of cadmium together with mounting toxicological implications[1] has spurred much activity to find reliable substitute coatings. This paper describes a plating process for producing zinc/graphite coatings which have frictional and corrosion performance properties comparable to those of electroplated cadmium coatings.

Experimental

Numerous plated deposits and composites have been reported to have low friction and/or anti-galling properties.[2-5] Using this information as a guide, steel fasteners were plated in the laboratory by conventional plating techniques. These systems included electroless nickel with and without molybdenum disulfide, electroplated zinc and electroplated cadmium with and without a chromate conversion coating. Plain steel, Teflon-coated, and

commercial phosphated and oiled fasteners also were used in the studies. In addition, fasteners were plated with a co-deposit of graphite in a zinc matrix by using a laboratory developed plating bath. This bath consisted of a conventional acid zinc formulation containing commercial proprietary addition agents and a refined grade of collodial graphite having a 2μm average particle size. The graphite content was varied from 5 to 75 g/l. Two of the bath formulations investigated are shown in Table 1.

BATH FORMULATIONS (g / l)

	POTASSIUM	SODIUM
$ZnCl_2$	78	78
KCl	210	—
NaCl	—	165
H_3BO_3	30	30
pH	5.0 - 5.7	5.0 - 5.7

Table 1

Unbagged anodes were used for both formulations. Steel nuts and bolts were processed through the baths either on racks or in barrels. The bath agitation cycle was found to be very critical to obtain deposits containing high graphite contents in the electrodeposit. Prior to plating, the bath was vigorously agitated to insure homogeneous graphite suspension. During the plating, the solution agitation -- and in the case of barrel plating the barrel rotation -- was interrupted for 30 seconds for every minute of plating time. About half of the plated fasteners were post treated with a chromate conversion film.

Of the two formulations, the bath made up with potassium chloride produced the brightest deposits. However, since specularity is not a requirement for fastener applications, and sodium chloride is plentiful and inexpensive, the sodium chloride formulation was used for most of the studies.

FORD PORTABLE JOINT ANALYZER

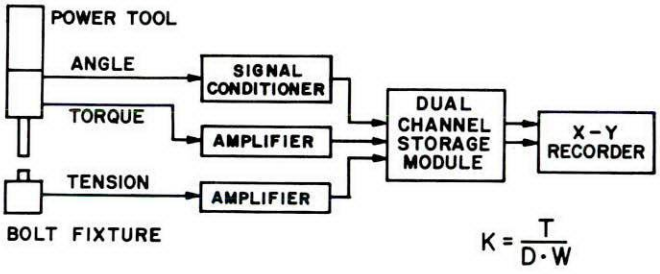


Fig. 1

The relative coefficient-of-friction-values for the various coated steel nuts were determined by using the Ford Portable Joint Analyzer. This equipment is shown schematically in Figure 1 and measures the relationship between angle of fastener rotation, applied torque and tension. For each measurement a nut was started on a bolt by hand in the fixture and then further tightened with a pneumatic power tool. The angle of rotation, which was measured by a torque-degree transducer, was electronically fed into the Encoder signal conditioner and stored in the Physical Data Channel Transfer module. Simultaneously, the tension and torque data were amplified and likewise stored in the memory module. The resulting data were then plotted out on an x-y recorder. From these plots the relative coefficient of friction value, K, was calculated at 40 ft.-lb. torque by the relationship K=T/DW where T is torque, D is the bolt diameter and W is the bolt tension.

Corrosion performance of cadmium plated and selected zinc/graphite composites was evaluated both by means of the ASTM B117 5% salt spray test and in one-winter mobile/road tests conducted in Buffalo and Detroit.

Results and Discussion

Figure 2 shows an x-y recorder plot of phosphated and-oiled fasteners displaying good and poor friction performance. In the case of poor performance, which is an illustration of stick-slip friction, excessive oscillation of the torque load results as the fastener is spun on the bolt. This oscillation is accompanied by a loud screeching noise. Furthermore the final tension achieved is insufficient. In the case of good performance of satisfactorily coated fasteners, the torque load is uniformly increased as the angle of fastener rotation is advanced, resulting in a firmly secured assembly with the required tension level.

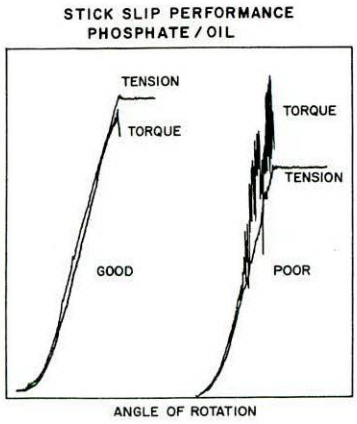


Fig. 2

Relative coefficient of friction values for steel nuts coated with various systems are given in Table 2.

RELATIVE COEFFICIENT OF FRICTION VALUES/ENGINE FASTENERS	
TEFLON	0.23
PHOSPHATE/OIL	0.20
ELECTROLESS NICKEL	0.17
ZINC ELECTROPLATE	0.16
ELECTROLESS NICKEL/MoS_2	0.16
BARE STEEL/OIL	0.15
ZINC/GRAPHITE	0.13
CADMIUM ELECTROPLATE	0.12

Table 2

From this table it is evident that both oiled phosphate coatings and zinc electroplate, which are commonly used in automotive fastener applications, are poor finishes in terms of uniform coating lubricity. Surprisingly, a Teflon finish was not even as good as phosphated-and-oiled fasteners. It was also found that uncoated steel was better than electroless nickel systems. As indicated in Table 2, the system with the greatest potential of matching the frictional properties of cadmium was a zinc/graphite composite which gave a value of 0.13 compared to 0.12 for cadmium. These zinc/graphite composite coatings were originally plated from a bath which contained 120 g/l of an unrefined grade of graphite. Additional improvements in friction levels were found by using a refined grade of graphite.

Coefficient of friction values for zinc graphite composite coatings as a function of the refined-grade graphite content, with and without a chromate conversion film, are shown in Figure 3.

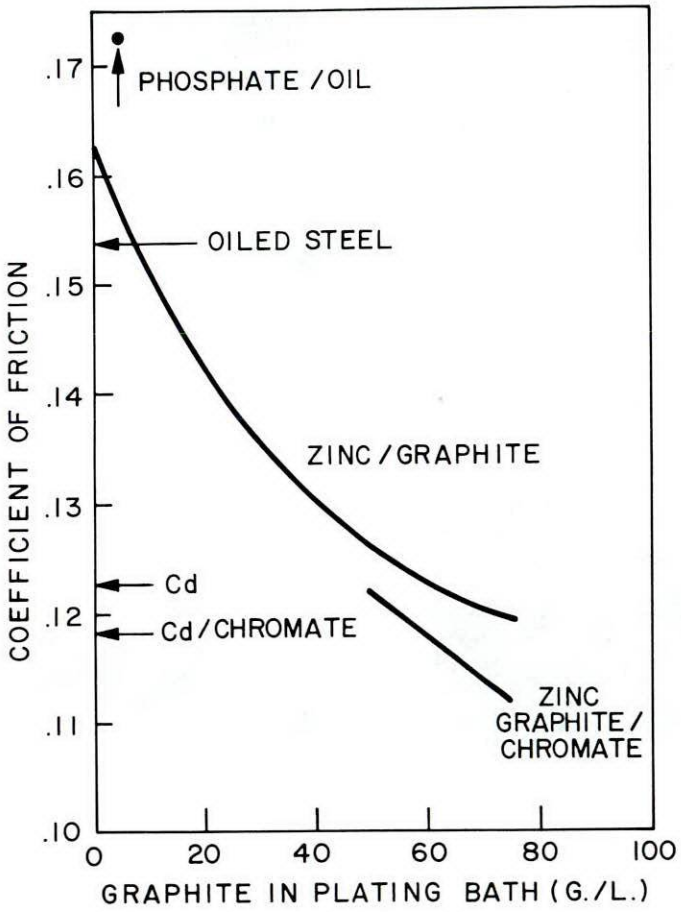
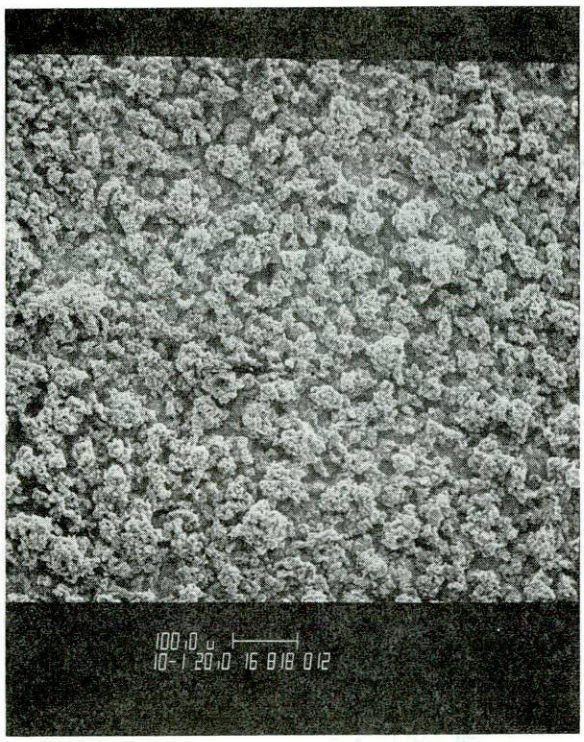


Fig. 3

Also shown in this figure, as points of references, are the coefficient of friction values for coatings of phosphate/oil and zinc which display inconsistent stick-slip performance. For phosphate and oil the average measured coefficient of friction was 0.20, while for zinc it was 0.16. Oiled steel, which is satisfactory for certain applications where minimal corrosion protection is required, had a coefficient of friction of 0.15.

With respect to the zinc/graphite composite the coefficient of friction decreased as the graphite content was increased from 5 to 75 g/l. At 20, 50 and 75 g/l the coefficient of friction values were 0.14, 0.13 and 0.12, respectively. The 0.12 value corresponded to the same value measured for cadmium. For the composite plated in the 75 g/l graphite bath, the coefficient of friction was reduced to 0.11 when the deposit was passivated with a chromate conversion film.



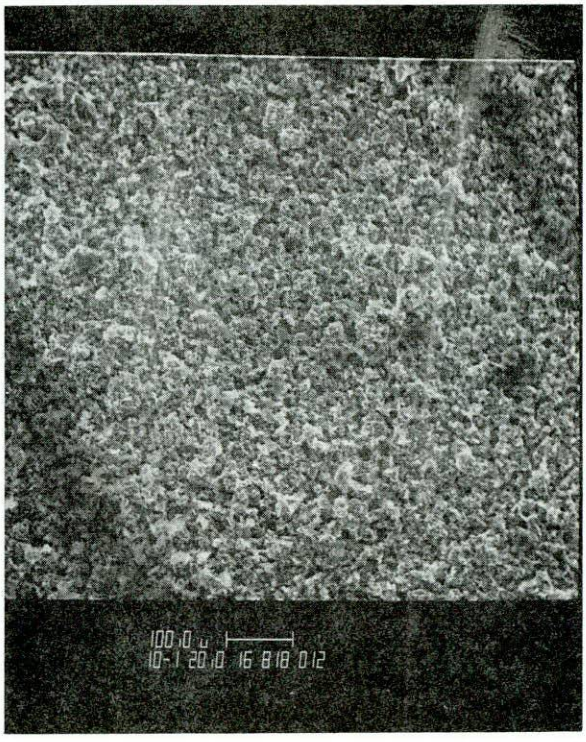


Fig. 4 - 20 g/l graphite bath Fig. 5 - 50 g/l graphite bath
Surface morphology of panels plated in vertical position

Figures 4 and 5 are SEM photographs showing the surface morphology @ 100X magnification of steel panels plated with zinc/graphite in a vertical position. Figure 4 shows a coated panel plated in a 20 g/l graphite bath, and Figure 5 shows a sample plated in a 50 g/l bath. Figure 6 and 7 show the surface morphology of steel nuts barrel plated in a bath containing 50 and 70 g/l respectively. These last two figures show a much smoother appearance than figures 4 and 5. Apparently, the tumbling action of the barrel plated nuts produced a burnished effect on the plated composite.

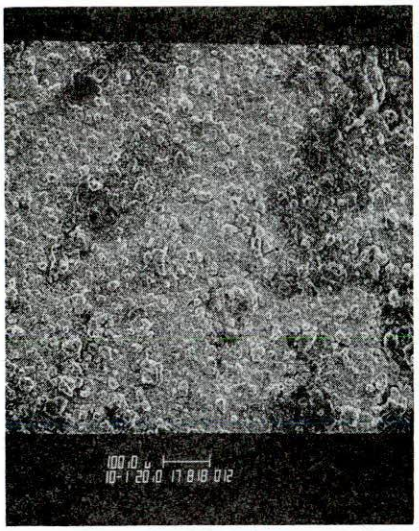


Fig. 6 - 50 g/1 graphite bath

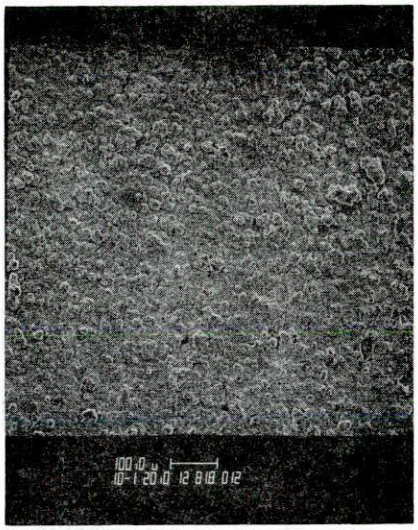


Fig 7. - 75 g/1 graphite bath

Surface Morphology of Barrel Plated Nuts

SALT SPRAY PERFORMANCE

COATING SYSTEM	g / l GRAPHITE	MILS	LIFE (HRS)
PO_4 / OIL	—	0.35	48
Zn / Gr	50	0.5	72
Zn / Gr / CrO_4	50	0.5	120
Zn / Gr	75	0.5	48
Zn / Gr / CrO_4	75	0.5	120
Zn / Gr	120	0.5	48
Zn / Gr / CrO_4	120	0.5	120
Cd / CrO_4	—	0.5	288

Table 3

Table 3 shows the salt spray performance of nuts coated with phosphate/oil; zinc/graphite; zinc/graphite (chromate film); and cadmium with a chromate film. Coatings of zinc/graphite and phosphate/oil provided minimal corrosion protection of the steel substrate (48-72 hr). The salt spray performance of the zinc/graphite composite was improved to 120 hours by passivating the composite with a chromate film. Cadmium plate with a chromate conversion film showed the best performance (280 hours).

Since salt spray data cannot be directly translated to snow belt road corrosion performance, one means of evaluating the corrosion resistance of

new plating systems is to expose the test samples on truck trailers driven in the Detroit and Buffalo area. Figure 8 shows the manner in which the exposure test was carried out.



Fig. 8. Truck trailer used for field corrosion studies

1 WINTER TRAILER EXPOSURE
(BUFFALO & DETROIT)

COATING	THICKNESS (MILS)	PERFORMANCE
ZINC / GRAPHITE	0.2-0.7	NO RUST
ZINC / GRAPHITE CHROMATE	0.2-0.7	NO WHITE OR RED RUST
CADMIUM / CHROMATE	0.5	NO WHITE OR RED RUST
PHOSPHATE / OIL	0.35	RED RUST

Table 4

Table 4 shows the corrosion performance of various coated steel nuts after one winter trailer exposure in the Detroit and Buffalo areas. As shown, the zinc/graphite composite and the cadmium deposit both protected the steel surface from corrosion. In contrast the nuts coated with phosphate and oil failed by red rusting. This test is continuing and it will be interesting to observe the results after two or more winters.

SUMMARY OF PROPERTIES

	PHOSPHATE/OIL	ZINC/GRAPHITE	CADMIUM
"Stick-Slip" Friction	Inconsistent	Low	Low
Salt Spray Performance	Inconsistent	Fair	Excellent
Field Performance	Poor	*	Good
Assembly Productivity	Inconsistent	Excellent	Excellent
Shelf Life	Poor	Excellent	Excellent
Bath Toxicity	Low	Low	High

*Tests in Progress

Table 5

Table 5 is a summary of coating properties, wherein the zinc/graphite composite is compared to commonly used automotive fastener finishes: phosphate/oil and cadmium electrodeposit. Both cadmium and the zinc/graphite composite show a marked superiority over phosphate/oil in "stick-slip friction," corrosion performance, and assembly productivity. With regard to plating bath toxicity, the zinc/graphite composite holds a decisive advantage over cadmium.

Summary and Conclusions

A laboratory plating process has been developed that produces zinc/graphite composites which have anti-friction and outdoor mobile corrosion properties comparable to cadmium. These results indicate that the zinc/graphite composite has the potential of replacing cadmium deposits currently used for automotive fasteners application. However costs, commercial reproducibility, and other possible limitations have not been evaluated for production usage of fasteners plated with the zinc/graphite composite.

Acknowledgements

We are grateful to J. R. Baughman for the assistance he provided in evaluating the coating lubricity properties of test samples used in this program.

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I-5

General Interest Session I

Analysis of Plating Baths by Differential Pulse Polarography

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ANALYSIS OF PLATING BATHS BY DIFFERENTIAL PULSE POLAROGRAPHY

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Polarographic techniques offer two important advantages in plating analysis: a large dynamic working range and the ability to determine both metals and nonmetals in a bath. The wide dynamic range allows these techniques to be used not only to determine major bath components, but trace contaminants and additives as well. Thus, the same technique used to monitor bath composition can also be used for troubleshooting and analysis of waste-water effluents. Detection limits of 10^{-8} M in differential pulse polarography (DPP) have been reported.[1] For Pb^{2+} in solution, this would correspond to 2 μg/L.

The range of applications of polarography is shown in Table 1. This list is far from comprehensive, but it serves to point out a few facts. First, it is often possible to determine the oxidation state of the metal being analyzed. For example, it is possible to determine the concentration of stannous and stannic tin in a bath, as well as the total tin. This ability to speciate metals is important in cases where only one of the species contributes to efficient plating.

Secondly, a variety of commmonly used organic additives with electroactive functional groups can be determined by DPP.[2] A few key classes of electroactive organics which are used as brighteners or levelers in the plating industry are aldehydes, aromatic nitro compounds and azo or diazo compounds.

Finally, it should be noted that anions such as cyanide can be measured by DPP. Although these anions are not themselves electroactive, their presence facilitates the oxidation of mercury, so they can be measured indirectly.

In addition DPP is easy to use and often requires little or no sample preparation. It is a low-cost alternative to other trace analytical methods. In this paper a brief description of the DPP technique and its applications to the analysis of plating baths are discussed. Also, the effect of key experimental parameters and the use of these parameters to solve analytical problems are explained.

Polarographic Apparatus

A basic system for polarographic analysis consists of a potentiostat, a sample cell with electrodes and a recorder. The potentiostat is used to apply a voltage ramp to the electrodes in the sample cell. The current passing through the cell as a function of voltage is then measured, and sent to the recorder. The amount of current which passes is used to determine the concentration of the analyte in the cell. The voltage at which the current appears is characteristic of the type of analyte present.

The sample cell is in some ways analogous to a small plating bath. The sample is mixed with a supporting electrolyte in the cell, and the electrodes are placed into the solution. A typical three electrode system is made up of a platinum wire counter electrode, a dropping mercury working electrode (DME) and a reference electrode. The platinum counter electrode is used simply as an inert anode in most polarographic work. It can also serve as a cathode, depending on the voltage applied to the cell, but the reactions at the counter electrode are not really of interest. It is there simply to complete the circuit.

The reference electrode is used to provide an accurate and reproducible measurement point for the applied voltage. The reference electrode contains an electrochemical half-cell, for example Ag/AgCl, which is separated from the sample solution by a salt bridge.

The working electrode is the one at which the analyte is oxidized or reduced. Mercury is used as a working electrode material because it acts as an excellent cathode for a variety of analytes. There are two key advantages to using a DME. First, the reduction of hydrogen ion to hydrogen occurs at a more negative potential at mercury than at most other electrode materials. This means that a wider voltage region can be scanned, allowing the investigation of a large variety of compounds. Secondly, each mercury drop presents a clean electrode surface to the sample solution. This means that the current measured will not depend on the previous history of the electrode.

The voltage waveform applied to the electrodes depends on the technique selected. The most commonly used technique for routine analysis is DPP, since it provides high sensitivity and easily measured peaks, when current is recorded as a function of applied potential. In the work reported here differential pulse polarography was done using commercially available equipment. *

Determination of Cu^{2+} in an Acid Sulfate Bath

In this first example, DPP is used to quantify a major bath component, Cu^{2+}, in an acid sulfate bath.[3] A typical set of polarograms is shown in Fig. 1. Five polarograms are shown, corresponding to a blank, sample and three additions of a copper standard. The analysis was performed by first placing 10 mL of supporting electrolyte in the polarographic cell, deaerating the solution by bubbling pure nitrogen through it for 5 minutes, and recording the blank scan. The supporting electrolyte is one of the main experimental parameters which the analyst can control. In addition to its basic function of providing solution conductivity, the electrolyte greatly affects the position of the polarographic peaks. Proper choice of electrolyte can often eliminate interferences and insure that the analyte peak is well

* IBM Instruments EC/225 Polarographic/Voltammetric Analyzer, with a 7424 X-Y Recorder.

defined. After the blank run, a small aliquot, 10 μL, of a bath sample was added to the cell, and a second scan was recorded. The peak due to Cu^{2+} occurred at about -0.5 V vs. the saturated calomel reference electrode (SCE). Three successive additions of Cu^{2+} standard were then made to the cell, and a polarogram was recorded after each addition. A plot of peak height vs. concentration of Cu^{2+} added was used to determine the sample concentration, as shown in Fig. 2. The result was reported as g/L $CuSO_4 \bullet 5H_2O$, since this was the salt used to replenish the bath. The instrumental parameters used for the analysis are shown in Table 2.

This entire analysis took less than 15 minutes. Each polarogram was recorded in 70 seconds. Even shorter analysis times could be achieved by using fewer standard additions, or by using a calibration curve method. The analysis time can also be cut down by deaerating enough supporting electrolyte for several runs at the same time.

Simultaneous Determination of Pb^{2+} and Sn^{2+} in a Plating Bath

In this analysis, a voltage window was chosen which allowed two peaks to be observed in each polarogram as shown in Fig. 3. The two peaks, at -0.48 V and -0.62 V vs SCE are due to the reduction of Pb^{2+} and Sn^{2+} respectively.[3,4] The instrumental parameters used in the analysis are listed in Table 3. A brief description of these parameters and their effect on the shape of the polarogram follows.

E initial and E final are simply the voltages at which the scan begins and ends. The scan rate determines the time required for each 'run'. The scan rate, together with the drop time, also determines the number of data points collected per polarogram. In DPP two current measurements are made near the end of each drop and the difference current is plotted. The previously measured current is held until the new value is measured. This accounts for the small steps observed in the polarogram. Generally, scan rates from 1-20 mV/sec are used in DPP, to minimize the width of these steps.

Drop time can also affect the sensitivity of the polarogram. Longer drop times result in larger electrode area, and thus higher current. Of course, since the drop is an expanding sphere, the increase in area is not linear with time. Drop times from 0.5 to 2.0 seconds are commonly used.

The last parameter is the pulse amplitude. To fully understand the effect of this parameter, it would be necessary to examine the DPP waveform in detail, which is outside the scope of this paper. An extensive literature on polarographic techniques exists for anyone interested in further study.[5-7] From a practical standpoint, however, the following rules hold: A large pulse amplitude results in peaks which are higher and broader. A small pulse amplitude results in shorter and narrower peaks. Pulse amplitudes typically range from 5 mV to 115 mV, with 50 mV giving a nearly optimum trade-off between sensitivity and resolution.

In the determination of Pb^{2+} and Sn^{2+}, resolution is a primary concern, and the choice of pulse amplitude can be used to good advantage. Since the two peaks are only about 150 mV apart, they can begin to overlap, particularly at high concentrations. By using a small pulse amplitude, 5-30 mV, and by diluting the bath sample sufficiently, good resolution between the peaks is obtained.

Determination of Formaldehyde in an Electroless Copper Bath

Figure 4 demonstrates the use of DPP to determine an organic constituent, formaldehyde, in an electroless copper bath.[3] Again, a standard addition experiment was done to quantify the formaldehyde. It should be pointed out that formaldehyde is unstable in highly alkaline supporting electrolyte, so the analysis should be completed quickly once the bath sample is added to the cell. Despite this minor disadvantage, the alkaline supporting electrolyte was the best choice for this particular bath. It provided a well defined peak, the height of which increased linearly with concentration in the range studied. In addition, the alkaline conditions insured that the cyanide, which was also present in the bath, did not evolve. The instrumental parameters used are listed in Table 4.

Determination of Cyanide in a Plating Bath

Certain anions can also be determined by DPP. Figure 5 shows the determination of cyanide in a plating bath.[8-10] The instrumental parameters used are listed in Table 5. This analysis is based on an indirect reaction, as shown below:

$$Hg + 2CN^- \longrightarrow Hg(CN)_2 + 2e^- \qquad (1)$$

The formation of the salt, HgCN, causes the mercury oxidation to occur at a less positive potential than usual. The height of the oxidation peak varies linearly with the cyanide concentration. Other anions which have this effect include chloride, bromide and iodide.[11] Certain sulfur containing organics, such as thiourea, can form insoluble complexes with mercury which have the same effect.[12]

Summary

DPP is a versatile, sensitive and rapid technique that offers several advantages for the analysis of plating baths. These few examples represent only a fraction of the plating analyses which can be handled by DPP. When other electroanalytical techniques, such as stripping voltammetry and voltammetry at various solid electrodes, are also considered, the potential applications are even greater. The ability of these methods to determine both metals and non-metals and the low cost of modern electroanalytical instrumentation make a powerful case

for adding these capabilities to any laboratory where plating bath analysis is done.

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Table 1

Applications of Polarography to Plating Bath Analysis

BASE METALS	PRECIOUS METALS	ORGANICS	ANIONS
Cd^{2+}	Au^{1+}, Au^{3+}	BENZALDEHYDE	CHLORIDE
Cu^{1+}, Cu^{2+}	Pd^{2+}	BENZOQUINONE	CYANIDE
Ni^{2+}	Pt^{4+}	CYSTINE	SULFITE
Pb^{2+}	Rh^{3+}	FORMALDEHYDE	
Sn^{2+}, Sn^{4+}		NAPHTHALENE-1-SULFONIC ACID	
Zn^{2+}		THIOUREA	

Table 2

Instrumental Parameters for the Determination of Cu^{2+}

E initial:	-0.35 V
E final:	-0.70 V
Scan Rate:	5 mV/sec
Drop Time:	1.0 sec
Pulse Amplitude:	50 mV
Supporting Electrolyte:	0.5 M NaOH, 0.05 M EDTA
pH:	13

Table 3

Instrumental Parameters for the Determination of Pb^{2+} and Sn^{2+}

E initial:	-0.30 V
E final:	-0.80 V
Scan Rate:	5 mV/sec
Drop Time:	1.0 sec
Pulse Amplitude:	30 mV
Supporting Electrolyte:	2 M Na Acetate, 2 M Acetic Acid
pH:	4

Table 4

Instrumental Parameters for the Determination of Formaldehyde

E Initial:	-1.42 V
E Final:	-1.82 V
Scan Rate:	5 mV/sec
Drop Time:	1.0 sec
Pulse Amplitude:	50 mV
Supporting Electrolyte:	0.5 M NaOH, 0.05 M EDTA
pH:	13

Table 5

Instrumental Parameters for the Determination of CN^-

E Initial:	-0.37 V
E Final:	-1.00 V
Scan Rate:	5 mV/sec
Drop Time:	0.5 sec
Pulse Amplitude:	50 mV
Supporting Electrolyte:	0.2 M KOH, 0.05 M EDTA
pH:	13

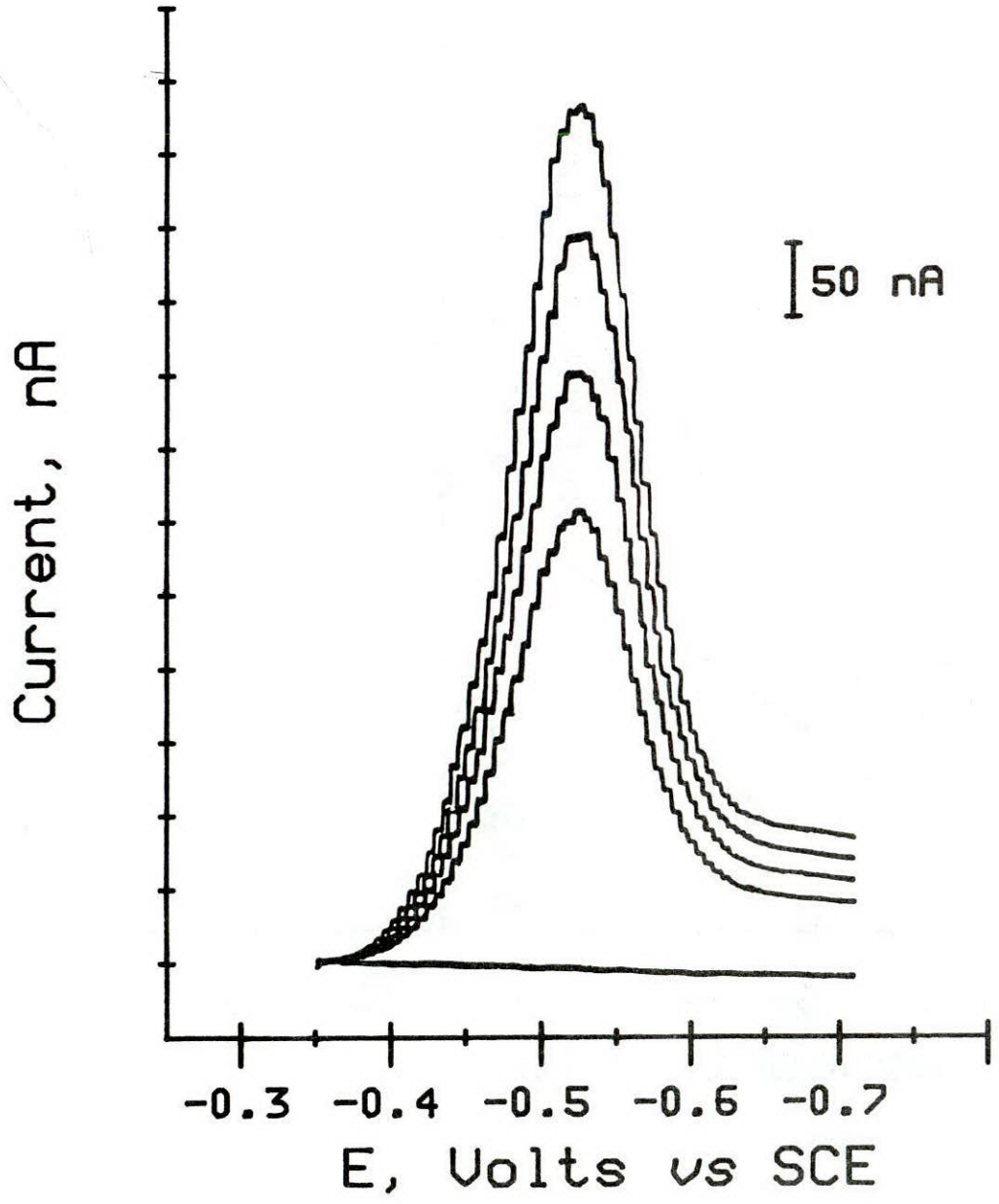

Fig. 1 - Determination of Cu^{2+} in an acid sulfate bath.

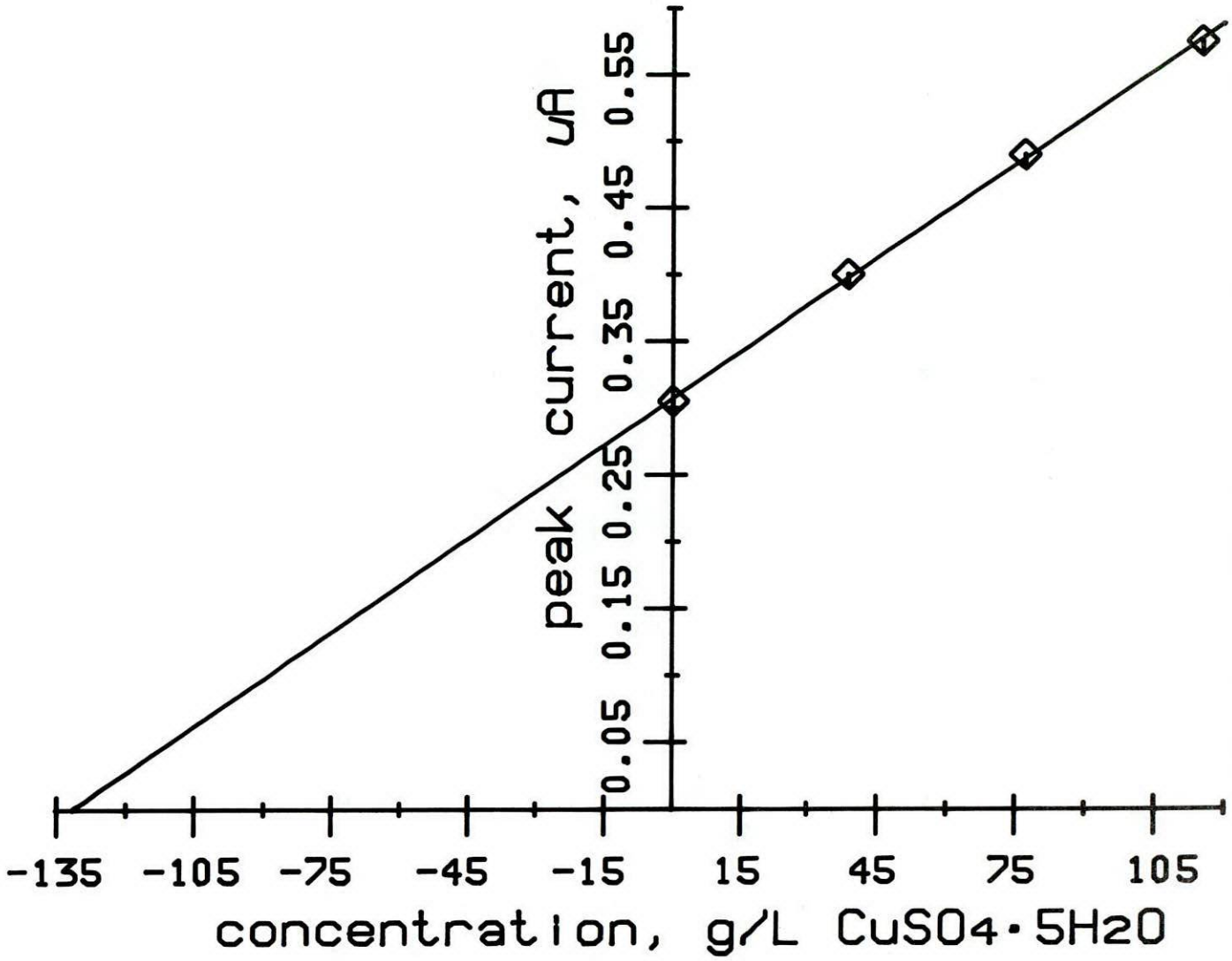

Fig. 2 - Standard addition plot for Cu^{2+} in an acid copper bath.

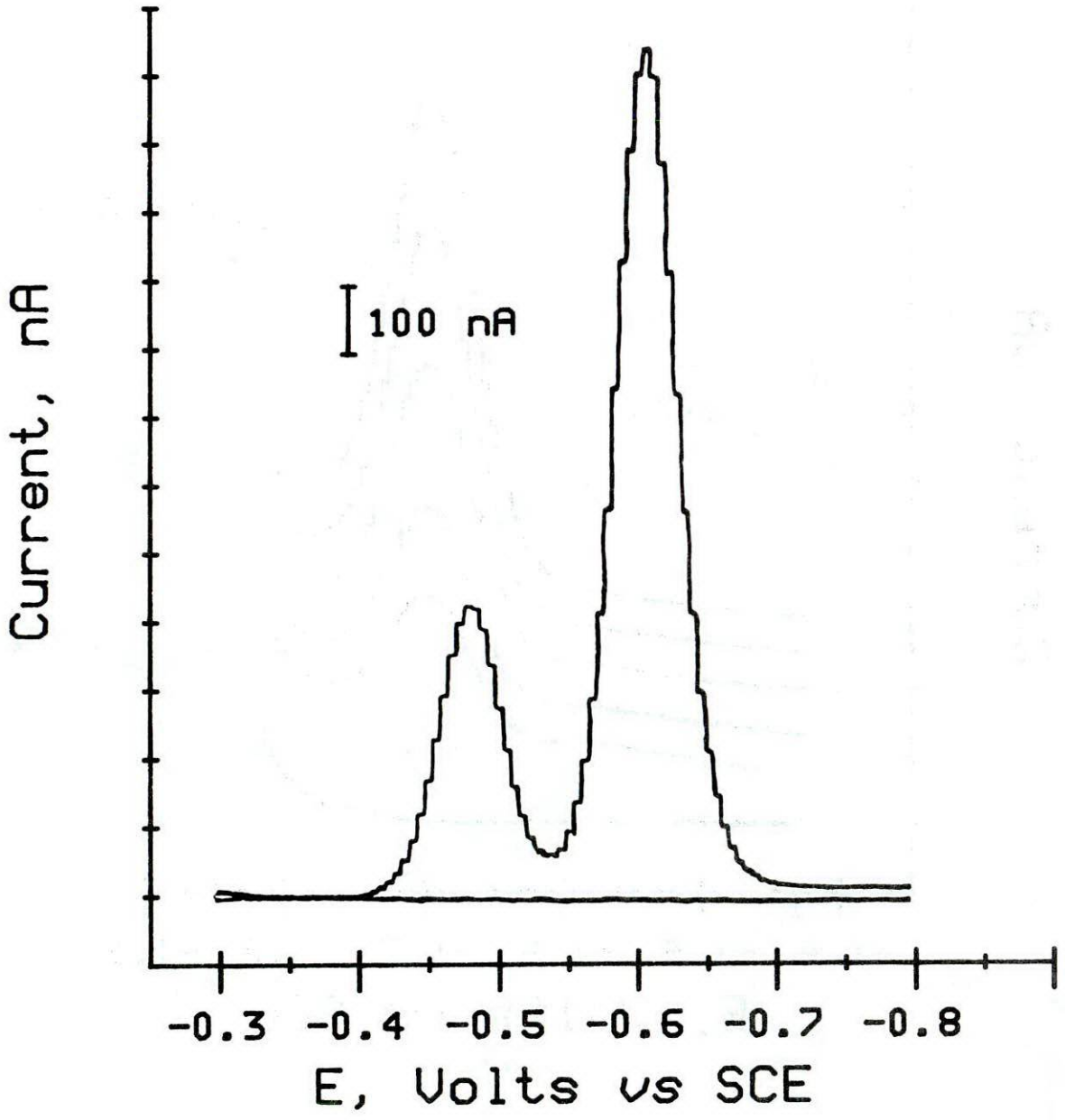

Fig. 3 - Simultaneous determination of Pb^{2+} and Sn^{2+} in a plating bath.

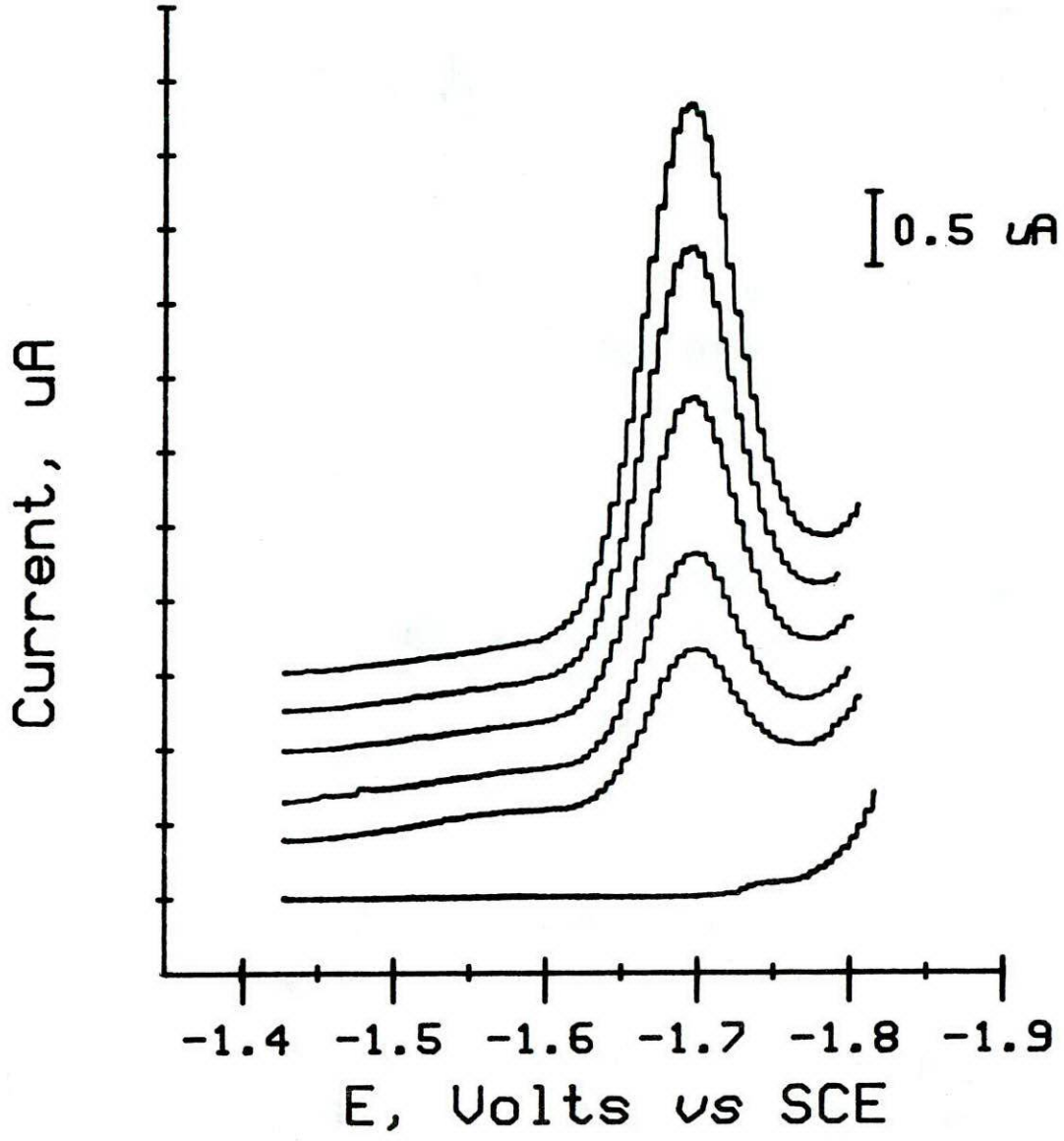

Fig. 4 - Determination of formaldehyde in an electroless copper bath.

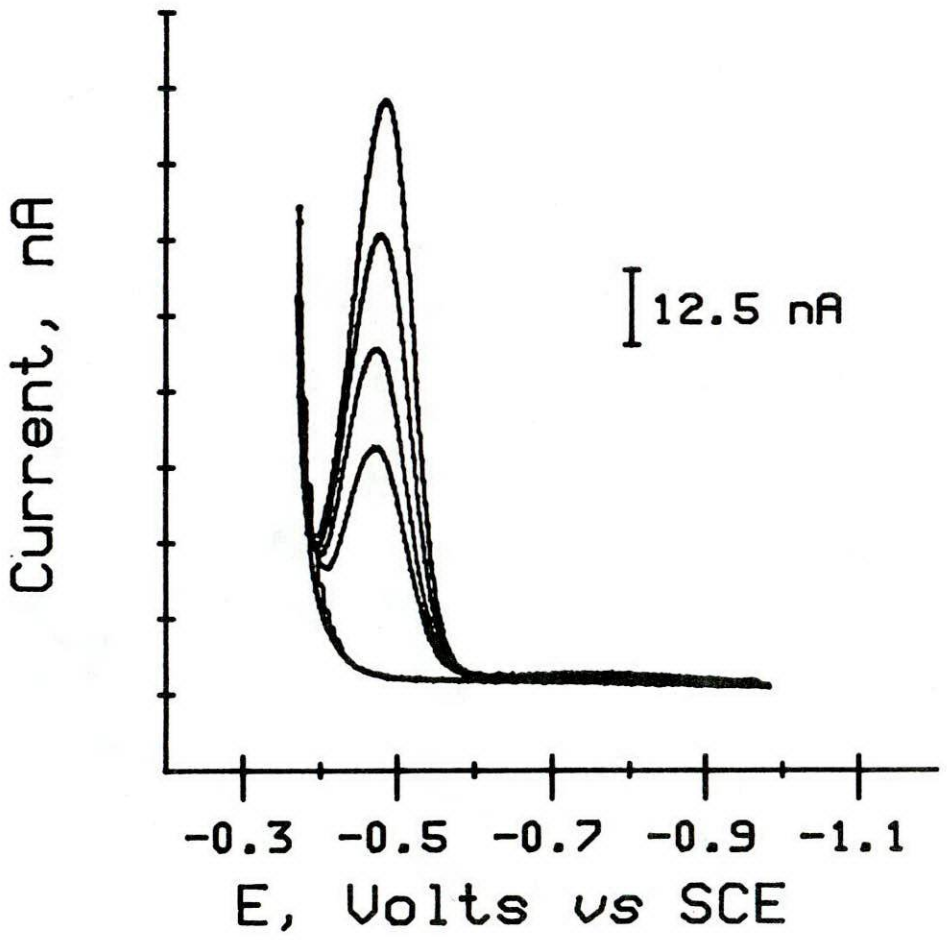

Fig. 5 - Determination of cyanide in a plating bath.

I-6

General Interest Session I

Rapid Analysis and Troubleshooting of Gold, Copper and Nickel Plating Bath Chemistry by Ion Chromatography

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RAPID ANALYSIS AND TROUBLESHOOTING OF GOLD, COPPER AND NICKEL PLATING BATH CHEMISTRY BY ION CHROMATOGRAPHY

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INTRODUCTION

The use of high speed plating processes impose higher demands on plating baths which in turn, require more rapid monitoring and control for optimum performance. Electroless processes also require frequent monitoring for replenishment purposes. Analytical techniques offering speed, versatility, and ease of operation are needed. The purpose of this paper is to demonstrate how Ion Chromatography has been and can be employed to monitor, control and troubleshoot critical chemical balances in plating solutions.

Ion Chromatography (IC) is a technique which can be used to rapidly detect, identify, and quantify a wide variety of plating solution constituents. Some species of special interest include metal complexes ($Au(CN)_2^-$, $Au(CN)_4^-$, $Co(CN)_6^{3-}$, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, $Ni(EDTA)^{2-}$, $Cu(EDTA)^{2-}$); common anions (Cl^-, Br^-, NO_3^-, HPO_4^{2-}, PO_2^{3-}, SO_4^{2-}, BF_4^-); cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}); organic acids (citric, formic, succinic) as well as carbonate and borate; transition metals (Fe^{3+}, Fe^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Pb^{2+}); and surfactants such as sodium lauryl sulfate.

Ion Chromatography has been extensively employed for analysis of various plating solutions, acid etchants, conversion coatings, and cleaning solutions. Although IC analysis is applicable to the control and troubleshooting of a wide variety of plating solutions, the specific examples in this paper will address only gold, copper, and nickel solutions.

PRINCIPLES OF THE TECHNIQUE

Ion Chromatography (IC) is a unique analytical technique which specifically addresses the chromatography of ionic species. The system, which is schematically depicted in Figure 1, consists of an eluent delivery mode, a spearation mode, and a detection mode. An eluent is pumped through the system and a liquid sample is introduced into the flowing eluent stream via an injection valve situated upstream of the separator column. The eluent flow carries the ionic species through an analytical column that contains a neutral, anionic or cationic resin. Since the respective ionic species present in the sample have different affinities for the resin, they are separated into discrete bands before entering the detector. Identification and quantification are determined by comparing the retention times and peak heights with those of known standard solutions. Data reduction is accomplished manually or by use of electronic integration.

The separation mode employed depends upon the ionic nature of the sample ions of interest. Three distinct separation modes can be employed and are summarized in Table I. High Performance Ion Chromatography (HPIC) is the

mode of choice for common inorganic ions such as F^-, Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, Mg^{2+}, Ca^{2+}, Fe^{3+}, and Zn^{2+}. The separation, based on ion exchange, is accomplished on a low capacity ion exchange resin. The theory of HPIC has been discussed by Small et al.[1]

Mobile Phase Ion Chromatography (MPIC) is the optimal separation mode for hydrophobic ions such as alkyl and aryl sulfonates and sulfates, metal cyanide complexes, SCN^-, BF_4^-, and quaternary and alkyl amines. The mechanism of separation is ion-pairing and adsorption which occurs on a neutral resin. This separation theory has been discussed in depth by Iskandarani[2] and Bidlingmeyer[3].

High Performance Ion Chromatography Exclusion (HPICE) is commonly used for the separation of weak organic acids such as formic, succinic, and citric. The mechanism is predominately dependent on pKa values and ion exclusion, however, adsorption also plays a role. Wheaton and Bauman[4] have discussed ion exclusion theory in detail.

The column packing material utilized in all of the separation modes, regardless of the resin functionality, is based on a polystyrene-divinylbenzene (PS/DVB) support. Unlike silica based packing, these resins are stable from pH 1-13. The excellent durability of the column packing material allows easy column clean-up with either strong acid or strong base.

Detection of the ions of interest can be accomplished in a variety of ways depending upon the chemical and optical properties of the sample ions. Four distinct detection modes are employed and these are summarized in Table II.

Suppressed conductivity is the most common detection mode used for ions with pK values <7. Highly conductive eluents are required to elute the sample ions from the separator column. If a conductivity detector cell was placed immediately after the separator column, the sample ions would be detected as small conductivity changes in a large background signal. Insertion of a suppressor, a second ion exchange device connected in series after the separator column, chemically converts the eluent to a less conductive form. The sample ions are thus detected as large changes in a low background conductivity. This increases sensitivity, extends the linear range, and promotes selectivity in detection. The actual suppression mechanisms differ depending on the chemical content of the eluent. Small et al[1] should be consulted regarding the actual mechanisms.

Three other detection modes are available in addition to suppressed conductivity. A UV/VIS detector can be used to detect ultraviolet or visible absorbing species in combination with any separation mode. Combined with a post column reactor utilizing a metallochromic indicator, this detector is used in the visible region for selective detection of the transition and heavy metals such as Fe^{3+}, Fe^{2+}, and Co^{2+}.[5] Amperometric detection is employed for species which can be oxidized or reduced, such as CN^-, HS^-, hydrazine, phenolics, carbohydrates, and mercaptans.[6 & 7] A fluorescence

detector can also be used following post column reaction for the sensitive and selective determination of amino acids. By use of multiple separation and detection modes, a wide variety of inorganic and organic anions and cations can be determined in complex matrices. Furthermore, trace level (ppm and ppb) analysis can be accomplished in the presence of high concentrations of other species, as is often the case in plating analysis where minor components or contaminants are of major concern.

PLATING BATH ANALYSIS

For plating bath applications, the sample preparation generally involves no more than a simple dilution step followed by, at times, a filtration. All the separation and detection techniques utilized in Ion Chromatography apply to plating analysis, depending upon the particular species of interest.

GOLD PLATING BATHS

Cyanide based plating solutions containing phosphate and/or citrate buffers are common gold plating solutions. Within the bath, the Au exists as stable gold cyanide complexes, with $Au(CN)_2^-$ the most prominent. With use, the Au^{3+} content increases forming a $Au(CN)_4^-$ complex and causes plating efficiency to decline significantly. Consequently, a convenient method of differentiating between the two gold cyanide complexes is a key monitoring tool. Although important, total gold values shed no light on oxidation states. Figure 2 illustrates a determination of the two gold cyanide complexes in a phosphate/citrate buffered gold plating bath. Sample preparation involved only dilution 1/200 with deionized water. Since the Au^{3+} levels in this sample were relatively low (100 ppm), the detector attenuation was changed to a more sensitive range. In this way, both gold species are determined from a single injection.

The cobalt content is also of interest in the gold baths that are alloyed with cobalt to impart hardness. The cobalt is usually added as the $CoSO_4$ or in chelated forms. If free CN^- is generated in the bath during plating, the Co^{2+} can easily convert to Co^{3+} and be present as the $Co(CN)_6^{3-}$ complex. In this form, the cobalt no longer functions as intended and the plate is affected. The $Co(CN)_6^{3-}$ is also a very strong complex and is easily determined in gold cyanide baths as illustrated in Figure 3. Other strong cyanide complexes which can be determined in Au cyanide baths include $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$.

Carbonate (Figure 4) present as a buffering agent in alkaline baths, is also easily determined using an alternate set of conditions. Other ions of interest in gold cyanide based baths that are readily determined by IC include the PO_4^{2-} and citrate content and trace Cl^- contaminents. Free cyanide is also easily determined by using the amperometric detector. If this detector is placed in series with the conductivity detector during the cyanide complex analysis, the free CN^- level would be determined simultaneously from a single injection. Although the majority of the methods developed to-date involve cyanide based baths, applications are being developed for sulfite, thiomalate and electroless gold baths.

COPPER PLATING BATHS

Copper Sulfate

When plating bright copper from a H_2SO_4 bath, a relatively small amount of Cl^- is necessary, as is commonly known, to increase the throwing power of bright copper baths. As illustrated in Figure 5, IC can be utilized for the determination of the low Cl^- level as well as the major constituent (sulfate) level from the same sample injection.

Many copper baths contain ppm levels of organic brighteners, levelers, or carriers. In some cases, these are anionic or cationic and are amenable to separation and detection by IC. Figure 6 illustrates the determination of an anionic brightener in a copper sulfate bath. In this particular case, UV detection was used due to excess sulfate which made conductivity detection impractical. The other peaks were not identified, however as bath use increased, the magnitude of these peaks also increased, possibly due to breakdown of some bath constituents or organic contamination. Although the chemical nature of many additives is proprietary, if some knowledge of the structure can be obtained and the additive is amenable to IC analysis, IC can be used in a monitoring capacity to quickly troubleshoot additive imbalances. The analysis of organic additives can also be applied to other types of plating baths.

In addition to copper, other metals can affect bath performance and plate quality. Figure 7 illustrates the determination of Zn^{2+} and Ni^{2+} contaminants in a $CuSO_4$ plating bath. By further dilution, the major metal content (Cu^{2+}) could also have been determined.

Copper Pyrophosphate

Ammonia improves the uniformity of the deposit in copper pyrophosphate baths as well as assisting in anode corrosion.[8] Since NH_3 is lost by evaporation, due to the bath's elevated temperature, frequent additions of NH_3 are necessary to maintain optimum conditions. Ammonia levels are rapidly determined as illustrated in Figure 8. The levels can then be adjusted if necessary.

Another common component of copper pyrophosphate baths is NO_3^- which increases the allowable maximum current density.[8] Figure 9 illustrates the determination of NO_3^- as well as the HPO_4^{2-} breakdown product of $P_2O_7^{4-}$ formed during the plating process. Using IC, a single sample analysis can determine the NO_3^- level as well as ensuring that the phosphate level is not excessive. Work is under way to develop a method for the determination of Cu^{2+} to $P_2O_7^{4-}$ ratios or the Cu pyrophosphate complex.

Electroless Copper

Major components of an electroless copper bath include formaldehyde and various chelators such as tartrate. During the plating process the formaldehyde is oxidized to formic acid. Both formic and tartaric acids are easily determined by IC (Figure 10). In this way, proper tartrate levels

can be maintained, as well as the detection of premature bath aging which is associated with rapidly increasing formate levels. IC is also commonly employed for industrial hygiene monitoring of formaldehyde which is measured as formate following a rapid oxidation with H_2O_2.[9] Although this method has not been applied to the determination of formaldehyde in an electroless copper bath, the approach appears feasible. Other applications that are under development for electroless copper baths include triethanolamine (Figure 11), EDTA, and the $Cu(EDTA)^{2-}$ complex.

NICKEL BATHS

Nickel baths investigated by IC to-date include nickel sulfamate, alloyed Ni/Fe and both electroless Ni and Ni/Co.

Nickel Sulfamate

Nickel sulfamate baths often contain chloride, sometimes added intentionally and other times present as a contaminent. Figure 12 illustrates the determination of Cl^- in a bath containing HCl. Note that the sulfamic acid as well as the SO_4^{2-} breakdown product of the sulfamic acid can be monitored in the same injection with 10 minutes. Trace level chloride determinations would be easily obtained by changing the eluent composition slightly and hence completely resolving chloride from sulfamate. If required, the NH_4^+ breakdown product of the sulfamic acid could also be monitored under different analysis conditions.

Alloyed Nickel Sulfate-Chloride

As well as containing significant levels of Cl^- and SO_4^{2-}, many of the Ni and Ni alloy baths contain H_3BO_3 as a mild buffer. The analytical methods of analysis for borate were previously lacking and most commonly, time consuming titrations with ill-defined endpoints were used. Figure 13 illustrates the determination of borate in a Ni/Fe bath. This technique is applicable to low level analysis as required for waste water. The concentration in the figure corresponds to 3.5 ppm, and the bath concentration is 35 g/L. If analysis of metals is employed, the Ni/Fe ratios can be determined under one set of conditions, or trace contaminents such as Cu^{2+} can be monitored as in Figure 14 and 15 respectively.

Electroless Nickel

Hypophosphite is used as the reducing agent in many pure or alloyed electroless Ni processes. As the bath is plated, the hypophosphite is depleted and phosphite is generated. Analytical methods for differentiation of phosphorous species have not been available and actual levels were commonly determined by difference. Figure 16 contrasts levels of the different phosphorous species in new and used electroless nickel baths. As expected, the hypophosphite level decreased and the phosphite level increased after a period of use. Hence, IC offers a rapid means for process monitoring of these species.

Organic acids are present in electroless nickel baths as mild chelators. Figure 17 illustrates the ease with which these organic acids can be determined. When plating from an alloy bath, the ratio of the metallic ions is an important parameter. Figure 18 illustrates the determination of the Ni/Co ratio in an electroless alloy bath.

Additives

Nickel bath additives include aromatic or alky sulfonic acids or sulfates, such as sodium lauryl sulfate. Although an IC method of analysis exists for these types of species, it has not yet been applied to a plating sample. Figure 19 illustrates a standard separation.

CONCLUSION

Ion Chromatography offers a fast, versatile and simple analytical procedure for determining a multitude of key plating components. Minimal sample preparation and rapid analysis times permit fast process troubleshooting. Furthermore, the comprehensive data generated by IC promotes a sound understanding of gold, copper, and nickel bath chemistry which can be used to optimize process control and economics. IC also permits the analysis of ionic components that were previously difficult or impossible to monitor, which may play a key role in bath performance.

TABLE I

SUMMARY OF SEPARATION MODES

	Predominant Separation Mechanism	Resin Functionality	Standard Eluents	Useful For:
HPIC	Ion Exchange			
Anion	"	$-N^+-R_3$	$Na_2CO_3/NaHCO_3$	Cl^-, NO_3^-, Br^-, SO_4^{2-}, PO_2^{3-}, PO_3^{3-}, CrO_4^{2-}, AsO_4^{3-}
Cation	"	$-SO_3^-$	HCl	Li^+, Na^+, NH_4^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}
Metals	"	$-N^+-R_3$ or $-SO_3^-$	Oxalic and Citric Acid	Fe^{3+}, Fe^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Pb^{2+}, Mn^{2+}, Cd^{2+}, Al^{3+}
MPIC	Ion Pairing and Adsorption	Neutral		
Anion	"	"	Tetrabutyl NH_4OH (TBAOH) CH_3CN	$Au(CN)_2^-$, $Au(CN)_4^-$, $Co(CN)_6^{3-}$ Alkyl sulfonates and sulfates BF_4^-
Cation	"	"	Hexane sulfonic acid (HSA) CH_3CN	Alkyl and quaternary amines
HPICE	Ion Exclusion	Totally functional $-SO_3^-$	HCl	Formate, citrate, tartrate, succinate, lactate, carbonate, borate

TABLE II

DETECTION MODES

	Principle	Most Useful For:
Suppressed Conductivity	Electrical conductivity	Anions or cations with $pK_{a \text{ or } b}$ values <7 eg. Cl^-, SO_4^-, Na^+
Amperometric	Oxidation or reduction at Ag or Pt electrodes	CN^-, S_2^-, mercaptans, OCl^-, hydrazine
Pulsed Amperometric	Oxidation or reduction at Ag, Pt, Au, or glassy carbon electrodes	Phenolics, carbohydrates, nitro aromatics
Direct UV VIS after PCR	Ultraviolet light absorption Visible light absorption after reaction with a post column reagent	Aromatic organics and select anions Transition and heavy metals after post column reaction with 4-(2-pyridylazo)-resorcinol (PAR) Polyvalents after reaction with $Fe(NO_3)_3$
Fluorescence after PCR	Excitation and Emission	Amino acids after reaction with o-phthalaldehyde

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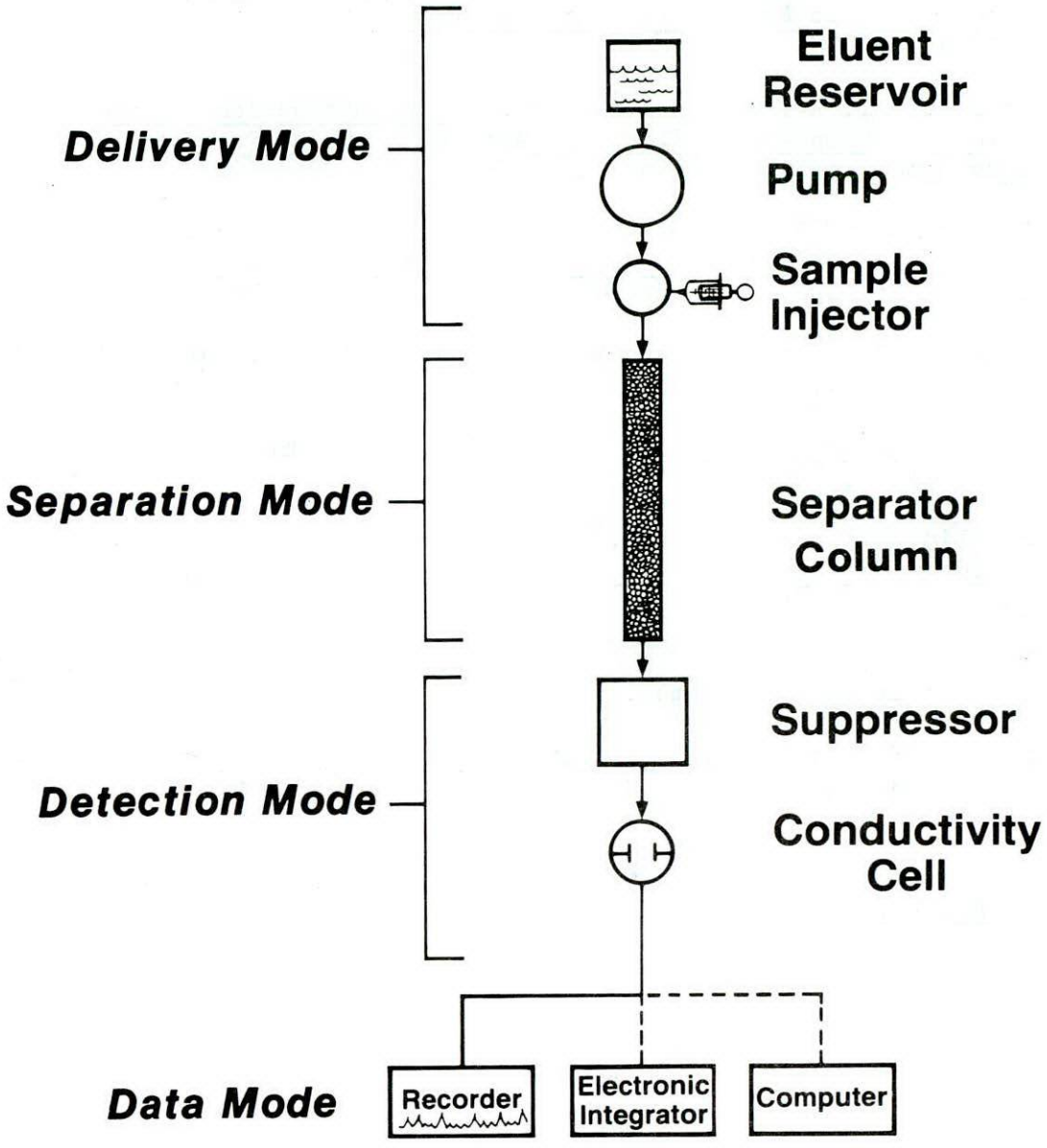


Figure 1. Schematic representation of the Ion Chromatographic system.

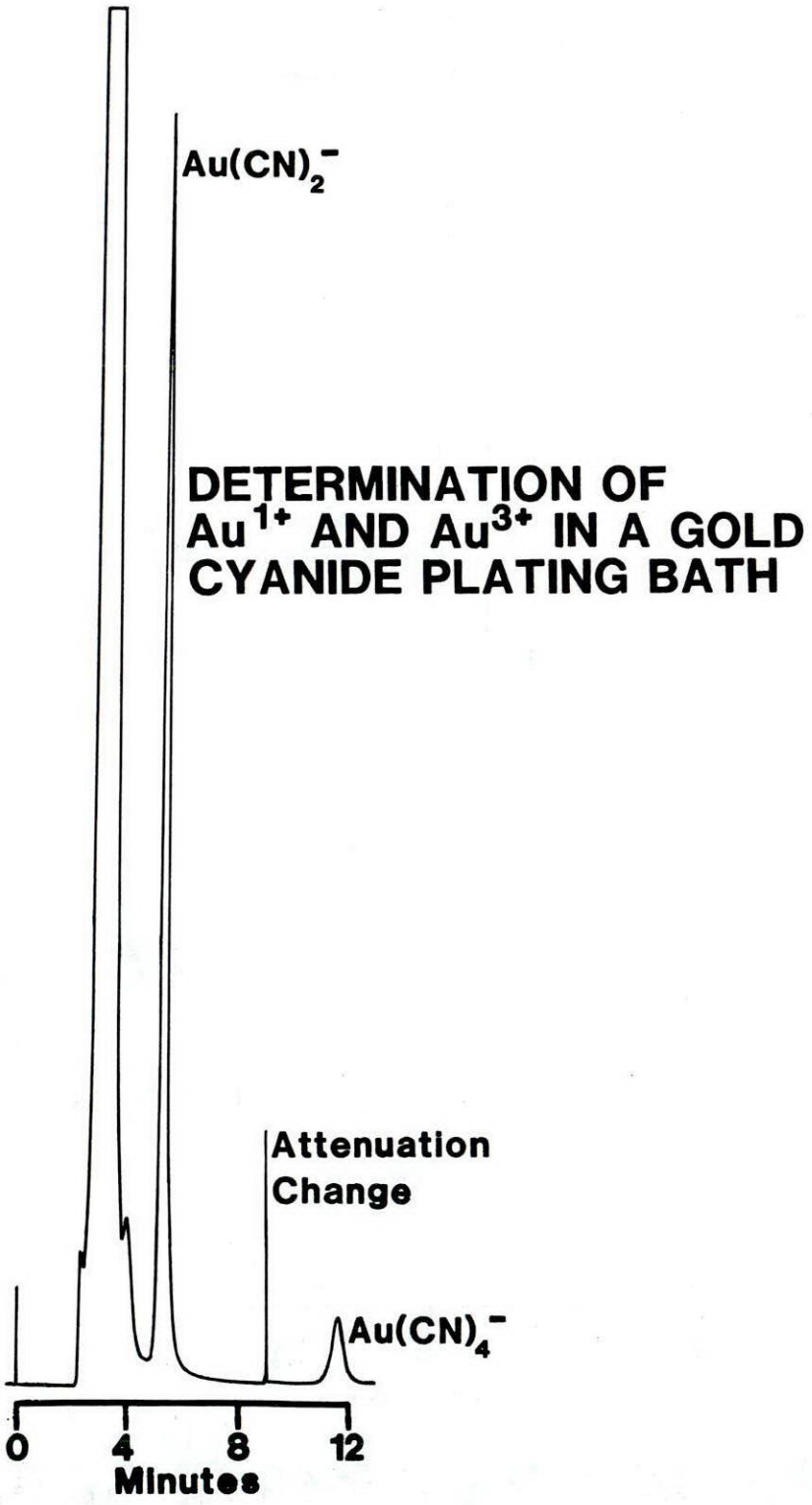
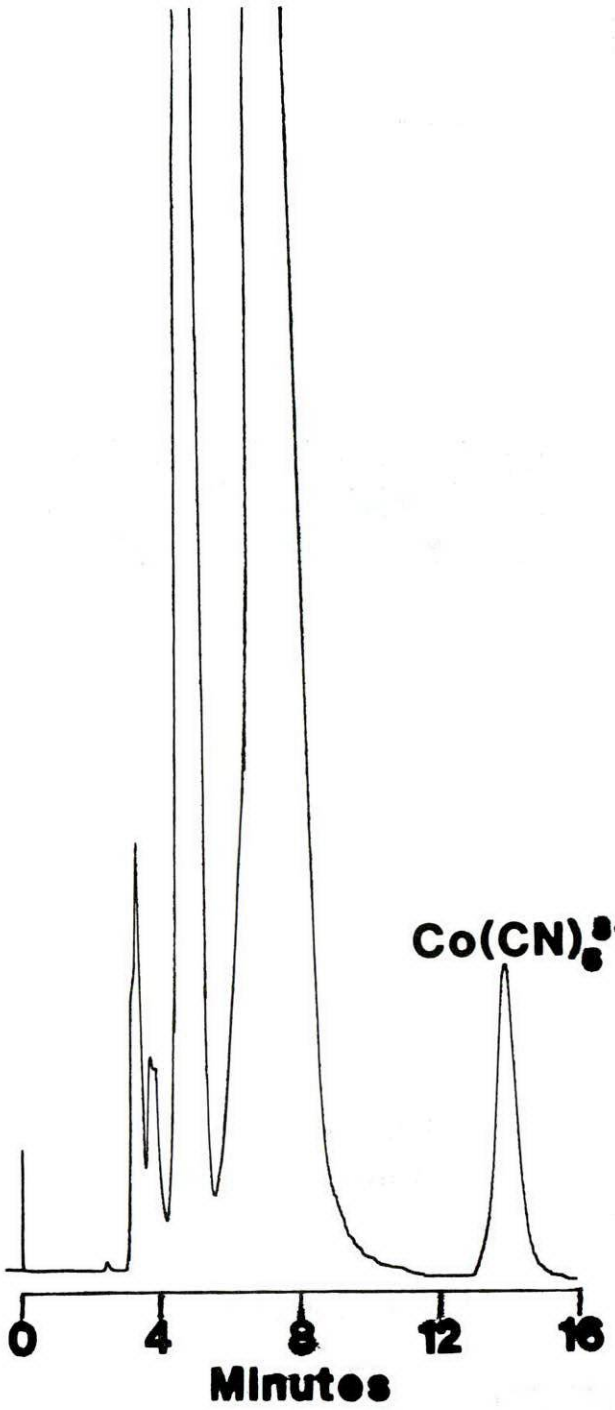
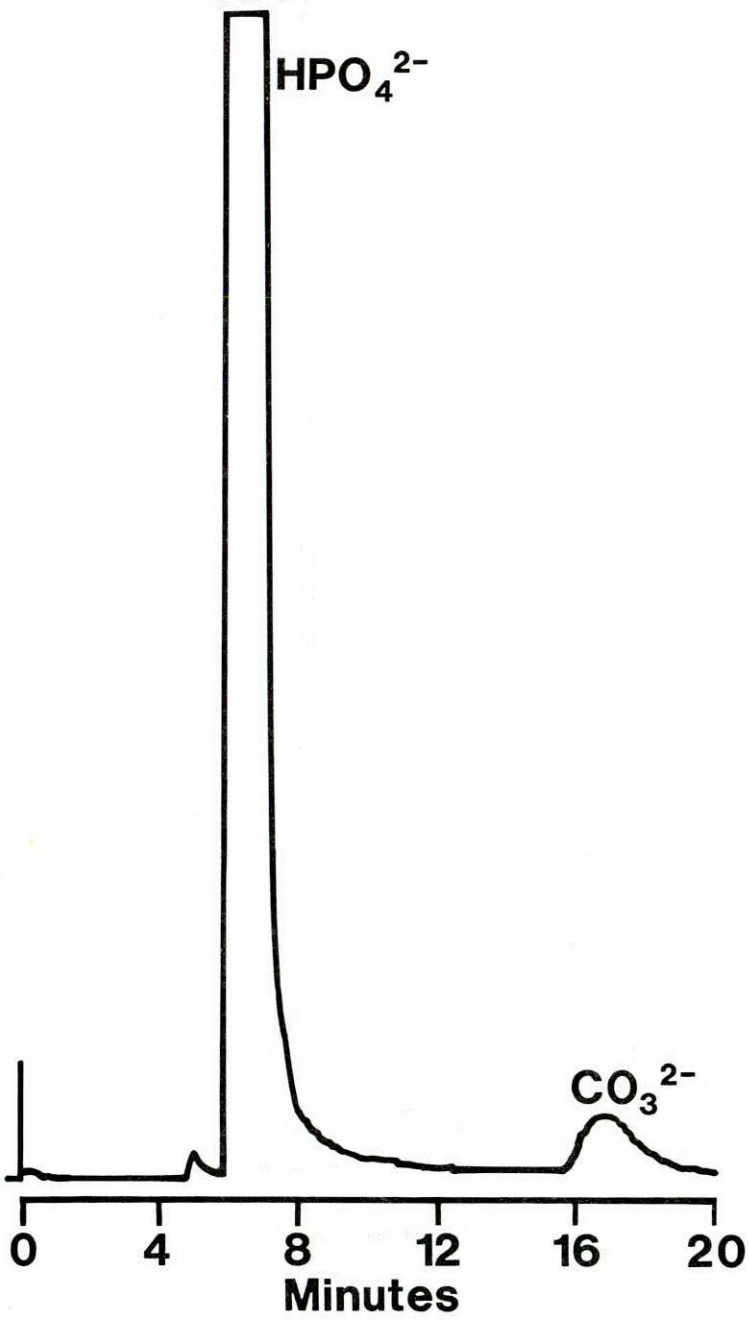


Figure 2. Columns: 1 MPIC-NG1 and 1 MPIC-NS1. Detection: ASC-1, conductivity at 30 and 3 μS. Sample: 50 μl of .5/100 dilution of bath. Eluent: 2 mM TBAOH, 40% CH_3CN, 1 mM Na_2CO_3.



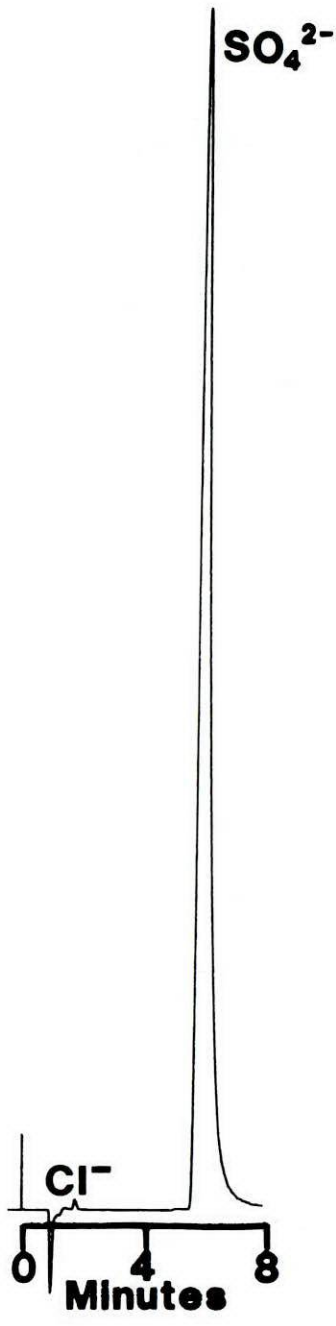
$Co(CN)_6^{3-}$ IN A PHOSPHATE-CITRATE BUFFERED GOLD PLATING BATH

Figure 3. Columns: 1 MPIC-NG1, 1 MPIC-NS1. Detection: ASC-1, conductivity at 10 µS. Sample: 50 µl of .25/100 dilution of bath. Eluent: 2 mM TBAOH, 10% CH_3CN.



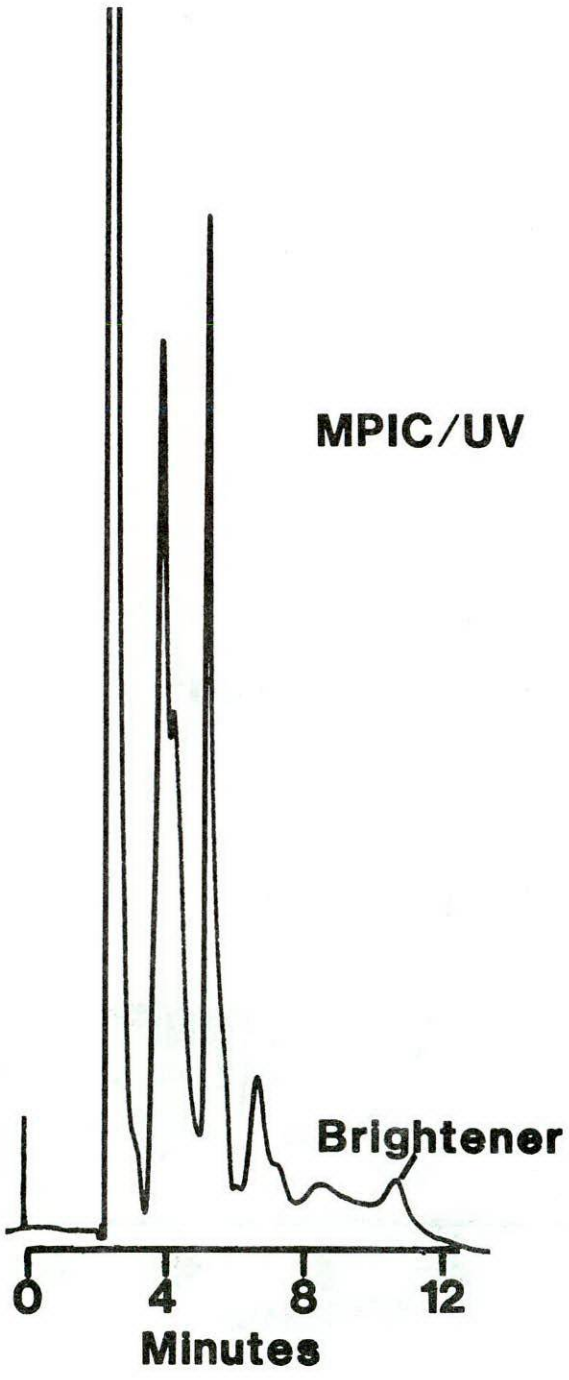
CARBONATE IN A GOLD CYANIDE PLATING BATH

Figure 4. Columns: 1 HPICE-AS1. Detection: ISC condictivity 10 µS. Sample: 50 µl of 1/100 dilution of bath. Eluent: .005 M HCl, .8 ml/min.



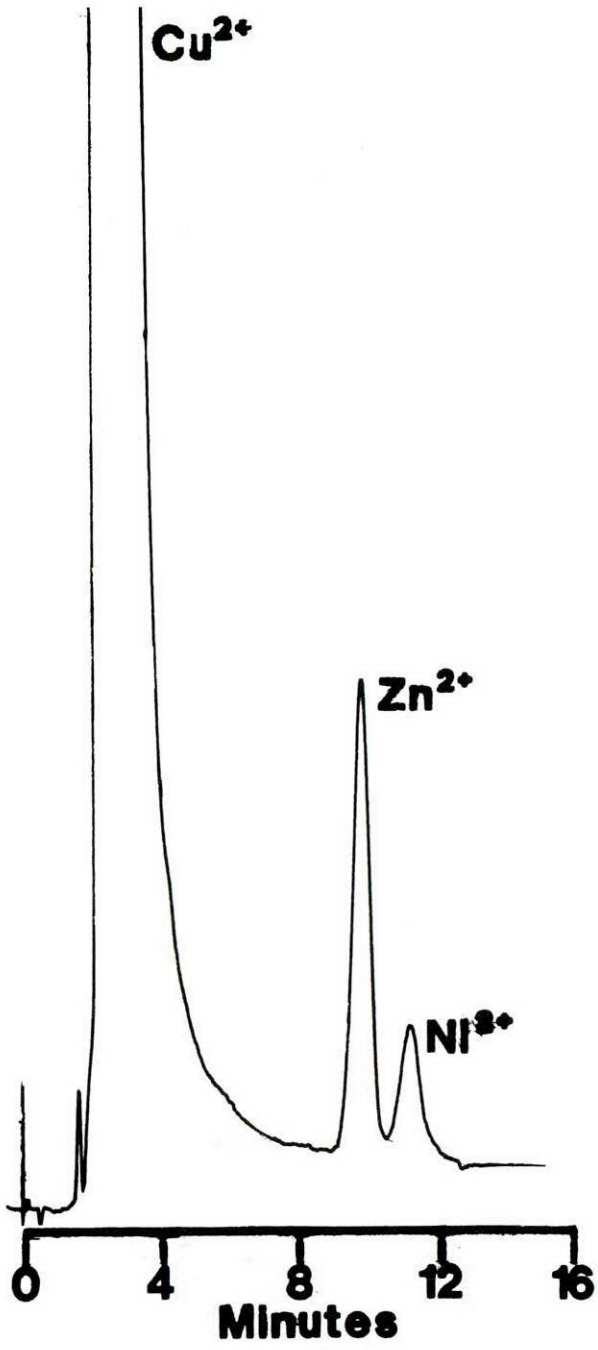
TRACE Cl^- IN A $CuSO_4$ PLATING BATH

Figure 5. Columns: 1 HPIC-AG4, 1 HPIC-AS4. Detection: AFS, conductivity at 30 μS. Sample: 10 μl of 1/1000 dilution of bath. Eluent: standard anion, .0028 M $NaHCO_3$/.0023 M Na_2CO_2.



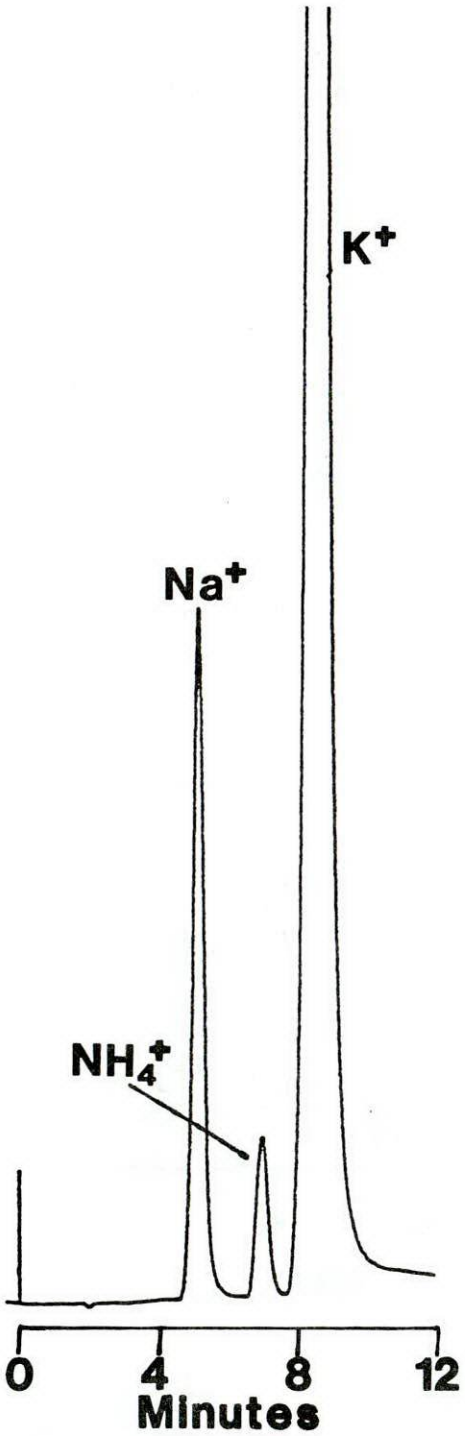
DETERMINATION OF A DISULFIDE ANIONIC BRIGHTENER IN A $CuSO_4$ PLATING BATH

Figure 6. Columns: 1 MPIC-NG1, 1 MPIC-NS1. Detection: UV, 215 nm .02 AUFS. Sample 50 µl of 1/2 dilution of bath. Eluent: 2 mM TBAOH, 25% CH_3CN, .2 mM Na_2CO_2.



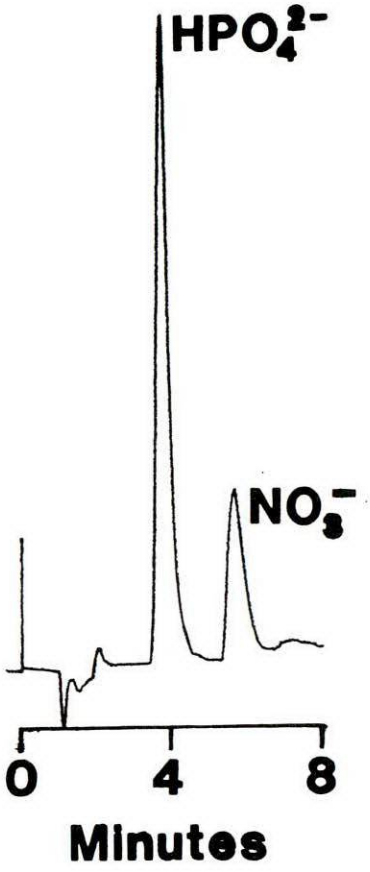
METAL CONTAMINANTS IN AN ACID COPPER PLATING BATH

Figure 7. Columns: 1 HPIC-AS4, Detection: Visible, 520 nm after post column reaction with PAR, 1 AUFS. Sample: 50 µl of 1/10 dilution of the bath. Eluent: 25 mM oxalic acid.



AMMONIA IN A COPPER PYROPHOSPHATE PLATING BATH

Figure 8. Columns: 1 HPIC-CS1, Detection: 1 CSC-1, 10 µS. Sample: 50 µl of 1/2500 dilution, Eluent: .005 M HCl.



ANIONS IN A COPPER PYROPHOSPHATE PLATING BATH

Figure 9. Columns: 1 HPIC-AG3, 1 HPIC-AS3. Detection: AFS, 10 μS. Sample: 10 μl of 1/1000 dilution. Eluent: .003 M $NaHCO_3$/ .0024 M Na_2CO_3.

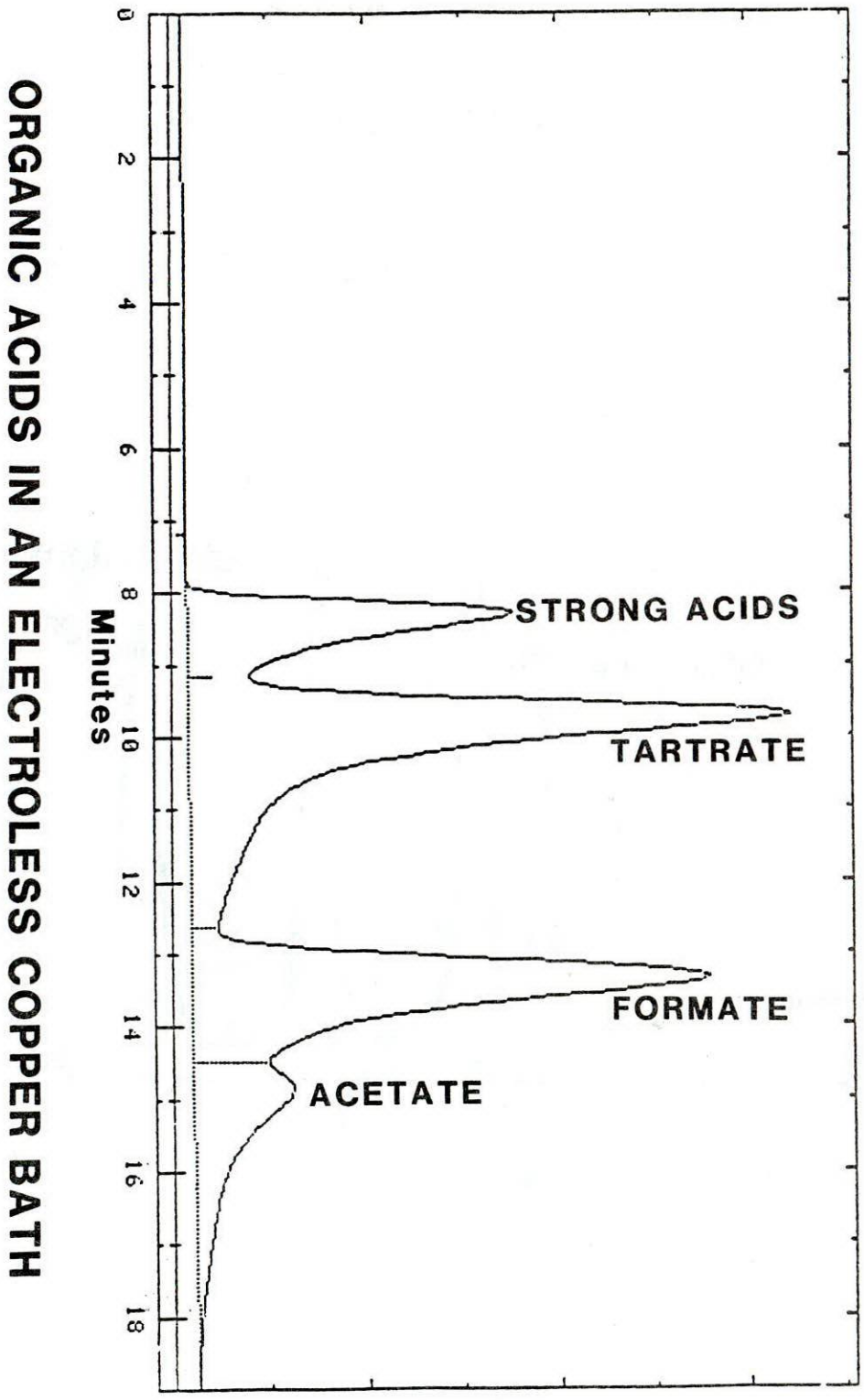


Figure 10. Columns: 1 HPICE-AS1, Detection: ISC, conductivity at 10 μS. Sample: 50 μl of 1/500 dilution. Eluent: .001 M HCl.

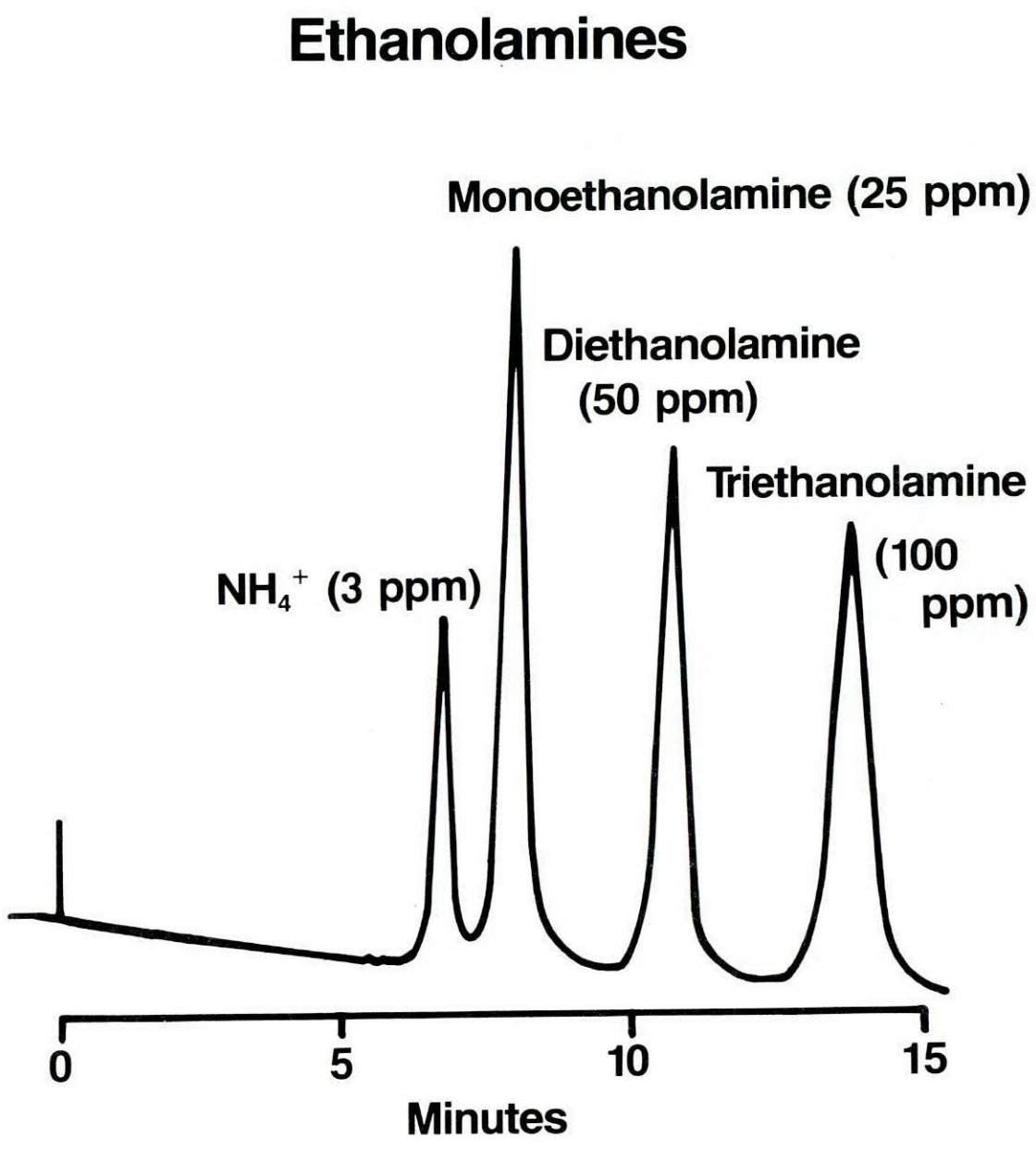
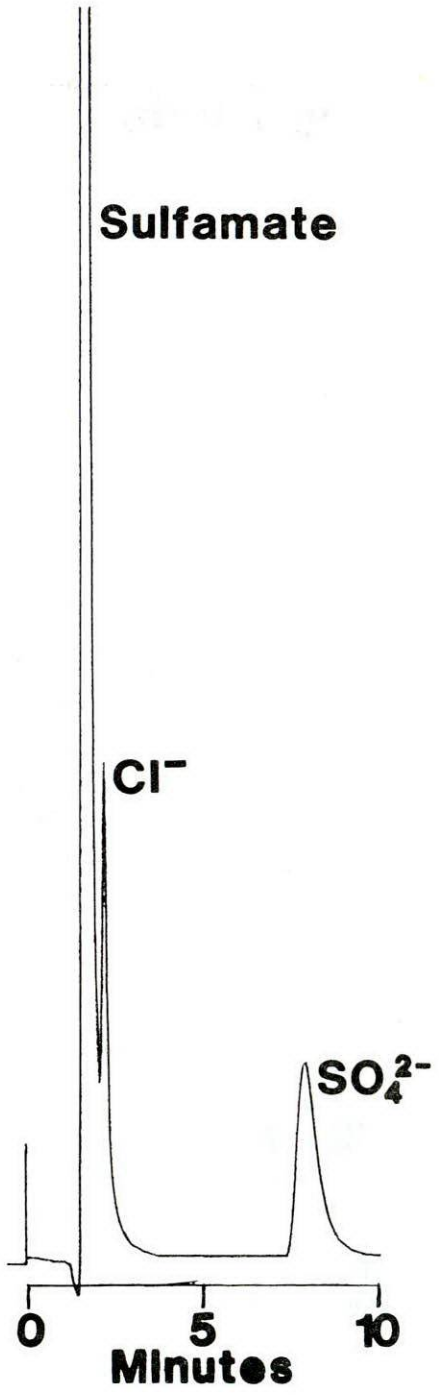


Figure 11. Columns: 1 MPIC-NG1, 1 MPIC-NS1, Detection: 1 CSC-1, conductivity 10 μS. Sample: 50 μl of standard ethanolamines. Eluent: 2 mM hexane sulfonic acid.



ANIONS IN A NICKEL SULFAMATE PLATING BATH

Figure 12. Columns: 1 HPIC-AG4, 1 HPIC-AS4, Detection: AFS, conductivity 10 μS. Sample: 50 μl of 1/500 dilution of bath. Eluent: .0028 M $NaHCO_3$/.0023 M Na_2CO_3.

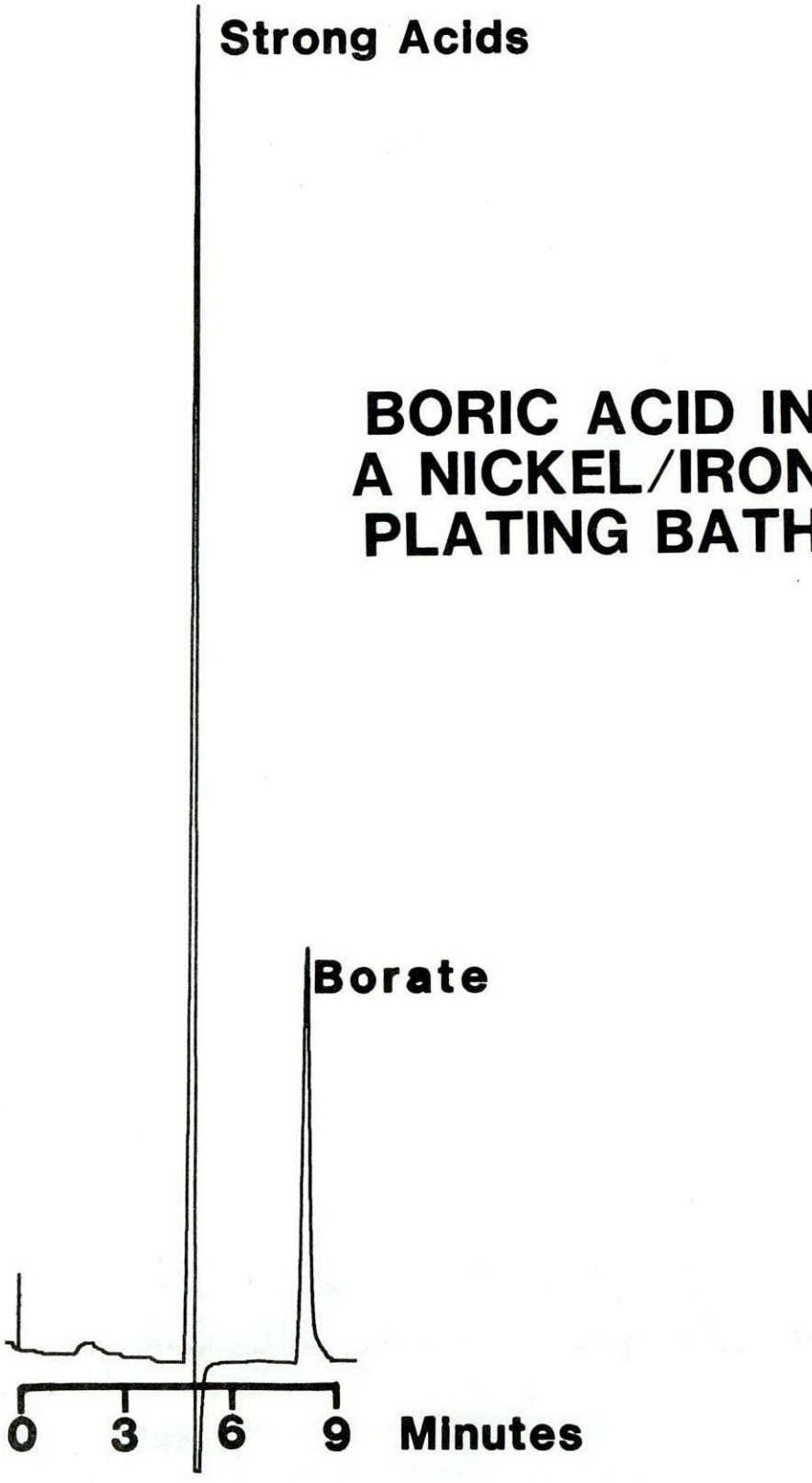
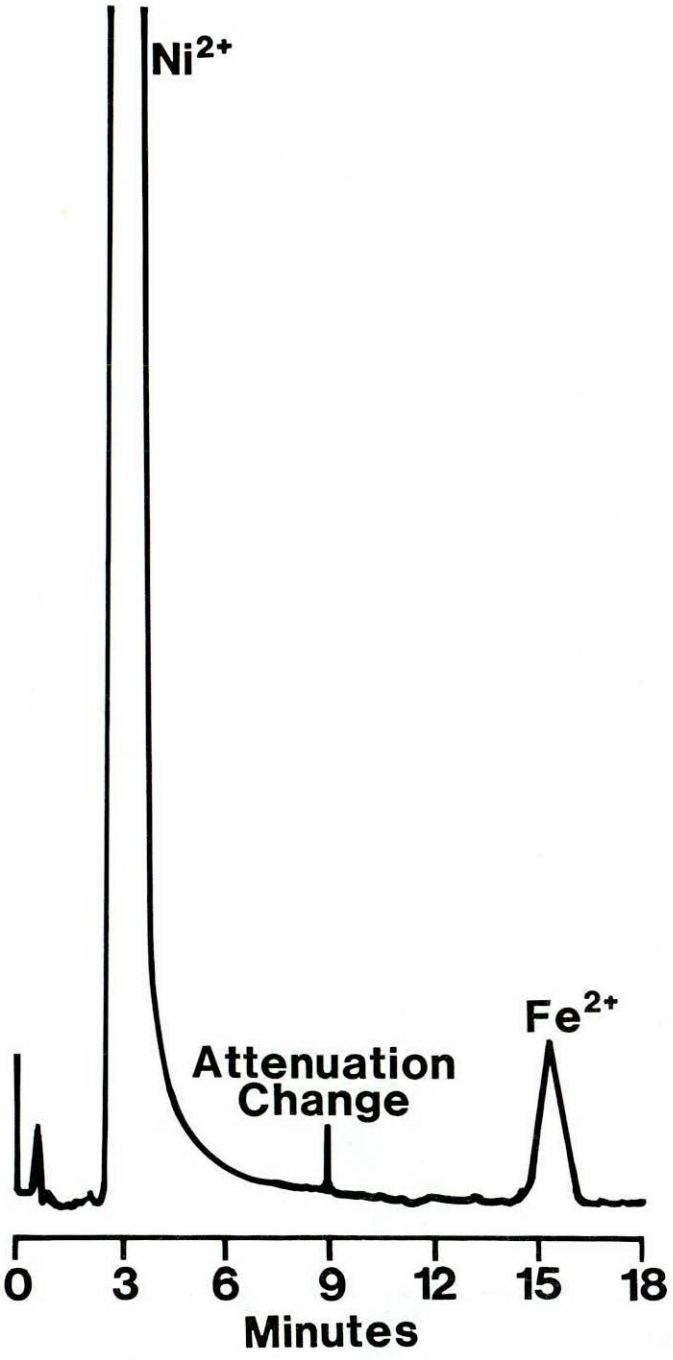


Figure 13. Column: 1 HPICE-1, suppressed conductivity, 10 µS. Sample: 50 µl of 1/1000 dilution.



TRANSITION METALS IN A NICKEL-IRON PLATING BATH

Figure 14. Columns: 1 HPIC-CG2, 1 HPIC-CS2. Detection: Visible, 520 nm after post column reaction with PAR. .2 AUFS, .1 AUFS. Sample: 50 µl of 1/500 dilution of bath. Eluent: 10 mM oxalic acid/7.5 mM citric acid, pH 4.30.

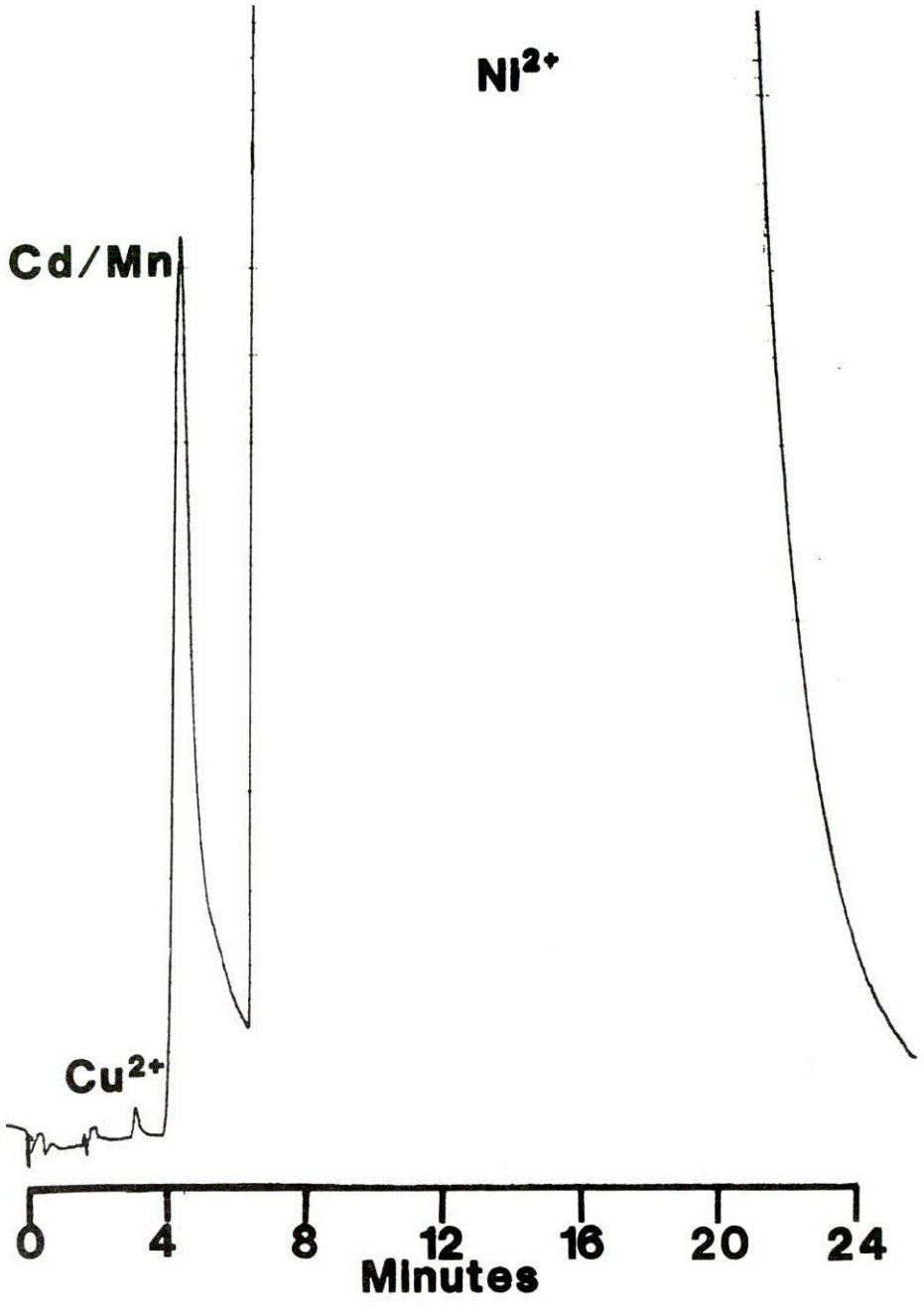
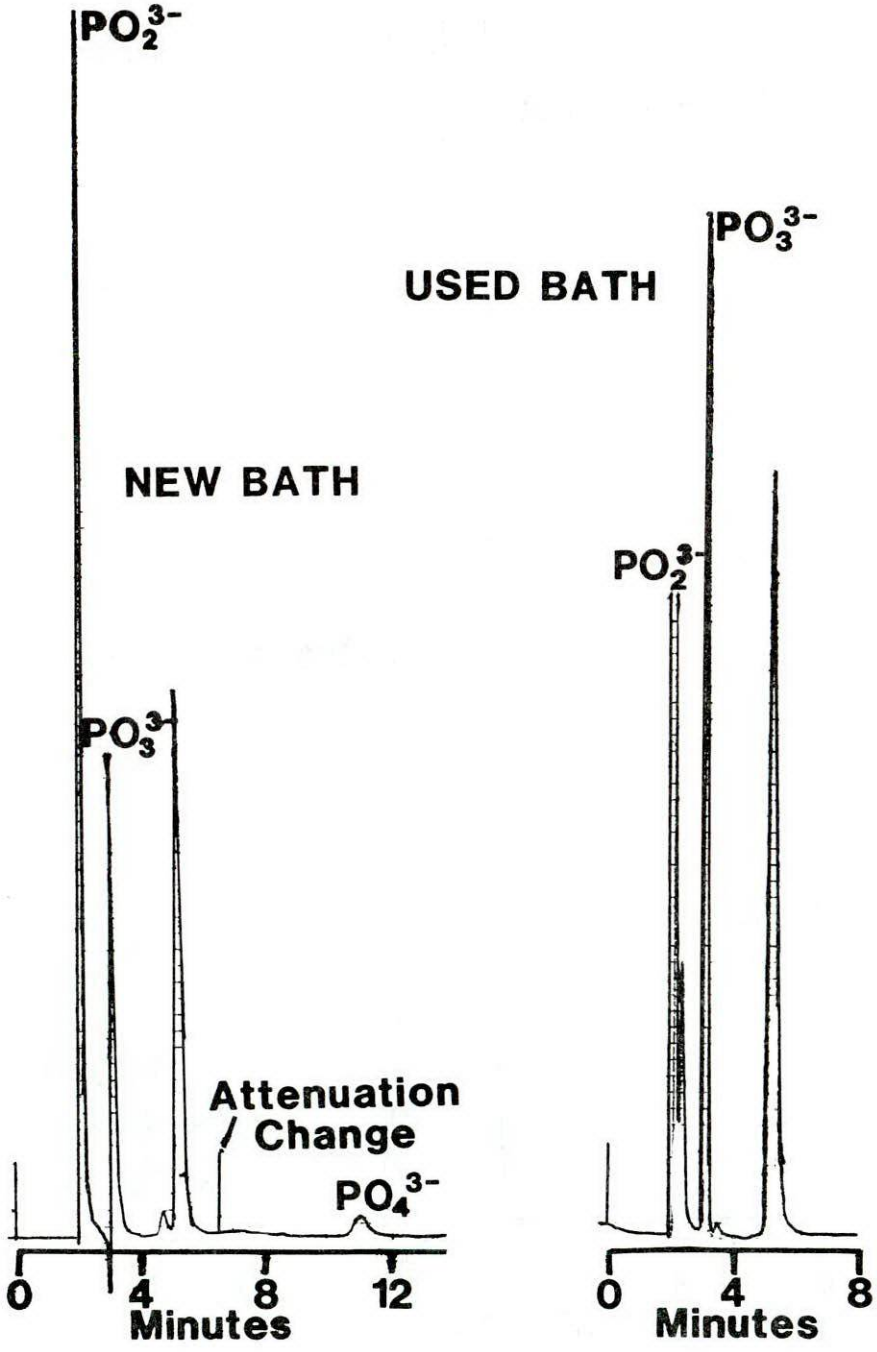
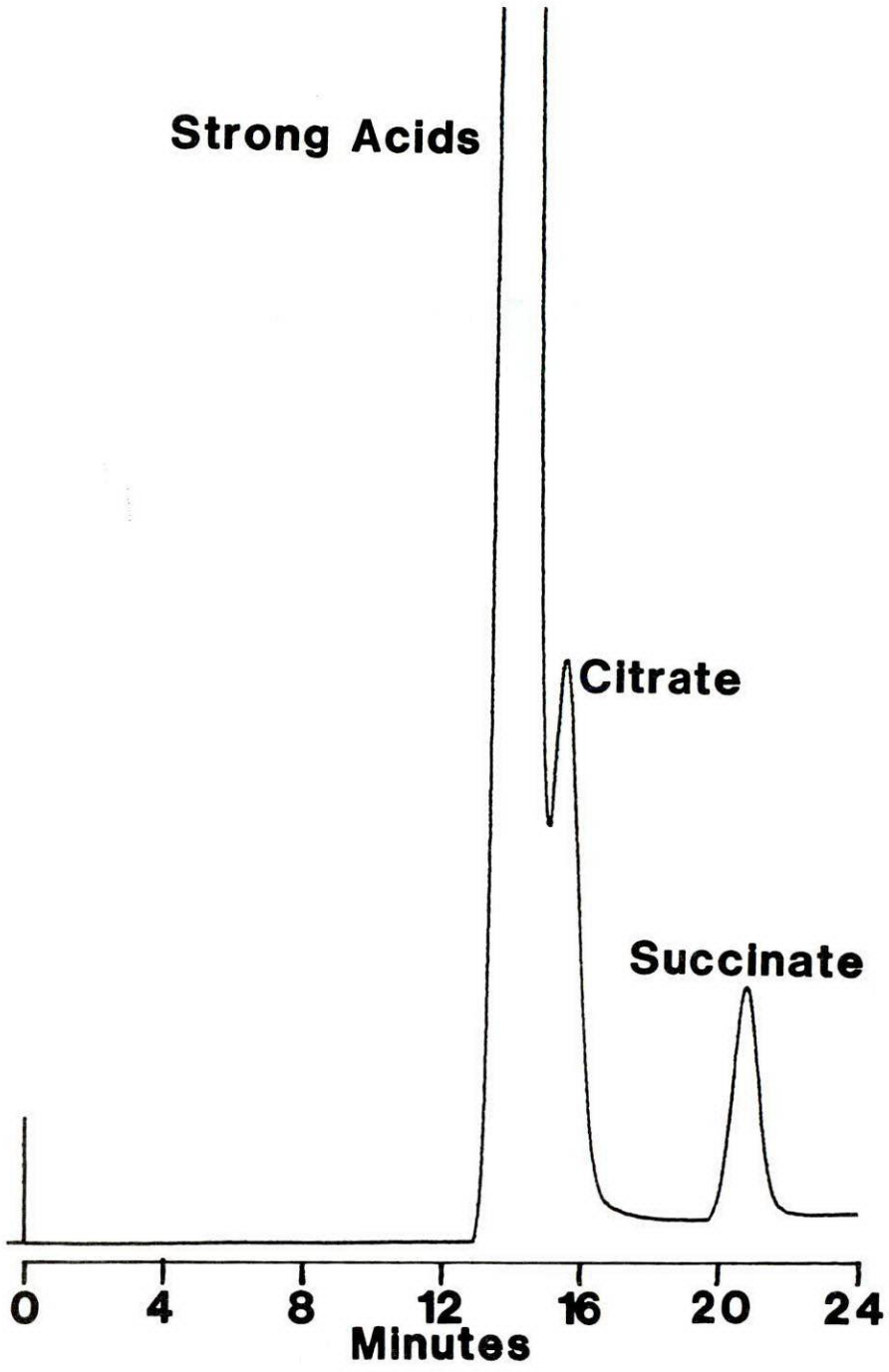


Figure 15. Column: 1 HPIC-AS4, Detection: Visible, 520 nm after post column reaction with PAR. Sample: 50 µl of 1/10 dilution of bath .1 AUFS. Eluent: 25 mM oxalic acid.



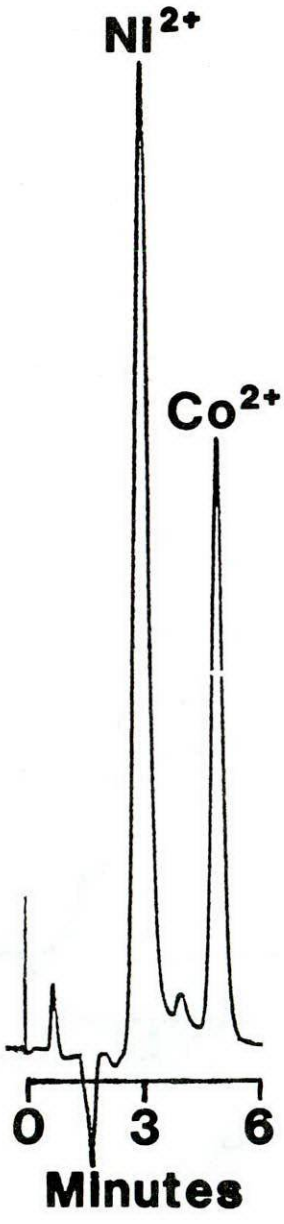
THE DETERMINATION OF HYPOPHOSPHITE, PHOSPHITE, AND PHOSPHATE IN ELECTROLESS NICKEL BATHS

Figure 16. Column: 1 HPIC-AG3, 1 HPIC-AS3. Detection: ASC-2 conductivity 30 μS. Sample: 50 μl of 1/5000 dilution, Eluent: 3 mM Na_2CO_3, pH 12 with NaOH.



ORGANIC ACIDS IN AN ELECTROLESS NICKEL PLATING BATH

Figure 17. Column: 1 HPICE-AS2, Detection: ISC, conductivity 10 µS. Sample: 50 µl of 1/1000 dilution. Eluent: .001 M HCl.



NICKEL & COBALT IN AN ELECTROLESS Ni/Co PLATING BATH

Figure 18. Column: 1 HPIC-CS2, Detection: Visible, 520 nm, after post column reaction with PAR. Sample: 10 µl of 1/1000 dilution. Eluent: 25 mM oxalic acid.

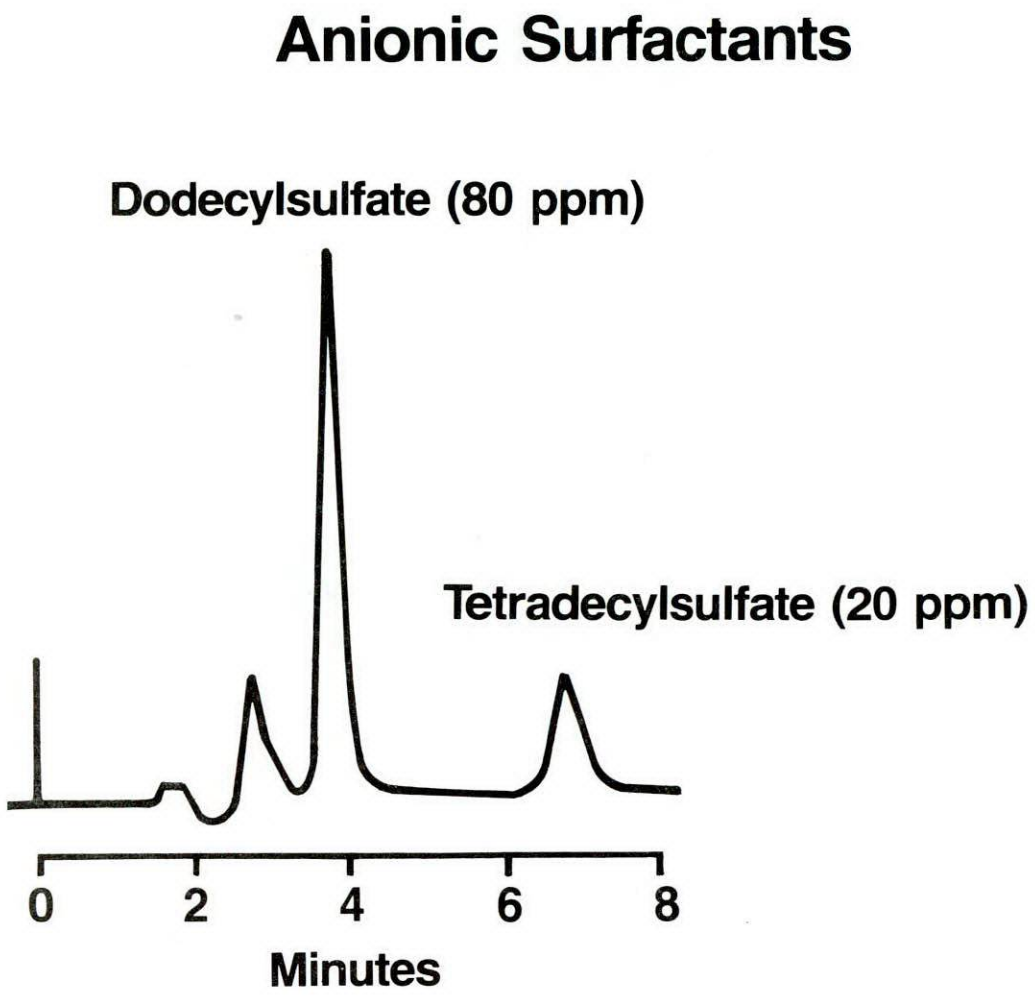


Figure 19. Column: 1 MPIC-NS1, Detection: 1 ASC-1, conductivity at 10 µS. Sample: 50 µl of standard solution. Eluent: 10 mM NH_4OH/32% CH_3CN.

J-1

Light Metal Finishing I
Session J

The Relationship of Electrolytic Coloring to Clear Anodizing Techniques

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THE RELATIONSHIP OF ELECTROLYTIC COLORING TO CLEAR ANODIZING TECHNIQUES

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Abstract

The two-step anodizing process, developed by Reynolds International, Inc, requires the production of a high-density aluminum oxide film followed by electrolytic impregnation at the base of the film pores by the metal form of a tin base metallic salt dissolved in a special electrolyte. This paper discusses some of the factors affecting the relationship between the quality of the film produced in the anodizing step and the rate of coloring which occurs in the electrolytic step as a function of voltage and time, as well as the independency of the ability to produce color from the thickness of the anodic film.

The Electrolytic Coloring Step

A simple description of electrolytic coloring is: The deposition of the metallic and/or metallic oxide form of a metal salt at the base of the pores of an aluminum oxide film by the passage of an electric current. This requires the use of a suitable electrolyte solution, in which the metal salt is dissolved, and a power supply, which is normally controllable alternating current. The A.C. power is supplied to the work load and counterelectrodes at the side of the tank act to complete the circuit back to the power supply. As in any electrolytic cell the current flows as the ion species in the electrolyte migrate to the appropriate electrodes.

A representation of the electrolytic coloring step is graphically shown in Figure 1. After a brief period to allow the solution to saturate the film (1), the power is supplied using a balanced voltage and the current flows in response to the electrical conditions of the circuit. Application of the voltage results in the movement of electrons through the barrier layer at the base of the film pore, which is the path of lowest resistance (2). As the electrons begin to flow into the pore the positive metal ions begin to migrate to the source of the electrons at the base (3). As the positive metal ions pick up the electrons they are reduced to metal particles which deposit at the bottom of the pore and pile up on each other (4). Even though the positive and negative components of the voltage are balanced, the electrochemistry of the process favors the reduction of the metal ion to metal and results in an excess of negative current over positive current. Buildup of the metal in the pore causes an accompanying increase in resistance which reduces total current flow (electron flow per unit time), reduces the ratio of negative current over positive current at the initial voltage, and slows down the deposition rate (5). There are two ways to increase the rate again:
1) Increase the total voltage to increase total current flow. This increases positive current, which does not contribute to metal deposition, along with the desired negative current. Or,
2) Increase the negative voltage and reduce the positive voltage through independent control of the half-wave potentials of the alternating current. This results in an increase in the ratio of negative current over positive

current which overcomes the resistance to electron flow into the pore and significantly increases the rate of metal deposition (6). As the layer of metal deepens, the effects of diffraction and absorption of light impart color to the surface of the workpieces (7). Control of the metal buildup to a desired color intensity is achieved by the amount of power supplied and by the amount of time it is supplied (8). In this manner it is possible to obtain color shades from champagne (9) to black (10) passing through a range of bronzes. The power supply rectifier to provide modulation of the half-wave potentials (Figure 2.) was first developed in the late 1960s[1] and has been modified and upgraded to allow for programming of the various shades of color desired.[2,3]

Controlling The Color

A program for a particular color is determined experimentally to establish the factors of time and voltage necessary to achieve that color. These values can then be electronically set into the power supply control system (Figure 3.) and can be expected to repeat time after time. The power supply and control unit only control the time, which is independent of the electrochemistry of the process, and the voltage, which, once programmed, does not control the fate of the current produced. Therefore, for a color program to be effective it is necessary to control the parameters which can affect the flow of current during electrolytic coloring.

The more important factors which affect coloring rate at a preset voltage are:

1) Concentration of the conductive electrolyte,
2) Temperature of the electrolyte,
3) Concentration of the metal ion,
4) Ability of the metal ions to flow uniformly to the workpieces, and
5) Size of the film pore.

Conductivity of the electrolyte is directly proportional to the first three parameters listed. Increases in any one or all will increase the rate of color formation and decreases will reduce the coloring rate. These factors are easily controlled through chemical analysis and proper refrigeration. The voltages used, the current densities generated, and the time in the coloring tank are such that high refrigeration requirements are not necessary and close temperature control is readily obtainable.

Workpiece Distribution

The fourth factor has resulted somewhat in a confusion of the capabilities of the two-step coloring process. A common method of racking is the horizontal attachment of workpieces to vertical bars or splines (Figure 4.). In the case of integral color anodizing a certain spacing of the parts is necessary to achieve color uniformity. In the case of clear anodizing, parts are racked more closely together because the effects of non-uniform anodizing are not clearly visible nor are the specifications nearly as demanding for their particular applications (Figure 5). With the integral color system it is possible to rack double-spline loads, with parts evenly spaced on each side, in conjunction with an internal cathode which is used in the anodizing tank to divide it into two separate cells and assure that the current will flow uniformly from all exposed surfaces. With the clear anodizing system the racking may be several parts across using multiple splines, twist racks, or stack racks (Figure 6.). An internal cathode is not used and generally

the inside parts will have less film thickness than those parts at the outside.[4]

One explanation of the differences which can occur is simply that resistance increases with distance from the source, and the inner surfaces, which are farther from the cathode, pass less current and receive less oxygen for film production. The use of the internal cathode in the integral color system balances those distances. Another possible explanation is that the current travelling along the workpiece generates a field around it which, in proximity with another part generating a similar field, serves to shield the current from flowing uniformly between the parts, thus reducing film growth on opposing and inner surfaces. Attention to proper spacing of workpieces becomes important in both clear and color anodizing processes in order to comply with specific requirements for uniform film thickness and color in a given application.

Rules of workpiece distribution similar to those for integral color anodizing (Figure 7.) apply in the electrolytic coloring step in order for the metal ions to flow uniformly to all exposed surfaces, and in the clear anodizing step in order to develop a uniformly distributed film in preparation for the coloring step. Dense racking of parts, as used in clear anodizing, will meet with the same resistances in the color system as occur in the anodizing system with the color rate varying directly with the degree of exposure of workpiece surfaces to be colored.

Misunderstanding of the two-step process arises as a result of the first step, which requires clear anodizing, and the desire to follow the same racking practices. However, recognition that the anodize and color steps require the free flow of current around and between workpieces for uniform film quality and color (Figure 8.) will help to eliminate this confusion. With specific or limited product mixes, it is possible to develop racking techniques, electrolyte chemistries, and color programming to provide color uniformity without the use of internal cathodes, while with large product mixes it is necessary to use internal cathodes.

What Electrolytic Coloring Isn't

It is important to recognize that, although it requires control of conductivity parameters similar to those of good anodizing practices, it has no relationship to the principles and objectives of anodizing; that is, it is not intended to add to or take away from the aluminum oxide film or its qualities. The coloring step is programmed to respond to those film qualities which have already been determined in the clear anodizing step.

The Clear Anodizing Step

A brief description of anodizing is: The generation of an aluminum oxide film on an aluminum surface by the passage of a direct current between the part and a cathode (making the part anodic) in the presence of a suitable electrolyte. The aluminum oxide film adheres to the surface of the aluminum and protects it with a highly non-corrosive finish. The durability and protective qualities of the finish have led to a wide range of applications on aluminum products.

Another quality which the film has permits the addition of color to the final finish to make it more attractive. The quality is that of porosity. The pores in the film provide sites whereby color can be added, such as in electrolytic coloring. However, the film pore is not something which is

constant, but is very dynamic and changes with the conditions used to generate the anodic film. It is an understanding and control of those conditions that will lead to a programmable color response.

Since the electrolytic coloring step responds to the existence of pores in the film, it is necessary that those pores be distributed uniformly over those surfaces which are to receive color. The practices which will provide that uniformity have already been discussed in conjunction with Workpiece Distribution. This then leaves the fifth item to be considered which will ultimately affect current flow in the coloring step--size of the film pore.

Control of Pore Size

Generation of the pore is a direct result of the solubility of aluminum oxide in a strong acid electrolyte. The dissolution effect occurs in competition with film growth. Part of the dissolution occurs generally over the film surface as it develops and part of it occurs in the form of penetration of the cellular structure of the aluminum oxide such that each cell grows in thickness but retains a void area or pore at its center. This growth occurs as a network of cells and pores over the workpiece (Figure 9.). The pore does not penetrate all the way to the aluminum base metal, but it does extend to the film surface. The barrier layer at the base of the pore is solid aluminum oxide which is formed in the initial stages of the anodizing cycle and is not subject to the dissolving action of the electrolyte. It is very thin and represents only a small fraction of the total film. As a result, the depth of the pore is almost equal to the thickness of the film. The competitive actions of film growth and cellular dissolution and the factors which affect the mechanics of those actions have been studied in detail and a large body of information is available about them.[5,6,7,8]

The solubility properties of the electrolyte are principally controlled by temperature and acid concentration. Increases in either one or both will increase dissolution rate and enlarge the pore. Decreases will result in smaller pores. For instance, as early as 1932 it was determined that non-uniform electrolyte temperature resulted in non-uniform porosity of the film on a load of parts. The ones higher up had larger pores which would take dye faster than parts lower down. The heat generated during the anodizing cycle was rising to create a warmer solution near the surface increasing its solubility properties. This led to a patent[9] for a system of mixing the electrolyte to maintain a uniform temperature by the use of air agitation distributed through tubing laid along the bottom of the anodizing tank.

Formation of the aluminum oxide cells is a function of the flow of current which creates the oxidation reaction, but it is the force behind the current which determines the density of the aluminum oxide produced at the cellular level. That force is the voltage driving the current to overcome the resistances of the system. As the voltage increases the unit volume of aluminum oxide in the cell increases and the size of the pore decreases, and likewise, lower voltages will result in a larger pore. The forming voltage of the film is affected by temperature and acid concentration and will vary inversely with changes in the same two factors which directly affect solubility.

Therefore, increases in temperature and acid concentration will simultaneously increase solubility and reduce voltage resulting in increasing pore size. Decreases in temperature and acid concentration will simultaneously reduce solubility and increase voltage resulting in decreasing pore size.

Relationship of Electrolytic Coloring to Clear Anodizing Techniques

Since the depth of the pore varies primarily as a function of the thickness of the film, the principal change in the size of the pore due to solubility and voltage factors occurs in its diameter, which is the passageway for the movement of the metal ions in the electrolytic coloring step (Refer to Figure 1.). As discussed previously, the deposition of metal is a result of the migration of metal ions to the source of electrons at the base of the pore. Keeping in mind that this process is occurring at the chemical level and that the pore diameter is extremely minute, the size of the passageway for the flow of metal ions begins to have significance. If the passageway (the pore diameter) is large, the migration or flow of metal ions will be faster than if the pore diameter is small. Returning to the factors which affect coloring rate in the electrolytic coloring step, the rate will vary directly with the size (diameter) of the pore. Consistent control of the parameters of temperature and acid concentration in the anodizing step will produce an anodic film of consistent porosity which will result in a reproduction of color from load to load utilizing a specific color program.

The other factor which is controllable in the anodizing step with respect to pore size is the pore depth. Although not as significant as the pore diameter, experience has shown that there exists a relationship between film thickness and coloring rate. A variation in the film thickness will vary the length of the passageway (pore depth) and thus the time necessary for the metal ions to reach the pore base. Consistent film thickness is readily achievable by controlling the parameters of current density and time in the anodizing cycle.

High Current Density Anodizing

Current density is the amount of current passing through a unit of surface area at any instant of time and is normally expressed as amperes per square foot or amperes per square decimeter. In anodizing it is determined from the total amperes passing through a load of workpieces having a known total surface area. Current density is a rate factor. The formation of the aluminum oxide film is directly related to the amount of current available in a given unit of time. Therefore, if the amount of current available is increased per unit area (current density), there will be an accompanying rate increase in the buildup of the film, reducing the time in the anodizing cycle. Increasing the current density also increases the voltage because of increased system resistance, if the other factors are constant (surface area) or controlled (temperature and acid concentration). As discussed previously, an increase in voltage will result in a denser aluminum oxide layer and a smaller pore. These last two factors produce the qualities of hardness and abrasion resistance in the film, which are desirable in many applications of architectural finishes--both colored and clear. The integral color anodizing process has utilized the practices of high current density, high voltage, low acid concentration, and moderate temperatures for some fifteen years to produce durable, hardcoated, colored finishes.

Another result of the increase in current density and voltage is an increase in heat generation from resistances in the system and from the electrochemical reactions. Refrigeration and air agitation are designed to take care of the first, but the reactions take place within the pore itself. An investigation begun in the 1960s estimated that the chemical reactions

taking place within the film pore generated temperatures which exceeded the boiling point of water. A study of the effects of various chemicals which might assist in the oxidation step to reduce heat generation at the chemical level led to a patent[10] for a combination of certain organic chemicals, which could be added to the anodizing electrolyte for temperature control in the pore. This resulted in a system which could operate at higher current densities and voltages in a clear anodizing process to generate hard, abrasion-resistant films and reduce anodizing time.

Two-step anodizing processes have been in commercial use almost as long as integral color anodizing processes, but they have only been predominant in Europe. In recent years the cost of electricity has increased dramatically in the U.S. and pushed up the costs of integral color anodizing. As a result the two-step process, which operates with lower energy requirements, began to be introduced into the U.S. in the late 1970s as a viable alternative to the energy-intensive integral color process. However, this required that the high current density clear anodizing process be used as the first step as assurance that the resultant finish would have hardcoat properties, could be produced rapidly, and would be energy efficient.[2,3]

Interdependency and Independency

In order to understand the importance of the interdependency of the two steps, it is necessary to remember that the purpose of the process is not to produce an anodized product but a color-anodized product. With the emphasis on color, it becomes important to control the factors which affect color formation. One way to point this out is to consider what happens if the parameters of the process are not controlled. The result is, first of all, an anodized film of varying quality. The second is a color program which cannot provide the desired color from one load to the next. Color will develop, but in order to match color, the process reverts to the "eye-of-the-beholder" method of color judgement, which is difficult to reproduce, is very time consuming, and reduces productivity. The choice is a manual operation or control of the parameters which will provide a consistent and uniform anodized finish with a color which has been developed automatically and reproducibly.

The independency of the two steps can be recognized by remembering simply that the parameters for the anodizing step can be independently selected to produce a film meeting the required finish specifications for coating thickness, coating weight, hardness, and abrasion resistance, and then a color program can be generated which will reproduce the desired color for that finish.

Conclusion

Recognizing the parameters in the clear anodize first step which have an effect on the quality of the anodic film and which will ultimately affect the rate of coloring in the second step leads to an understanding of the relationship of electrolytic coloring to clear anodizing techniques and to the importance of control. If the parameters are controlled consistently, which is possible with present state-of-the-art technology, then the color process will respond consistently and uniformly according to the color program developed.

The flexibility of the process is realized in the same way. Because the anodizing step is independent from the coloring step, it is possible to

establish and utilize whatever parameters are desirable to produce a particular quality of finish or coating thickness. Once the parameters are established and a particular film is generated, it only requires that the voltages and times of a color program be determined for the color desired.

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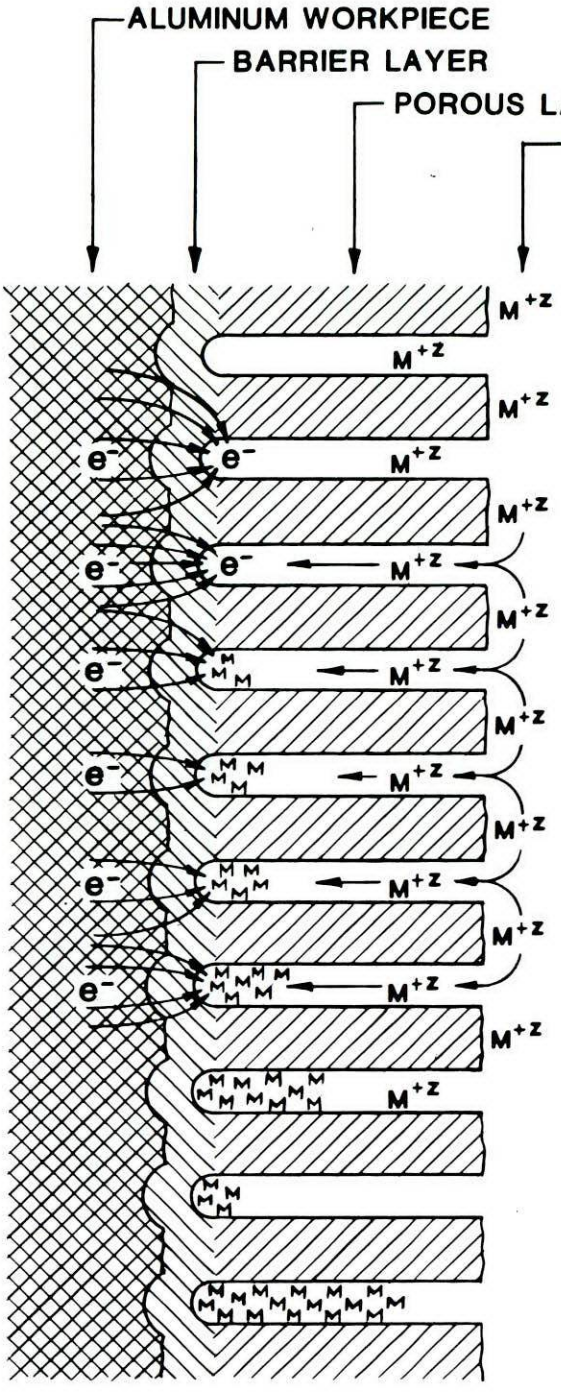
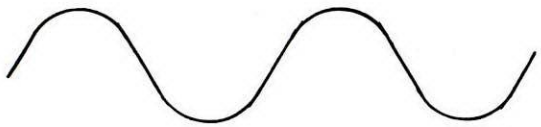


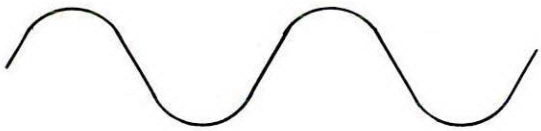
1. FILM PORE - ELECTROLYTE AND METAL IONS DIFFUSE INTO PORE.
2. <u>POWER ON</u> - ELECTRONS (e^-) FLOW INTO PORE AT BASE.
3. METAL IONS MIGRATE TO ELECTRON SOURCE.
4. METAL IONS PICK UP ELECTRONS AND DEPOSIT AS METAL (M).
5. RESISTANCE INCREASES TO ELECTRON FLOW. (INCREASE NEGATIVE VOLTAGE OVER POSITIVE VOLTAGE.)
6. POWER ADJUSTED - MIGRATION OF METAL IONS INCREASES.
7. AS METAL DEPOSITION CONTINUES COLOR INCREASES.
8. <u>POWER OFF</u> - FINAL COLOR IS ACHIEVED.
9. EXAMPLE - CHAMPAGNE
10. EXAMPLE - BLACK

THE ELECTROLYTIC COLORING STEP

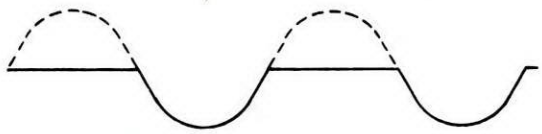
FIGURE 1.



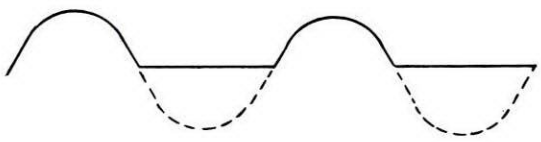
POWER LINE TO RECTIFIER.



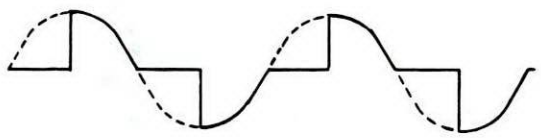
POTENTIAL SUPPLIED TO LOAD (AT FULL POWER).



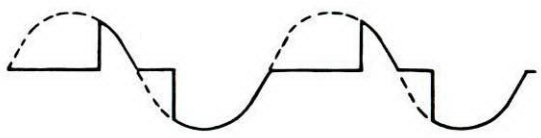
NEGATIVE POTENTIAL SUPPLIED TO LOAD.



POSITIVE POTENTIAL SUPPLIED TO LOAD.



INITIAL BALANCED (POSITIVE/ NEGATIVE) POTENTIAL SUPPLIED TO LOAD (AT PARTIAL POWER).



MODULATED (INCREASED NEGATIVE/REDUCED POSITIVE) POTENTIAL TO LOAD.

CONTROL OF ALTERNATING CURRENT

HALF - WAVE POTENTIALS

FIGURE 2.

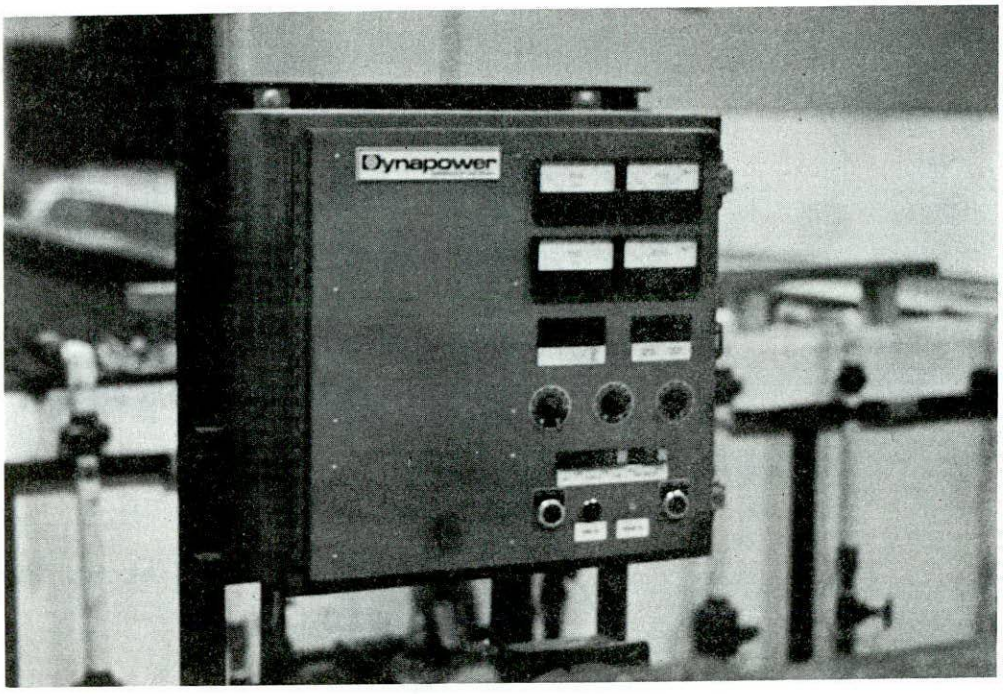


FIGURE 3.
Programmable Control Unit
For Electrolytic Coloring Power Supply

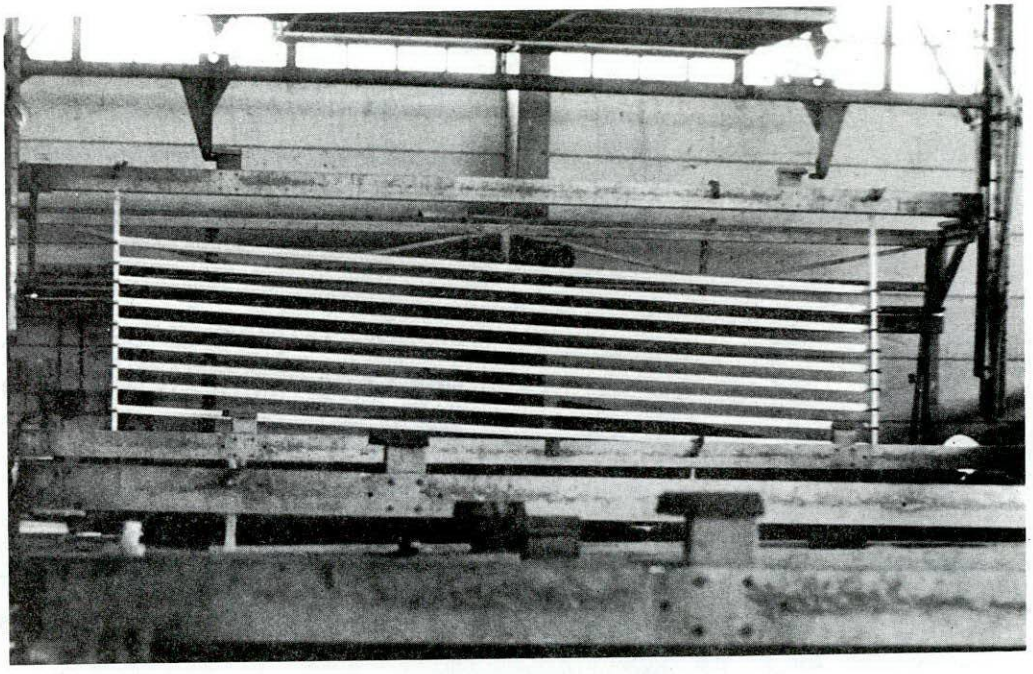


FIGURE 4.
Typical Method of Single-Spline Racking
For Color Anodizing

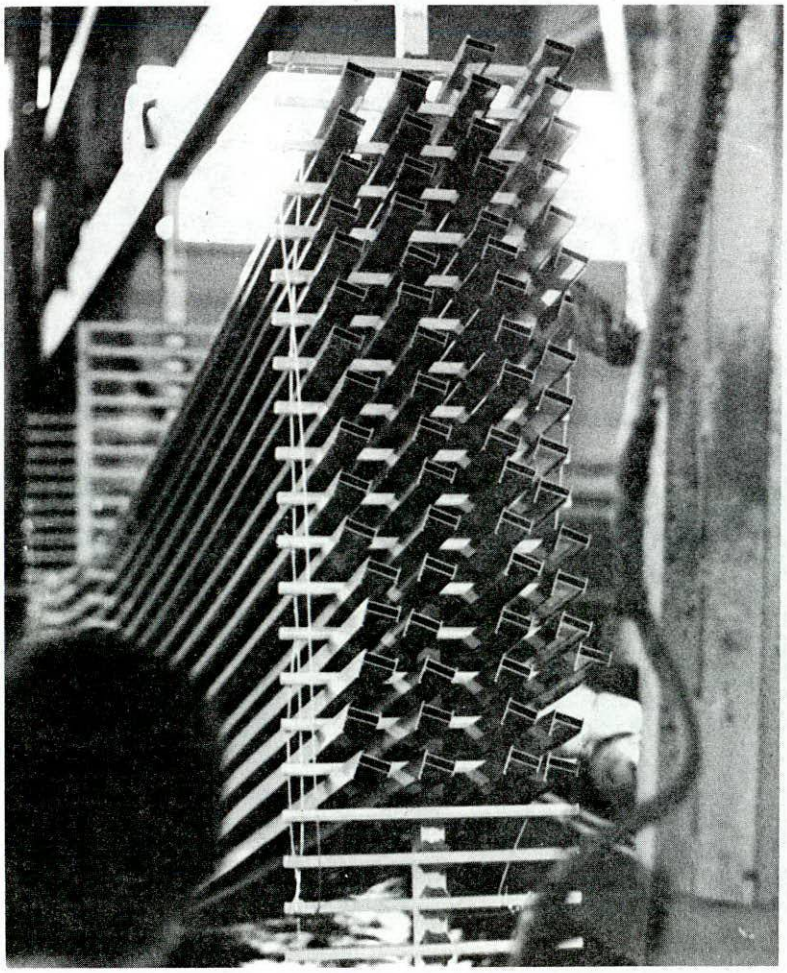


FIGURE 5.
Typical Method of Racking
For Clear Anodizing

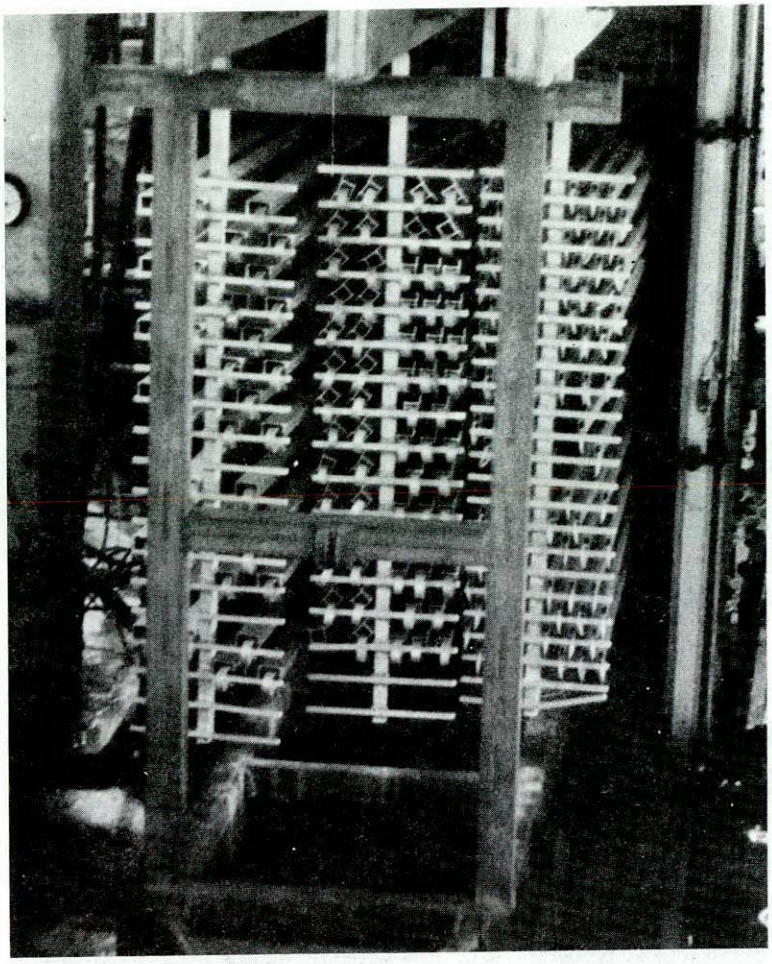


FIGURE 6.
Various Racks Showing Multiple Loading
of Workpieces for Clear Anodizing

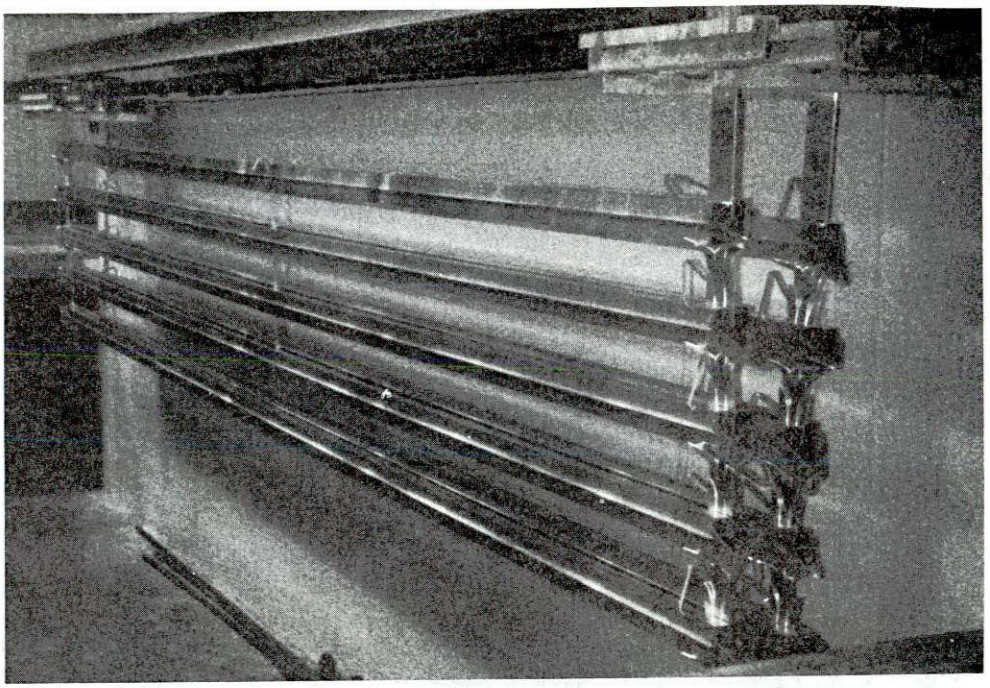


FIGURE 7.
One Method of Racking
For Electrolytic Coloring

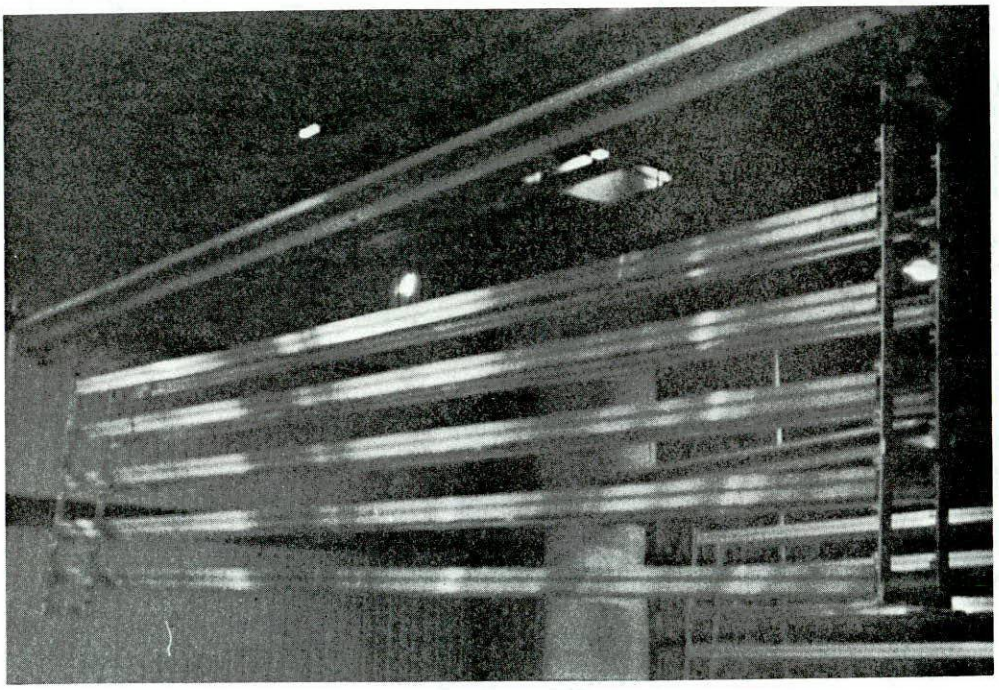
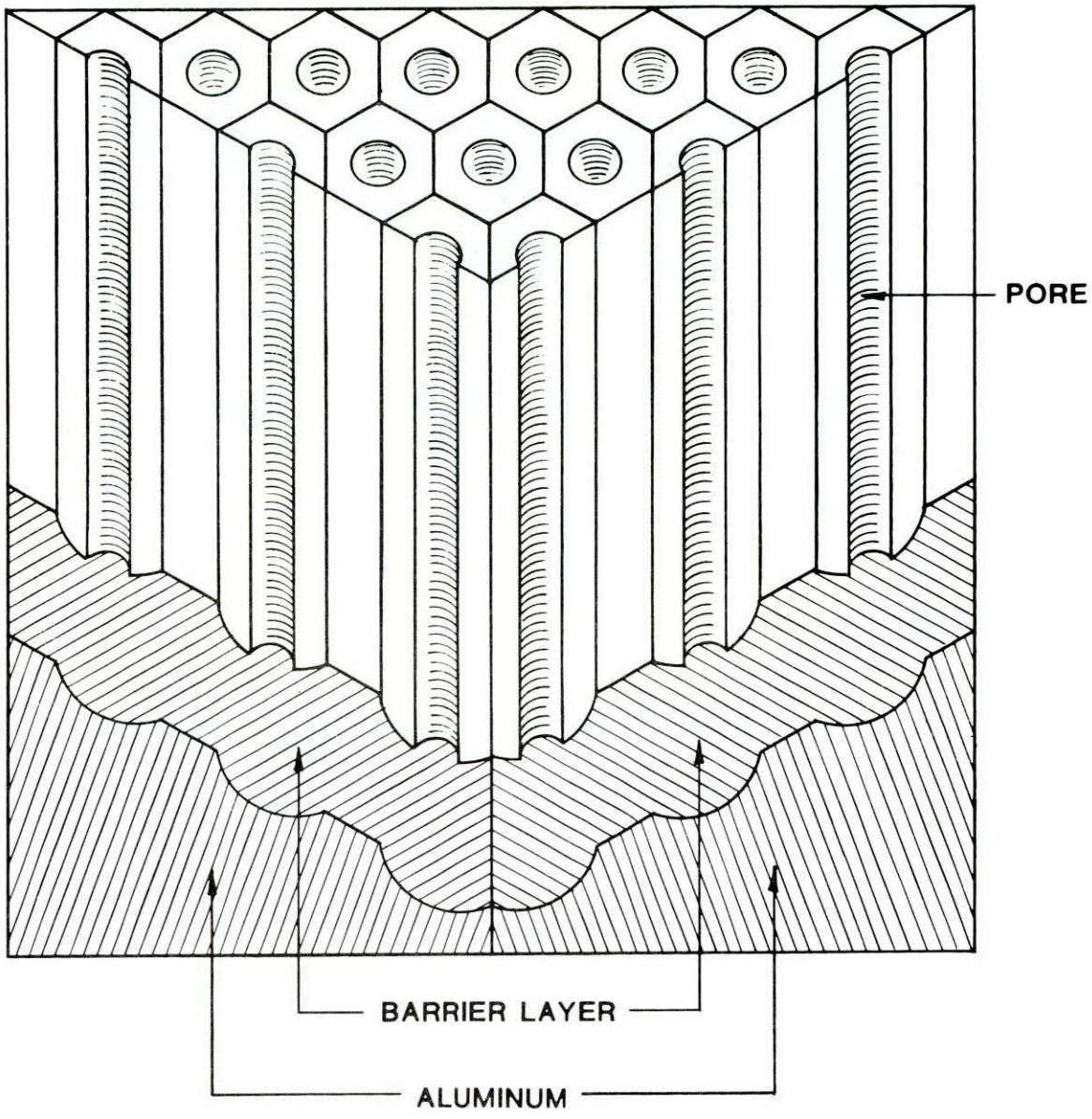


FIGURE 8.
Rack Load For Clear Anodizing
To Be Followed By Electrolytic Coloring



THREE - DIMENSIONAL SCHEMATIC OF ALUMINUM OXIDE FILM

FIGURE 9.

J-2

Light Metal Finishing I
Session J

The Production and Properties of Cobalt-Based Electrolytic Finishes

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THE PRODUCTION AND PROPERTIES OF COBALT-BASED ELECTROLYTIC FINISHES

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The paper describes the experience gained over a 12-year period in the production of cobalt-based electrolytic color finishes on aluminum. It gives indications of the equipment required and the operating costs involved, and describes the properties of the finishes produced, particularly their excellent light fastness and corrosion resistance.

THE PRODUCTION AND PROPERTIES OF COBALT-BASED ELECTROLYTIC FINISHES

P. G. Sheasby and W. M. Kellermann
Alcan International Limited

INTRODUCTION

Electrolytic coloring of anodized aluminum is now a well established production process that has been used in large-scale plants producing architectural finishes in many parts of the world since the late 1960's. Today electrolytic coloring processes are so strongly established in many areas that they have replaced the older integral-color anodizing processes. In contrast to integral-color anodizing, where color is developed during the anodizing process itself, electrolytic coloring is a two-step process involving first the production of a conventional clear anodic film, typically in a sulfuric acid electrolyte. The work is then transferred to a suitable metal salt solution and again treated electrolytically, usually under a.c., rather than d.c., conditions. This causes metal particles to be deposited at the base of the pores of the anodic film and these deposits act as scattering centers for light, in a similar way to the intermetallic particles present in integral-color coatings. The color and depth of shade produced depend on the metal being deposited and the coloring conditions used, but most metals produce a range of bronze shades and black. While many different metals and coloring electrolytes can theoretically give a variety of colors, in practice most industrial processes use electrolytes based on salts of nickel, cobalt or tin or mixtures of these salts[1,2]. In recent times electrolytes based on tin and tin-nickel mixtures have become used extensively and while outside Japan, the use of nickel-based electrolytes has become less common, cobalt-based electrolytes continue to be widely used, particularly in association with Alcan's ANOLOK* finishes.

Applications of Electrolytic Coloring

The major application of such finishes is in the architectural field where long-term durability is of prime importance. It is the ability of electrolytic coloring

*ANOLOK is a Registered Trademark by Alcan companies in many countries.

processes to provide this durability at a reasonable processing cost that has made them attractive to architectural finishers. In particular, the fact that in comparison with integral finishes they are relatively low-energy processes is now of considerable importance. This is mainly because the electrical energy used to produce an anodic film of a particular thickness in a sulfuric acid electrolyte is very much less than that required to produce a similar thickness in an integral-color process. Typically a 20 micron (0.8 mil) film produced in sulfuric acid requires about 2.2 kW hr/m^2 (0.2 kW hr/ft^2) and coloring of such a film in an electrolytic coloring process adds less than 0.2 kW hr/m^2 (0.02 kW hr/ft^2). In contrast an integral color anodizing process uses about 7.5 kW hr/m^2 (0.7 kW hr/ft^2) for a similar film thickness.

Another interesting aspect of electrolytic coloring is that the color is independent of the anodic film thickness, so the full range of colors can be produced with relatively thin films, say 5-10 microns (0.2 - 0.4 mil). This makes the finishes of interest for many other applications, especially for decorative trim components in the automotive field[3] where the ability to produce durable black finishes at a thickness of about 8 microns (0.3 mil) is of particular interest, as is the possibility of producing both high lustre or matte color finishes as required.

The Cobalt-Based Coloring Electrolyte

Electrolytes based on cobalt salts have been in widespread use since the early 1970's and their attractive features are the ability to produce a full range of bronze and black finishes, their relative insensitivity to contamination and the very high bath stability. Many baths of this type have been in continuous use for more than 10 years, and they normally need no filtration or regeneration procedures. Formulation of the electrolyte is important in order to cope with increasing aluminum content and to achieve an electrolyte with good throwing power, but properly formulated baths give excellent results. The pH of cobalt-based electrolytes is normally high (between 4 and 6) and this can be important, as highly acidic coloring electrolytes can cause some attack of the anodic film during the coloring operation.

The make-up cost for cobalt-based electrolytes is currently about 49¢/liter ($1.90/U.S. gallon). Typical consumption rates give a current operating cost of about 9¢/m^2 of surface colored (0.8¢/ft^2). It is important, however, to realize that more than 80% of the cobalt salts

used in a typical plant are lost through drag-out rather than deposition, so recovery of these salts from rinse waters can be an attractive proposition. Ion-exchange systems for doing this are available[4] and are in operation in a number of plants around the world. Use of such a recovery system can reduce chemical consumption costs to about 3¢/m^2 (0.25¢/ft^2).

Equipment for Coloring

The equipment required for electrolytic coloring with cobalt-based electrolytes is relatively simple and inexpensive (typically less than $40,000). It essentially consists of an appropriate tank, power supply and electrodes. The tank required is similar to that used for normal sulfuric acid anodizing operations, and is usually steel or concrete, lined with an acid-resistant plastic, fibreglass or rubber material. Air agitation of the electrolyte is necessary, but as the process operates at ambient temperature, means for cooling or heating the electrolyte are not normally required. Fume extraction equipment is also unnecessary. Rinsing between anodizing and coloring is important and this may necessitate an extra rinse tank at this stage.

The power supply is a continuously variable, single-phase, a.c. unit having a range of 0-25 V and a current capacity of about one-third the capacity of the anodizing rectifiers used. Appropriate controls to allow voltage or current/time programmes to be preset for particular shades of color are usually incorporated.

As the electrolytic coloring process is an a.c. process, current is passed between the work and suitable counter-electrodes. These are normally graphite or stainless steel and the use of appropriately spaced electrodes can be advantageous[5]. The electrodes are placed at the sides of the tank as in anodizing but, in addition, a central counter-electrode system is usually used to ensure good color uniformity throughout the load (Figure 1).

Properties of the Colored Finishes

In general, electrolytically colored finishes produced in cobalt-based electrolytes have properties that are similar to those of conventional sulfuric acid coatings, as the deposition of the metal within the pores of the film has little effect on the film structure itself. Thus properties such as abrasion resistance and sealing

characteristics are little affected by the coloring process.

The light fastness of the finishes produced is excellent, and even under very severe U.V. light conditions in the Microscal apparatus (I.S.O.6581:1980), the finishes have been shown to withstand more than 100 hours' exposure without change. Other work[6] has shown that 24 hours' exposure in this test is equivalent to 6-8 years' actual sunlight exposure.

In many applications corrosion resistance is the property that is most important, and the corrosion properties of cobalt-based electrolytic finishes are very good. This is borne out by their performance on many hundreds of storefronts, schools, hospitals and offices that were built throughout the United States during the last 12 years using only 10 micron (0.4 mil) thick anodic films (AA-Class II). Such finishes, with an anodic film thickness of 25 microns (1 mil), have also been exposed at our most severe industrial site in Sheffield (England) for more than 10 years, and are still in excellent condition with no pitting of the anodic coating. Other workers[7] have compared the performance of cobalt-based finishes with that of integral-color finishes at several exposure sites and have shown no significant difference in performance, all the finishes being in good condition after 5 years' exposure.

This good exposure performance is reflected in accelerated test performance in acidified salt spray tests (I.S.O.3769:1976 or ASTM Method B287-74), where the whole range of finishes, including the black, withstand more than 500 hours' exposure without significant pitting (anodic film thickness 25 microns (1 mil)). These good results are associated with the fact that cobalt, when deposited within the pores of an anodic film, is concentrated towards the base of the film and does not, even with black finishes, spread more than about 10 microns (0.4 mil) from the aluminum/aluminum oxide interface (this is not necessarily the case with all electrolytically colored finishes).

These, then, are the most important properties of cobalt-based electrolytic color finishes, and it is this combination of good properties and process economy that continue to arouse such widespread interest in these attractive finishes.

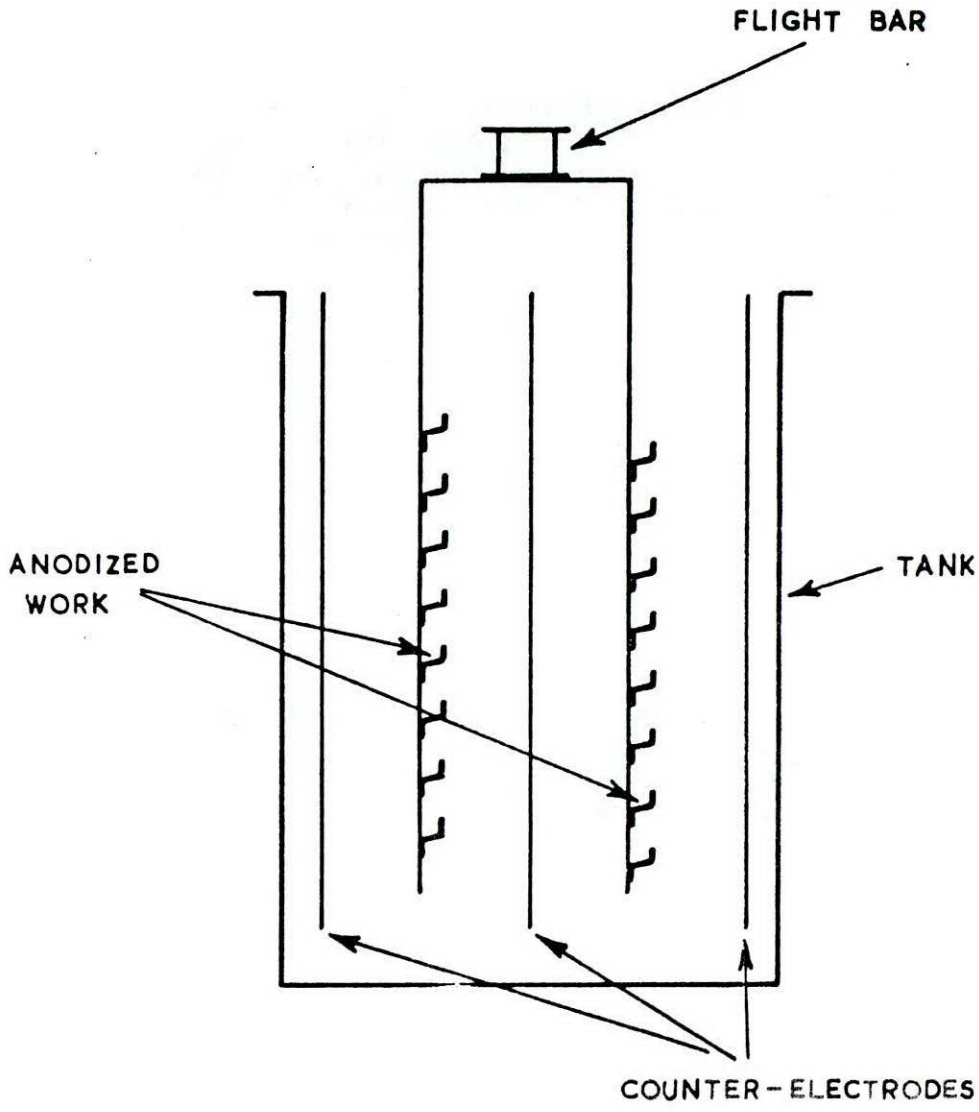

FIGURE I. LAYOUT OF COUNTER-ELECTRODE SYSTEM FOR ELECTROLYTIC COLOURING

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J-3

Light Metal Finishing I
Session J

Electrolytic Coloring of Anodized Aluminum Using Tin Electrolytes

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ELECTROLYTIC COLORING OF ANODIZED ALUMINUM USING TIN ELECTROLYTES

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and Glenn C. Schoener, Amchem Products, Inc., Ambler, Pa.

Comparison of Different Coloring Methods

Anodic oxide coatings on aluminum can be colored by one of three different methods which are distinguished by the nature of the coloring matter and its location within the oxide film (Fig. 1).

In adsorptive dyeing, organic dyestuffs or inorganic pigments are introduced into the openings of the pores in the oxide coating and are adsorbed in the region adjacent to the surface of the oxide coating. A wide range of colors with good uniformity and reproducibility can be obtained by adsorptive dyeing. Several dyestuffs exhibiting excellent lightfastness are currently available but their application under production conditions require much care and extensive controls in order to insure proper application and color matching. The problems of color control as well as earlier problems with lightfastness have led to the abandonment of this method of coloring in the field of architectural finishes in spite of the multitude of available color shades.

Integral color processes have dominated the architectural marketplace for many years. In an integral colored film, finely divided particles are situated inside the bulk oxide coating. These particles produce shades ranging from light bronze to black as a result of scattering of the incident light. These particles can be constituents of the base alloy, non-oxidized aluminum or decomposition products of the organic acids used in the color anodizing electrolytes. The depth of color produced is very dependent upon film thickness and alloy composition. The nature and location of the coloring particles make lightfastness a minor problem with the integral color process. Additionally, the high current densities and anodizing voltages employed in the integral coloring process result in the formation of an extremely hard,abrasion resistant oxide coating. These properties have resulted in the wide acceptance of integral colored finishes in the architectural field. However,a major drawback of the integral color processes is the extremely high energy consumption resulting from the high voltages and current densities required by the integral coloring process.

In electrolytic coloring, a clear anodized film is first produced. During a second step, small particles of metal are deposited irreversibly at the bottom of the pores of the oxide film by the application of an A.C. current in a metal salt solution. Most metals which can be electrodeposited from an aqueous solution may be used in electrolytic coloring but only some of them have gained practical importance. These are tin, nickel, cobalt and, to a lesser extent, copper. As in the integral colored film, the color is produced by light scattering phenomenon caused by the metallic particles. Therefore, the same range of light bronze to black color is obtained with all

metals except copper which produces red finishes if applied alone. The depth of color is determined by the quantity of metal deposited and is independent of film thickness and alloy composition within certain boundries. After initial uncertainties about the exact chemical nature of the deposits obtained, their metallic character has been proven independently by several researchers[1-3]. As with the integral color process, the nature and location of the coloring particles make lightfastness a minor problem with the electrolytic processes. Tin finishes, for example,have shown no fading after 2000 hours of cyclic Ultraviolet Weather-O-Meter testing.

All three coloring methods are still applied in the anodizing industry today. However, if we look back on the last 10 to 15 years of anodizing history, a clear shift in emphasis can be recognized, going from adsorptive dyeing to integral color processes and most recently to two-step electrolytic processes. Some of the factors used to assess the technical and economic value of a coloring method are: reproducibility of colors; uniformity of colors (throwing power); lightfastness of colors; corrosion resistance of colored finishes; ease of application; and cost per surface area. From these important considerations, the observed trend toward electrolytic coloring processes have their justification.

Compared to adsorptive dyeing, electrolytic processes provide greater color uniformity and reproducibility, as well as, improved lightfastness. Compared to integral color processes, electrolytic coloring produces equivalent color shades of greater uniformity and reproducibility on a wider range of alloy compositions. This fact coupled with the ability to obtain equal corrosion and abrasion resistance at much lower production costs have resulted in the rapid growth of two step coloring processes at the expense of the integral color process. By the introduction of an electrolytic coloring process, about DM 1.50 (about $0.62) in electrical cost can be saved per sq. meter. Therefore, it is not surprising that in Europe, integral coloring is continually being replaced by electrolytic coloring processes. This same trend is beginning to occur in the United States as demonstrated by the ever increasing number of anodizers installing two-step coloring processes.

As was mentioned earlier, the metals most frequently used for electrolytic coloring are tin, nickel and cobalt. Nickel based electrolytes, despite their low throwing power and sensitivity to contamination by foreign ions, are still widely used in Japan. Anodizers in Europe, on the otherhand, have demonstrated a clear preference for tin based electrolytes. These are relatively easy to operate, do not require expensive equipment, are insensitive to most contaminating ions and provide excellent throwing power. The following sections of the paper describe the method of operation of the tin based electrolytic coloring processes, the theoretical and practical problems originating in the relatively high acid content of these electrolytes, and the ways to overcome these potential problems.

Equipment and Coloring Procedure

Figure 2 shows a cross-section through a typical electrolytic coloring tank. The tank itself should be constructed from acid resistant material, preferably fiberglass or rubber lined mild steel. The most important feature

is the two sets of counter-electrodes running the length of the two long sides of the tank. In the case of tin based coloring electrolytes, the counter-electrodes are fabricated from stainlesss steel strips or tubes but carbon or tin can also be used. The counter-electrode system should have approximately the same surface area as the aluminum work load to be colored. The distribution of the counter-electrodes along the sides of the tank should be as uniform as possible. The fence-like construction visible in this drawing has given the best results in regard to color uniformity. The installation of a center counter-electrode, if the coloring tank is wide enough, will permit the processing of larger workloads. The center electrode should contain the same number of strips or tubes as the outer electrodes. The compressed air supply indicated in the drawing is used for mixing the coloring electrolyte after the addition of chemicals but times of air agitation should be kept as short as possible to prevent losses of divalent tin by air oxidation. The drawing does not show circulation and filtration equipment which can be installed to continuously remove any insoluble tetravalent tin compounds which may be formed during operation of the bath. The drawing also does not show any installation for heating or cooling. This equipment is only necessary if substantial deviations from the normal working temperatures of 18° - 24°C are to be expected due to climatic influences.

Normally, sinusoidal AC current with a frequency of 50 or 60 HZ is used for coloring. The transformer should have a maximum output of 25 volts with an amperage capacity corresponding to 75% of the anodizing amperage. Different attempts to improve the coloring efficiency have been made by employing solid-state thyristor based electrical equipment to control separately both the anodic and cathodic half cycles of the AC waveform. To date, these have not resulted in much benefit to the relatively easy-to-run tin coloring processes, making them, instead, unnecessarily complicated and extremely expensive to install.

The tin electrolytes used for coloring have a pH of 1.0 to 1.6. They normally contain between 8 and 10 g/L divalent tin as tin sulfate and between 16 and 22 g/L sulfuric acid. Organic stabilizers are often present to retard the air oxidation of divalent tin and to improve the throwing power of the process. Several proprietary stabilizers are available, some of which contain phenolic substances.

There are two alternative methods of producing a desired color shade. The coloring can be carried out for a constant time period using varying voltages, or the voltage can be kept constant and the time period varied. Normally, the second method is employed in most production facilities. To insure consistent color reproduction from load to load the anodizer must work with fixed coloring cycles. After anodizing, the rinsed parts are introduced into the coloring bath and are left there without voltage for about one minute. Following this immersion period the voltage is slowly increased from zero to a specific value between 10 and 18 volts within approximately one minute. This step must always be carried out in the same manner to insure color reproducibility. Coloring times range from 10 seconds for light champagne to 15 minutes for black. The current density at the beginning of the coloring process can be as high as 10 A/ft^2. Within 30 to 40 seconds it will drop to about 40% of the peak value and remain constant for the remainder

of the coloring time.

Influence of Coloring Voltage

Theoretically one would expect that the speed of coloring would be increased by increasing the coloring voltage. Surprisingly, this is only partly true as can be seen from Figure 3. In this figure the total reflection measured with a device similar to the PRS head[4] is plotted as a function of coloring voltage. The total reflection is given as a percentage of the reflection of a white barium sulfate plate. Using this method, the lower percentage figures represent darker shades. The two curves represent coloring times of 2 and 5 minutes in an electrolyte containing 10 g/L tin,20 g/L sulfuric acid and 20 g/L of proprietary stabilizer. It can be clearly recognized that the coloring speed is highest at about 15 to 16 volts. This is very important to know, particularly for the production of dark finishes, since the coloring time should be kept as short as possible.

The same test series was run at different concentrations of sulfuric acid. This was done to determine whether the position of the maximum coloring speed was influenced by the composition and the conductivity of the electrolyte. As can be seen in Figure 4, this was not the case. The two curves were obtained using a coloring time of 2 minutes. Darker shades were produced at all voltages with the lower sulfuric acid concentration of 15 g/L as compared to 30 g/L. The speed of coloring was highest at about 15 to 16 volts in both cases. A variation of the tin concentration leads to the same results.

We suggested, therefore, that the position of the maximum coloring speed might be influenced by the initial barrier layer thickness, which is a function of anodizing voltage. According to a previous work[5], the barrier layer thickness of oxalic acid films is reduced to a value which is determined by the coloring voltage and the acid concentration of the coloring electrolyte at the start of electrolytic coloring. It is certainly not wrong to theorize that similar changes will take place within a sulfuric acid film as well. Therefore, films of 20 to 21 µm were prepared with anodizing voltages ranging from 12 to 18 volts. These films were colored for a constant time of one minute in an electrolyte containing 10 g/L tin and 20 g/L sulfuric acid at 14, 16 and 18 volts. From the theoretical barrier layer thickness of 9 A°/V for d.c. anodizing and 10.9 A°/V (peak) for a.c. anodizing, an increase of the barrier layer thickness during coloring ranging from 54 to 170 A° was calculated. However, no correlation between these changes and the depth of color could be detected. Figure 5 shows that the darkest color was obtained at a coloring voltage of 16V independent of anodizing conditions.

One possible explanation for the fact that the voltage of maximum coloring speed is not influenced by the composition of the electrolyte or the properties of the anodic oxide coating can be given. In the first part of the curves, between 10 and about 14 volts, the speed of metal deposition increases linearly, similar to electroplating, whereas at still higher voltages the redissolution of tin during the anodic half-cycle of the a.c. wave becomes increasingly noticeable.

Contamination of the Coloring Electrolyte

It has been mentioned earlier that nickel based coloring electrolytes are extremely sensitive to contamination by foreign ions, especially sodium and potassium. This is not the case with tin based processes. However, no quantitative data has been published concerning the maximum permissible concentrations of impurities. In order to fill this gap, increasing amounts of chemicals normally encountered in an anodizing facility were added to a tin based coloring electrolyte. The electrolyte employed contained 10 g/L tin and 20 g/L sulfuric acid. The changes in coloring efficiency, that is the depth of color obtained after a fixed coloring time of 2 minutes, were observed. The ions investigated were sodium, potassium, calcium,magnesium, ammonium, nitrate, chloride, borate and oxalate. The tin is precipitated by phosphate ions, therefore they will not build up to a significant concentration. The influence of trivalent chromium ions and silicate ions were also investigated.

The results for sodium, potassium, nitrate and chloride are shown in Figure 6. The depth of color obtained after 2 minutes at 16V is plotted as a function of the concentration of the contaminating ion. It can be seen that sodium and potassium ions show an effect only at concentrations above 2 g/L. The coloring current density showed a significant increase at potassium ion concentrations above 5 g/L. Presumably such concentrations will rarely be attained by simple carryover from other pretreatment baths. Nitrate ions, on the other hand, reduce the coloring efficiency at concentrations as low as 0.2 g/L. In the presence of 1.5 g/L nitrate, no color was obtained. It might be concluded from the graph that chloride ions had no influence whatsoever. However, at a concentration of about 2 g/L chloride, the total film started to separate from the base aluminum. Simultaneously, the current density showed a tremendous increase. Chlorides, therefore, must be included among the dangerous ions, especially if the concentration approaches 1 g/L.

The other ions investigated are shown in Table I. Their influence on coloring efficiency is rather small. Very slight fading was observed with ammonium, borate, silicate and magnesium ions when their concentrations exceeded 5 to 10 g/L. Oxalic acid precipitated the tin and calcium was precipitated as calcium sulfate at rather low concentrations. Trivalent chromium was added in the form of a 1% solution of chromium-III sulfate. Only low concentrations were studied in order not to dilute the coloring electrolyte. No detrimental effects were observed to the maximum 0.8 g/L studied.

As a whole, these results confirmed the high tolerance of tin based coloring electrolytes toward contamination by foreign ions. Only nitrate and chloride proved to be dangerous at concentrations below 1 g/L. All other ions showed an effect only at much higher concentrations. Due regard has to be given to the quality of the coloring chemicals since chloride is a frequent contaminant of commercially available tin salts. Additionally, the chloride content of the make-up water must also be considered.

The Problem of Spalling

A local chipping off of the anodic oxide coating during the electrolytic coloring, called 'spalling' was a severe problem during the early development of electrolytic coloring processes. This phenomenon can occur with all electrolytes, independent of their acidity and the metal used for coloring. Possible reasons are too high coloring voltages and too fast an increase in voltage at the beginning of the coloring cycle. Spalling seems to occur at lower voltages in the less acidic nickel and cobalt electrolytes than in the more acidic tin electrolytes. Recently it has been recognized that the composition of the alloy is another important factor. Sheet alloys containing more than 1.5% magnesium proved to be especially susceptable to spalling.

Film Quality and Corrosion Resistance

The predominant point of dispute in comparisons of different electrolytic coloring processes has been and continues to be the question whether or not the relatively high acid content of tin based electrolytes is harmful to the quality of the anodic oxide coating. Conclusions have been drawn from purely theoretical considerations that, due to the high redissolution of the oxide film, tin finishes should show reduced abrasion resistance and inferior corrosion protection properties. The question of how much metal must be deposited or, in other words, how far the pores must be filled in order to obtain a dark color, has gained some importance in regard to the corrosion resistance problem. Electron microscopic investigations[6] have indicated that new pores are formed inside the original barrier layer due to reanodizing during the a.c. treatment in acidic electrolytes. This phenomenon is thought to increase the danger that the deposited metal might come into contact with the substrate aluminum thereby reducing the corrosion resistance.

In the following sections an attempt will be made to provide answers to all these questions. All the experimental variables involved in anodizing, coloring and sealing were closely controlled in order to be able to make a judgement on the basis of samples with defined properties.

Alterations of the Barrier Layer

Electron microscopic investigations on the structure of sulfuric acid anodized films are extremely difficult since the thickness of the barrier layer and the cell walls is only 100-150 A° if normal anodizing voltages are applied. Therefore, films anodized in oxalic acid or phosphoric acid at voltages ranging from 50 to 80V have been preferred for this type of work. Only under these conditions could the formation of branched pores under the original barrier layer during electrolytic coloring in acid electrolytes and the deposition of metal inside these new pores be demonstrated[5,7]. Simultaneously, a thinning of the barrier layer to a value corresponding to the much lower coloring voltage was observed. According to a Japanese work[8] on the structural changes inside the barrier layer produced by a sudden voltage

drop during anodizing, a strong branching of new pores is only to be expected if the voltage is reduced to less than two-thirds of the original anodizing voltage. In all other cases the new film grows uniformly below the original barrier layer. Conditions are even more favorable in the case of anodizing in sulfuric acid and subsequent electrolytic coloring. Since the coloring voltage is generally higher than the anodizing voltage, the thickness of the barrier layer is actually increased. This should make corrosion originating from a contact of the deposited metal with the aluminum substrate less probable.

Salt Spray Tests and Outdoor Exposure Results

An investigation into the corrosion resistance of tin based finishes was performed using different color shades. The samples were anodized in an electrolyte containing 200 g/L H_2SO_4 at 18°C using a current density of 15 A/ft^2 to a film thickness of 20 microns (0.8 mil). The coloring electrolyte contained 10 g/L tin and between 15 and 30 g/L sulfuric acid. The color shades produced were light bronze, medium bronze and black. All samples were sealed for 3 min/micron in boiling deionized water at a pH of 5.8. Fig. 7 shows the black samples after 1500 hours of exposure in an acidified salt spray test[9]. The upper test sheets were merely rinsed after leaving the test cabinet. The lower ones of identical pretreatment were cleaned with a slightly abrasive cleaner. The salt spray caused some greyish discoloration and only very slight pitting. No correlation between the number of pits, the depth of color and the sulfuric acid concentration could be detected. This becomes obvious from Table II which gives the number of pits observed on the cleaned samples having a surface area of 50 cm^2. Pits situated directly at the cut edges of the samples were not considered in the evaluation. The black sheet colored with the highest sulfuric acid concentration showed the largest number of pits. However, the medium bronze sample prepared using the same pretreatment did not develop any pits at all. The black test specimen colored with the next lowest sulfuric acid content also did not develop any pits. Therefore, the differences noted must be attributed to statistical variations. Furthermore, the pits which did develop had a very small diameter (less than 0.3 mm). This means that even in the worst case, only 30 ppm of the total surface area was covered with pits.

These very favorable results are in accordance with outdoor exposure tests carried out in France[10] and Germany[11]. In the latter country a comparison between dark tin based finishes and integral colored finishes was conducted in maritime, industrial and mixed maritime/industrial climates. No differences in corrosion resistance could be observed on samples with a minimum film thickness of 20 microns when evaluated after 5 years of exposure. A conclusion might be drawn from these results that the concentration of the sulfuric acid in the coloring electrolyte is of no importance whatsoever. This is certainly not entirely true. It has been shown previously that the acidic coloring electrolytes do not reduce the abrasion resistance of the anodic oxide coating if the anodizing is carried out under proper conditions[12]. This is demonstrated by Fig. 8 in which the thickness reduction in the abrasive wheel test is plotted as a function of the number of double movements with a constant contact pressure. It can be seen that the same curve is obtained for clear anodized, electrolytically colored and the organically dyed

sample if anodizing is performed at 18°C. Figure 9 shows, however, that a small increase in anodizing temperature of only 3°C produces a significant reduction in abrasion resistance if the film is colored in an acidic electrolyte. These differences have been explained as indicating that the coloring step will show a harmful effect only if the outermost zones of the anodic oxide coating have already been weakened or softened during anodizing.

Anodizing temperature is only one factor affecting the hardness of the anodic oxide coating. Another factor is the current density, by which the porosity of the film and the contact time in the anodizing bath are determined. It is known that extended anodizing times and elevated film thicknesses will result in an oxide coating with reduced strength and wear resistance especially in the outermost zones. Samples were anodized at current densities of 12 and 15 A/ft^2 to a film thickness of 25 microns to determine whether the resistance to an acidic coloring electrolyte is reduced by these effects. One set of the test samples were colored black in a cobalt electrolyte. Two other sets were colored to a dark bronze and a black shade in a tin electrolyte containing 20 g/L H_2SO_4. The film quality was determined after sealing by means of the chromic-phosphoric acid weight loss test and the abrasive wheel test and compared to that of clear anodized samples produced under identical conditions. The results summarized in Table III show only very slight effects of current density and coloring treatment on the acid resistance, though the weight losses of the cobalt colored samples tend to be somewhat higher. The influence of current density on the abrasion resistance is more distinct. A significant reduction, especially in the case of the black tin finish, is observed if the current density is lower than 15 A/ft^2. It can be concluded from previous work by one of the authors[12], that under the test conditions used, all thickness reductions below 4 to 5 microns must be regarded as satisfactory. Abrasion resistance can be obtained with black tin finishes which come close to that of integral colored films if the current density is further increased to 24 A/ft^2. In these cases, however oxalic acid must be added to the anodizing electrolyte in order to avoid the negative effect of local overheating (burning) of the film.

Metal Distribution Inside the Pores

The dark bronze and black samples on which the location and amount of metal inside the pores were determined had not been prepared in the laboratory but were taken from the production of an anodizing plant. The scanning electron micrograph in Fig. 10 shows the cross-section of a 20 µm film colored dark bronze in a tin electrolyte. The line scan with the electron microprobe was run along the white line and the tin concentration profile in the pore is given by the dotted curve. It can be clearly recognized that the maximum of this curve is situated at the oxide/metal interface and that only the lower 25% of the pores are filled with tin. Identical results were obtained on a sample colored to the same shade using a cobalt electrolyte with the only difference being a slightly narrower distribution.

More metal must be deposited in the pores for the production of a black finish. This becomes obvious from Fig. 11 which shows the tin distribution inside a black 20 micron thick film. The deposited metal extends about 10 microns into the coating leaving the pore openings free for sealing. Its

absolute concentration decreases steadily from the barrier layer in the direction of the film surface. The corresponding distribution of cobalt is somewhat different (Fig. 12). Here again the pores are about half-filled with metal. The concentration profile, however, shows a much sharper increase as compared to tin and a plateau with a width of about 5 µm where the pores seem to contain the maximum possible amount of cobalt. These results are in accordance with the observation that over-coloring, that is, overfilling the pores with metal; is more likely to occur with tin than with cobalt. On the other hand they also prove that this possibility is by no means an unavoidable characteristic of tin based coloring processes. It can be overcome and therefore avoided by limiting the coloring times to the minimum necessary to produce the required shade. Admittance measurements provide a fast and accurate means of determining whether or not the pores have been overfilled with metal. The coloring parameters and admittance values of different dark tin finishes are summarized in Table IV. A black film with an admittance of 77 µS was obtained after 8 min. coloring at 16 Volts. The Table shows that an extension of the coloring time to 15 min. did not bring about any change in color but caused the admittance to rise in increments to 200 µS. It is advisable, therefore, for an anodizer to establish internal standards defining maximum permissible admittance values for dark finishes.

It has been claimed[10] that the deposition of nickel inside the pore is able to enhance the corrosion resistance of the anodic oxide coating. Occasionally, therefore, mixed tin/nickel coloring electrolytes are used adjusted to a pH of about one. Fig. 13 shows the nickel distribution inside a film colored to a dark shade according to one of these processes. There is only a very small amount of nickel present at the bottom of the pores which presumably has been co-precipitated together with the tin. No nickel at all could be detected in other areas of the same sample. Significant amounts of nickel can only be introduced into the film if the pH of the coloring electrolyte is raised to a value more favorable for the electrodeposition of this metal. This change requires special means for preventing the precipitation of tin salts as well as bringing about a remarkable decrease in throwing power.

Conclusions

Tin based electrolytic coloring processes are predominant in Europe for the production of bronze to black architectural finishes due to their high throwing power, ease of operation, low cost and high tolerance to contaminating ions. More than ten years of field experience have given proof of the excellent lightfastness and corrosion resistance of tin colored films. The tin based electrolytic processes are very rapidly becoming the standard choice of anodizers in the United States for the same reasons stated above. Tin based coloring processes have achieved this wide acceptance in spite of the relatively high acid content of the coloring electrolytes.

Possible negative effects of the acid concentration can be avoided by controlling the anodizing conditions and by applying as short as possible coloring times. Anodizing should be carried out at a maximum temperature of 19°C and at current densities not much lower than 15 A/ft^2.

The preferred coloring voltage is 15 to 16 V a.c., since in this region maximum speed of coloring is obtained. The pore must be almost half filled with tin in order to produce a black color on a 20 µm Class I architectural film. Production of black Class II work will require anodizing to approximate 12 µm to insure that empty pore space is available for adequate sealing. The dangerous overfilling of the pores which can occur at extended coloring times can be detected by means of the admittance test.

Samples anodized and colored under conditions quoted above and sealed for 3 min./micron in deionized water showed excellent results after 1500 hrs. of acidified salt spray testing. The test results were independent of the color shade and a wide variation in acid concentrations in the coloring electrolyte.

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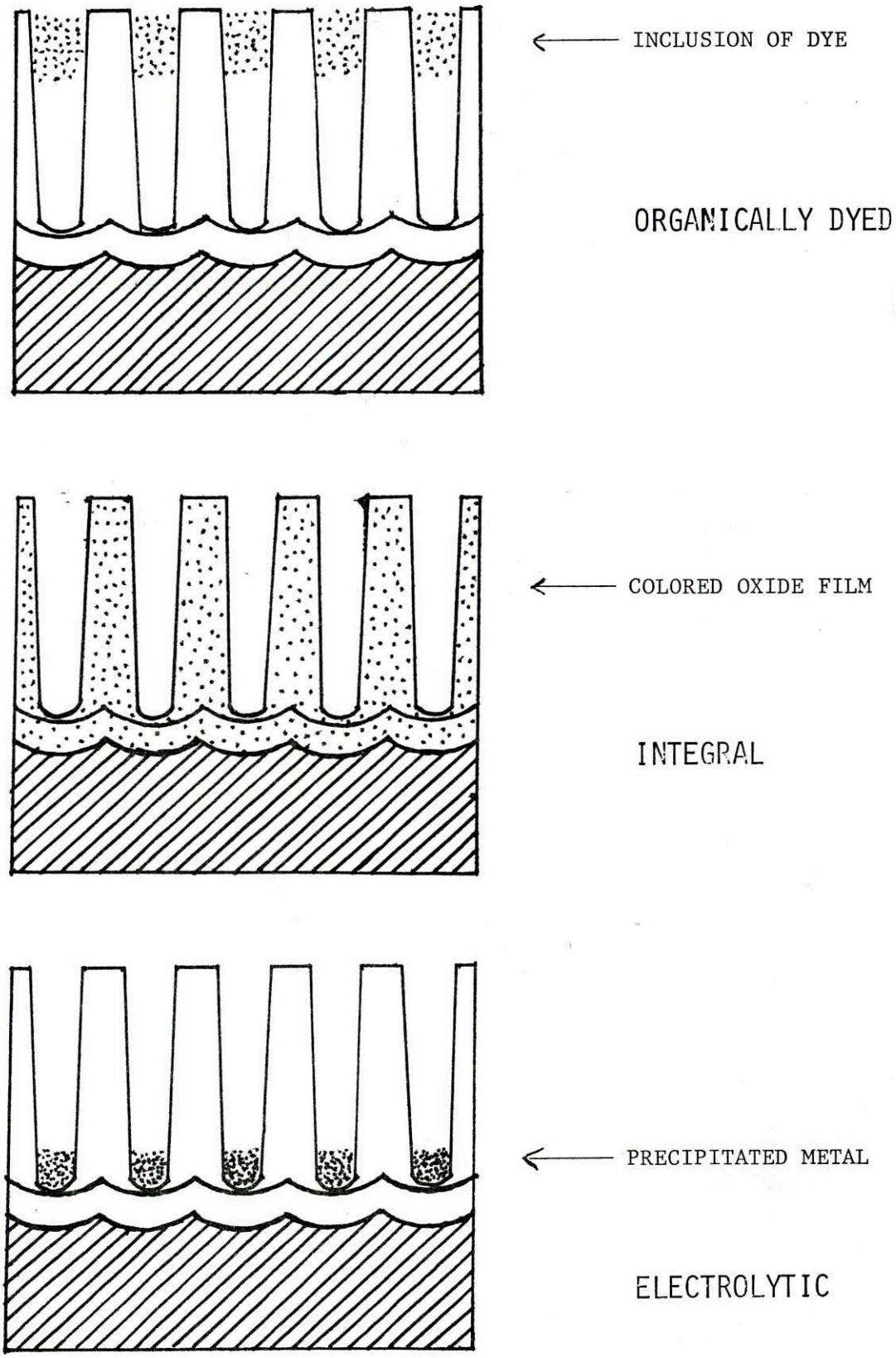

Fig. 1 Comparison of Various Methods for Coloring Anodized aluminum.

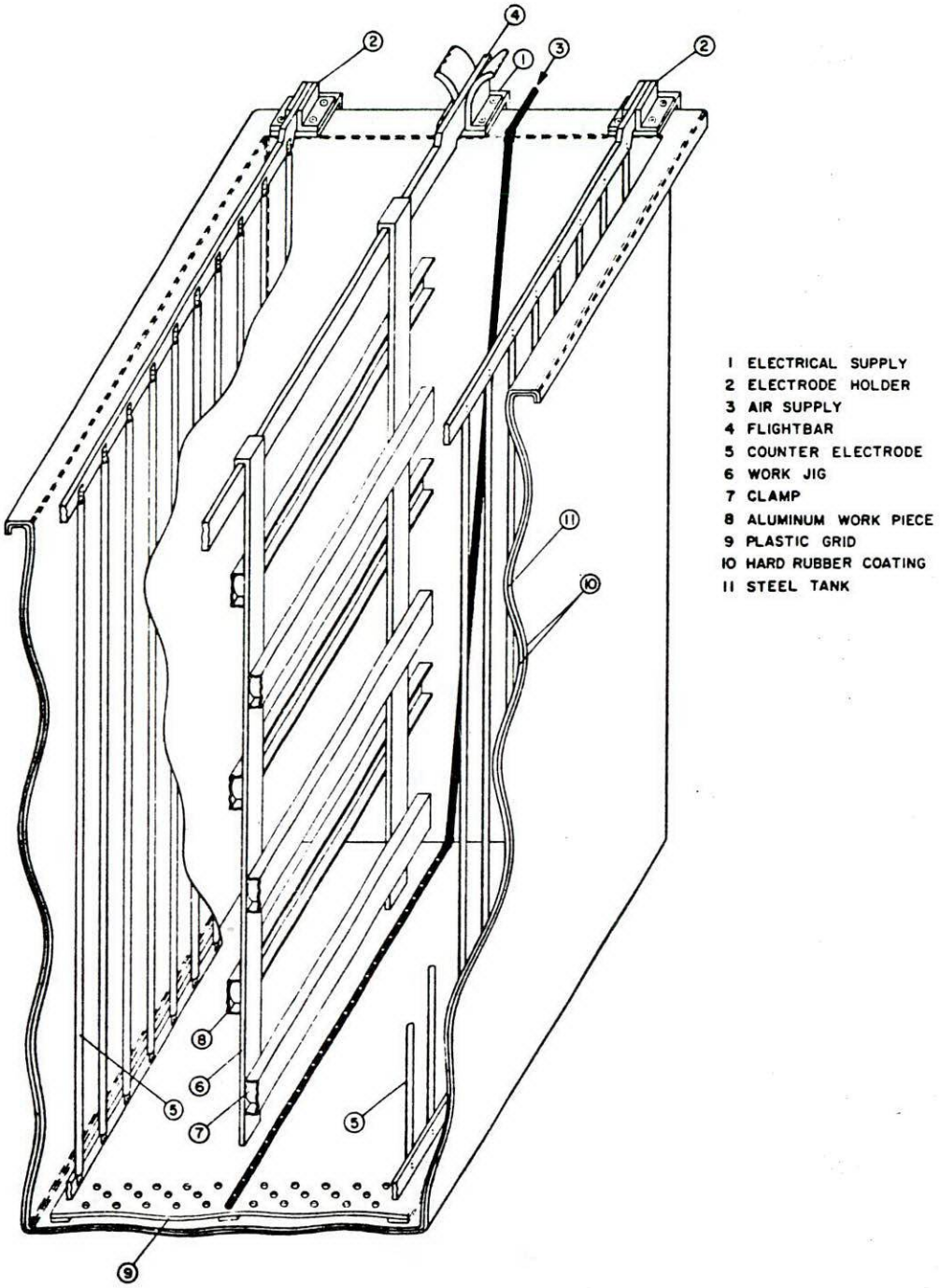

Fig. 2. Schematic drawing of a typical electrolytic Coloring Tank

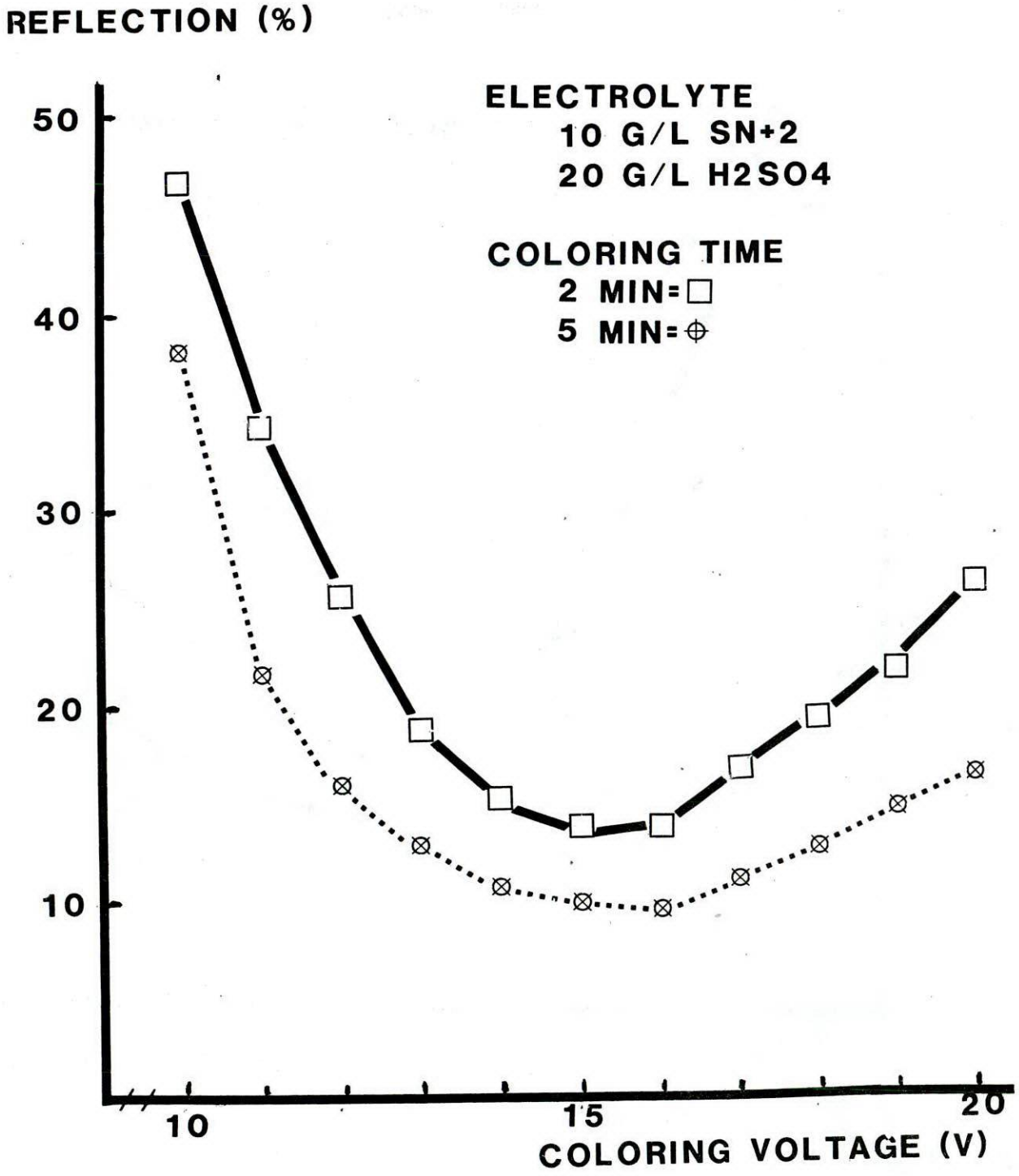

FIG 3. INFLUENCE OF COLORING VOLTAGE ON COLORING TIME

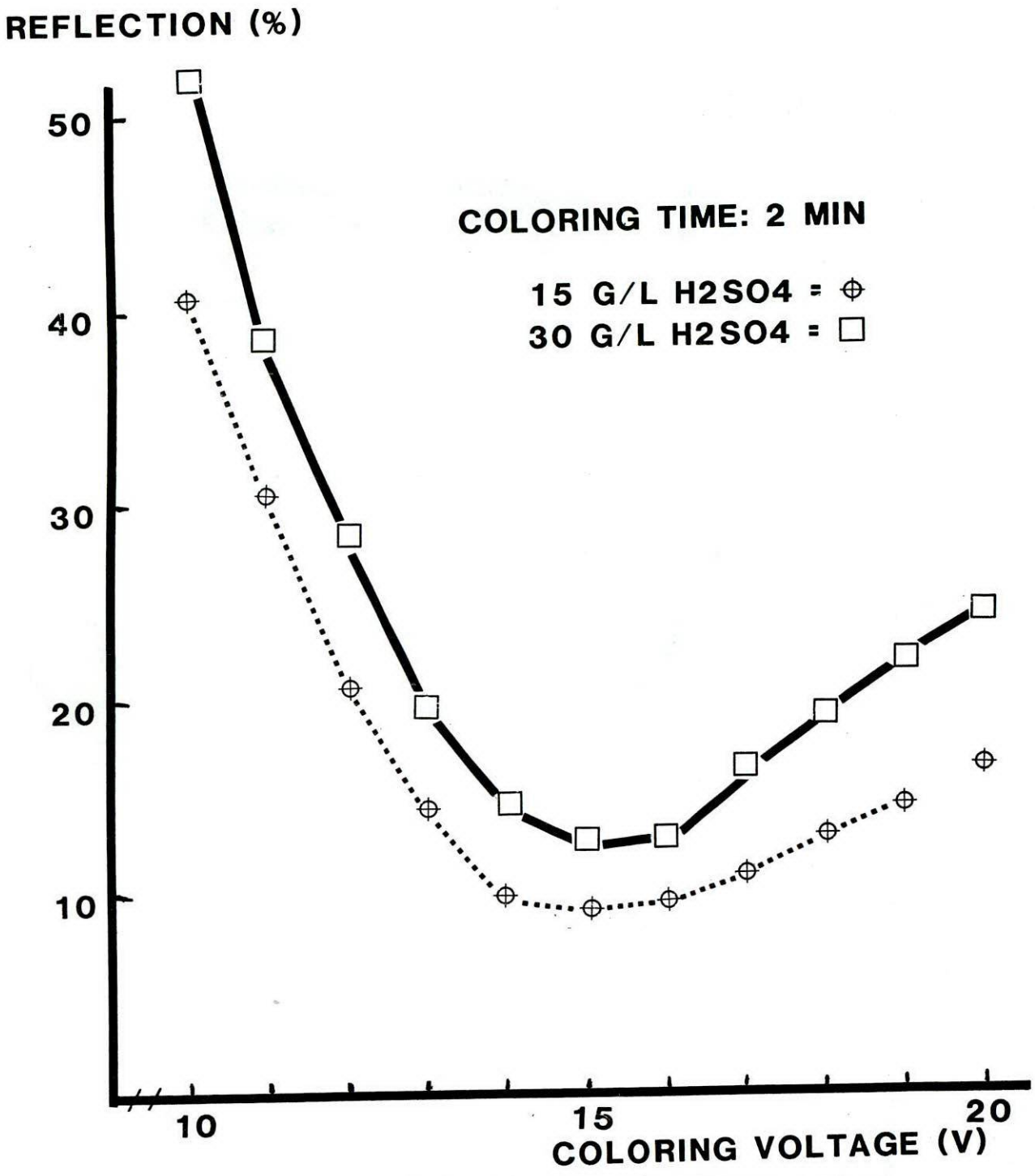

FIG 4. INFLUENCE OF SULFURIC ACID CONCENTRATION AND VOLTAGE ON COLORING SPEED

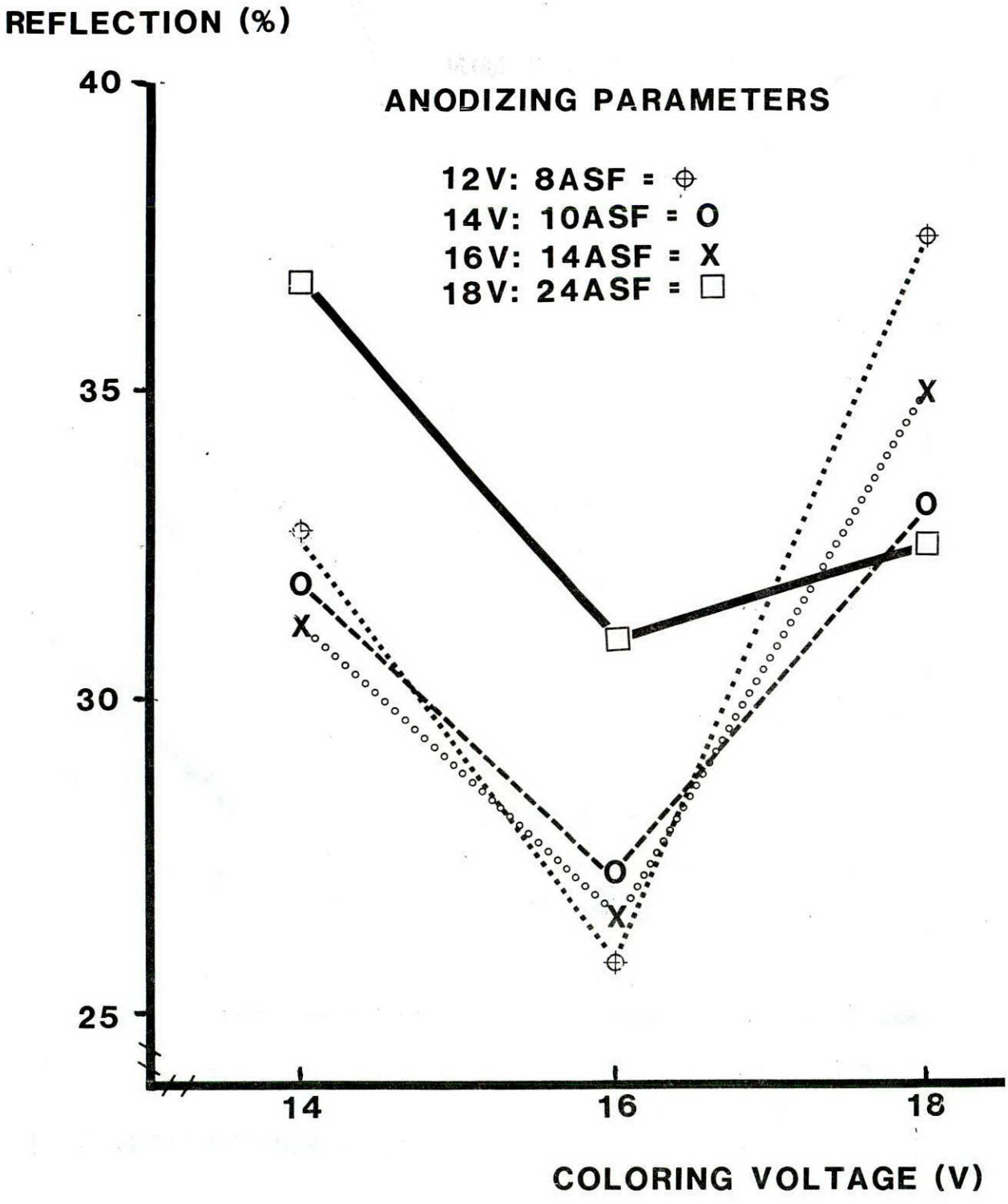

FIG 5. INFLUENCE OF ANODIZING AND COLORING VOLTAGES ON COLORING SPEED

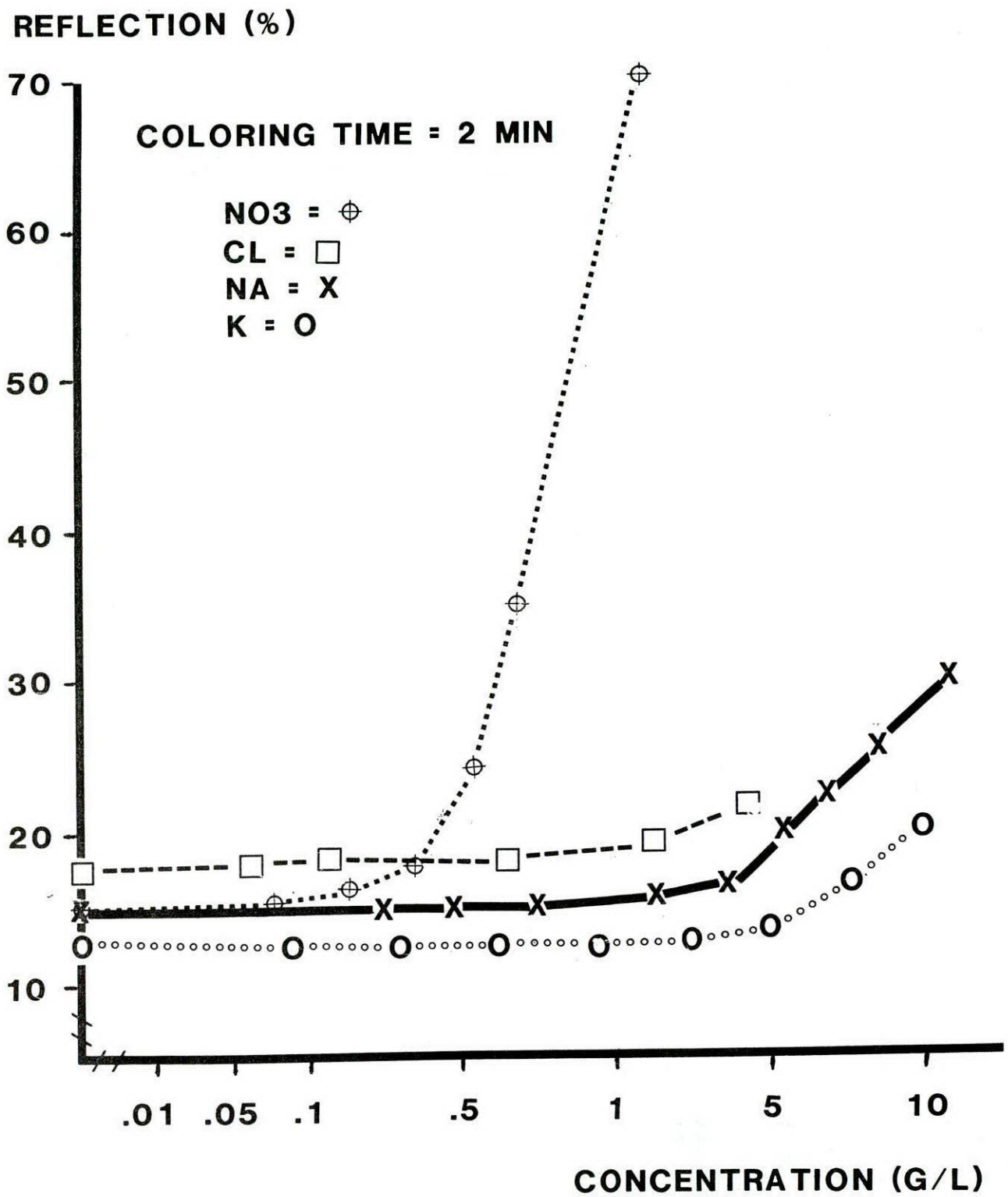

FIG 6. EFFECTS OF CONTAMINATING IONS ON COLORING EFFICIENCY

TABLE I INFLUENCE OF CONTAMINANTS ON COLORING EFFICIENCY

Contaminant	Maximum Concentration Studied (G/L)	Tolerable Concentration (G/L)	Remarks
NH_4^+	27	5	Slight Fading
B_2O_3	18	7	Slight Fading
Ca^{+2}	2.5	2.5	Precipitates
Mg^{+2}	10.1	10.1	
Oxalic Acid	50	2	Precipitates
Cr^{+3}	0.8	0.8	
SiO_2	10	5	Slight Fading

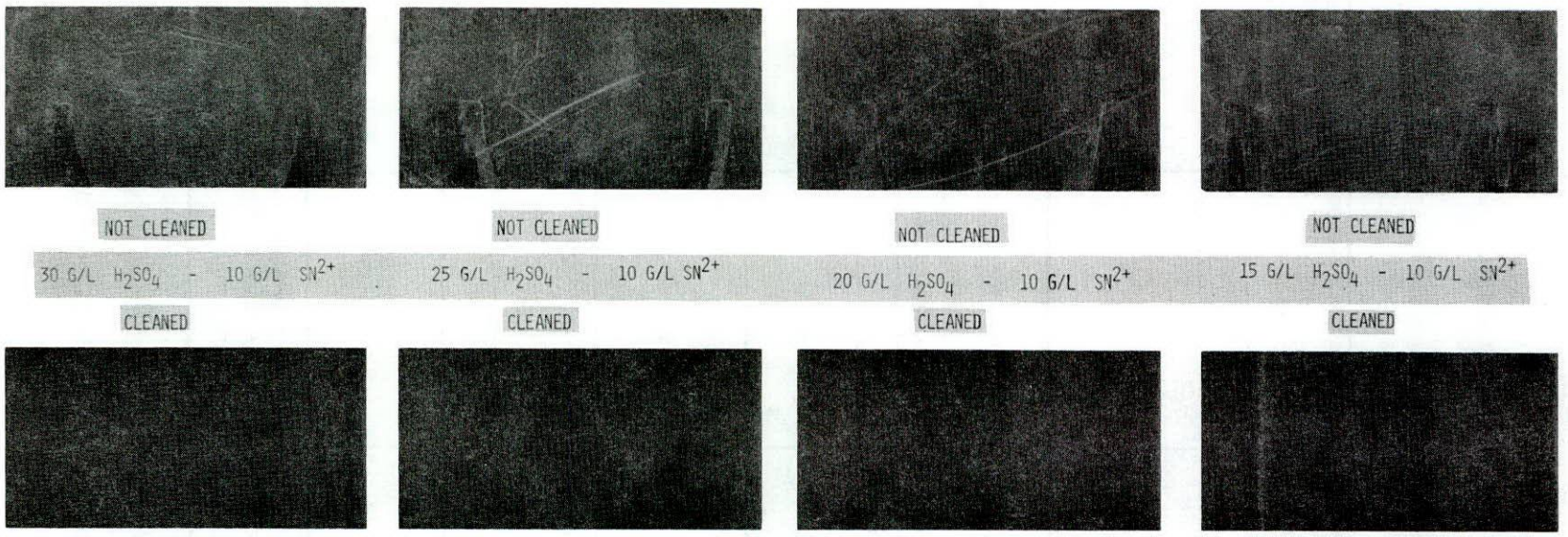

Fig. 7: Black Tin Colored Samples After 1500 hrs. Acidified Salt Spray Test

TABLE II PITTING CORROSION ON DIFFERENT TIN FINISHES AFTER 1500 HRS ACIDIFIED SALT SPRAY TEST

Sample No.	Coloring Electrolyte	Color Shade	Number of Pits
2	10 G/L SN^{+2} 15 G/L H_2SO_4	Light Bronze	0
4		Medium Bronze	2
6		Black	2
8	10 G/L Sn^{+2} 20 G/L H_2SO_4	Light Bronze	5
10		Medium Bronze	1
12		Black	3
14	10 G/L Sn^{+2} 25 G/L H_2SO_4	Light Bronze	1
16		Medium Bronze	0
18		Black	0
20	10 G/L Sn^{+2} 30 G/L H_2SO_4	Light Bronze	6
22		Medium Bronze	0
24		Black	9

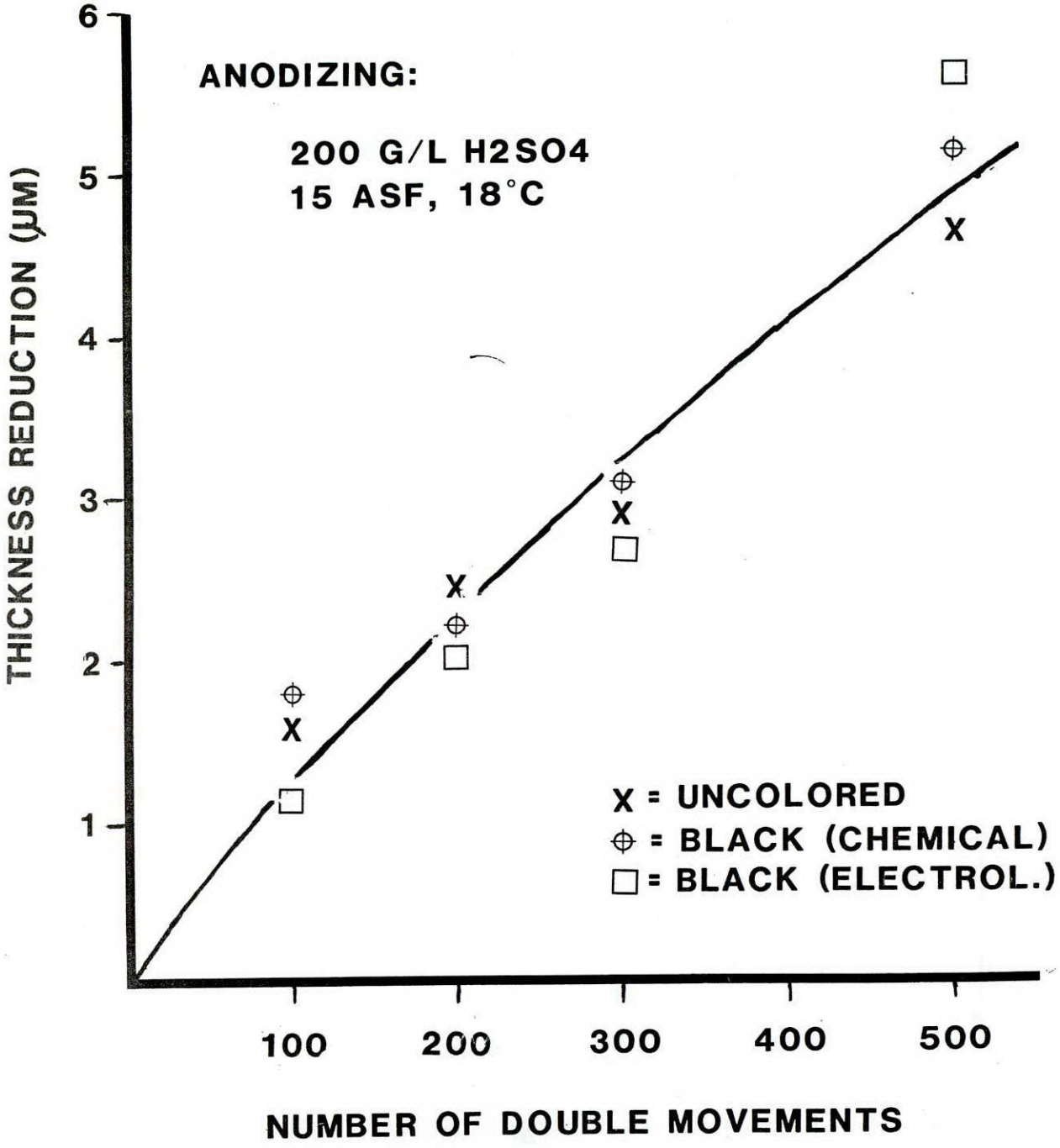

FIG 8. INFLUENCE OF CHEMICAL AND ELECTROLYTIC COLORING ON ABRASION RESISTANCE

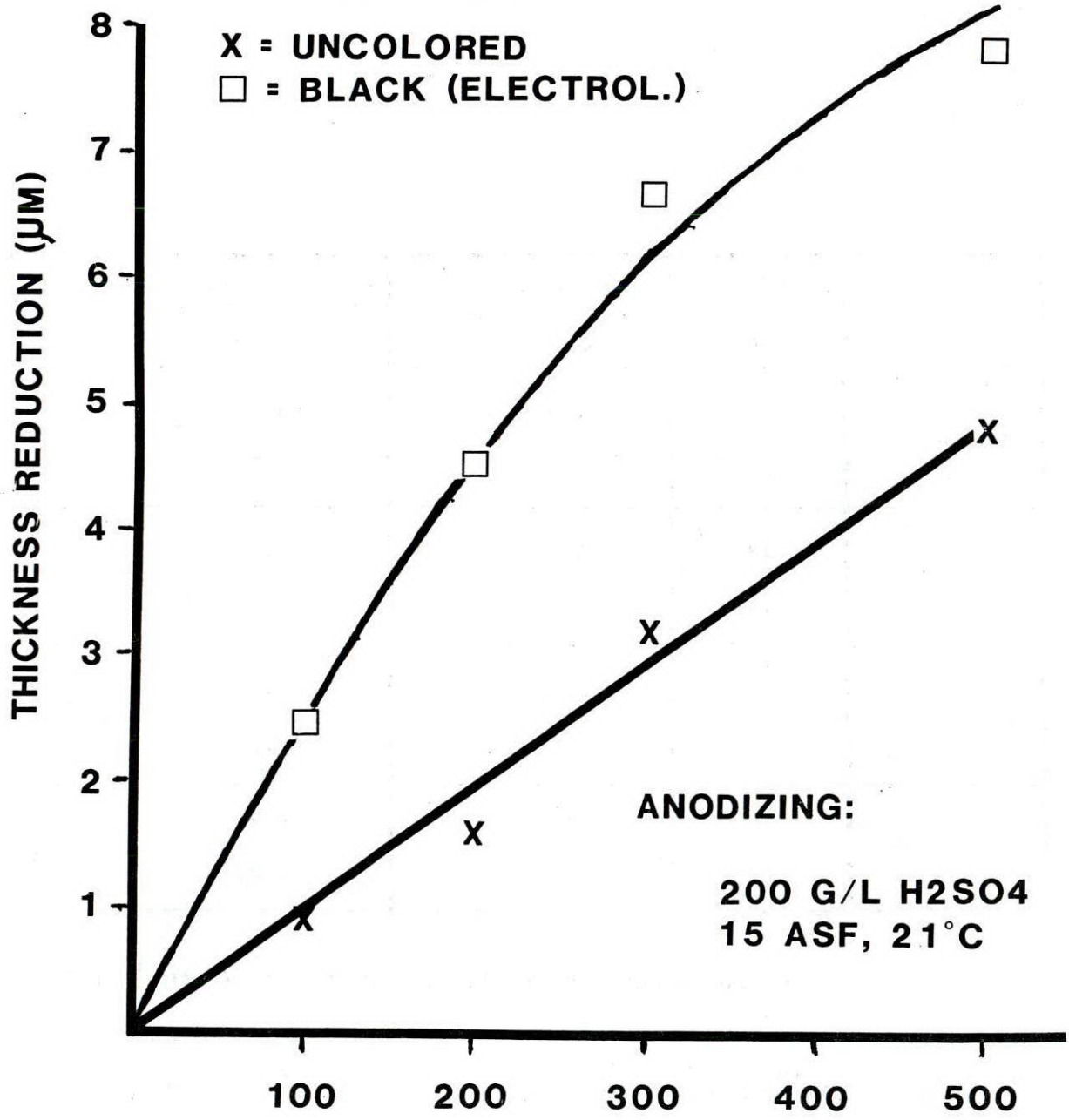

FIG 9. INFLUENCE OF ANODIZING TEMPERATURE ON ABRASION RESISTANCE

TABLE III INFLUENCE OF ANODIZING CONDITIONS ON TIN AND COBALT FINISHES.

Finish	Anodizing Conditions (ASF)	Acid Dissolution Weight Loss Test (Mg/ft^2)	Thickness Reduction Abrasive Wheel Test (um)
Uncolored	12	1.5	3.4
	15	1.3	1.7
Sn^{+2}, Black	12	1.5	3.7
	15	1.3	2.6
Sn^{+2}, Black	12	1.6	10.7
	15	1.4	2.7
Co^{+2} Black	12	1.8	3.0
	15	1.4	1.8

Anodizing Electrolyte: 160 g/L H_2SO_4; 7 g/L AL^{+3}; 19°C

Film Thickness - 25 um

Sn^{+2} Coloring Electrolyte: 10 g/L Sn^{+2}; 20 g/L H_2SO_4

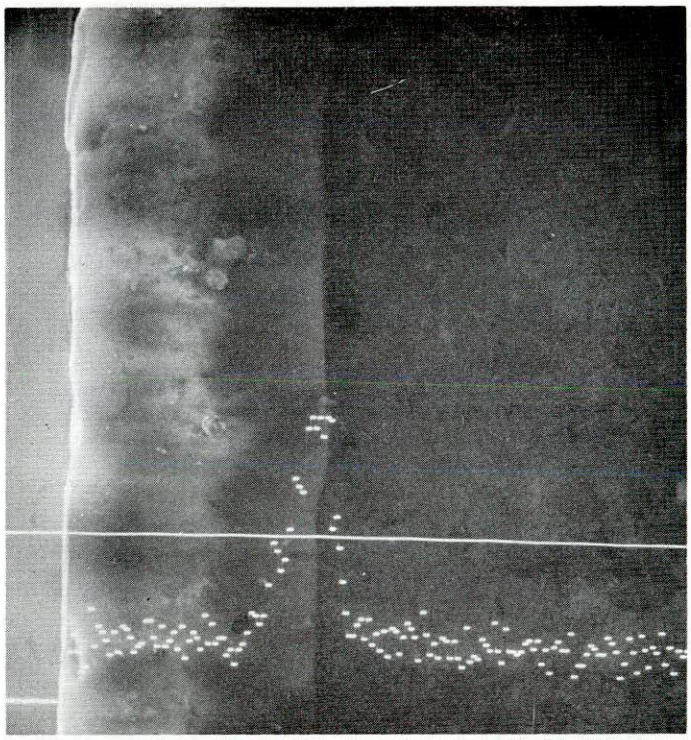

Fig. 10: Tin distribution inside a dark bronze film

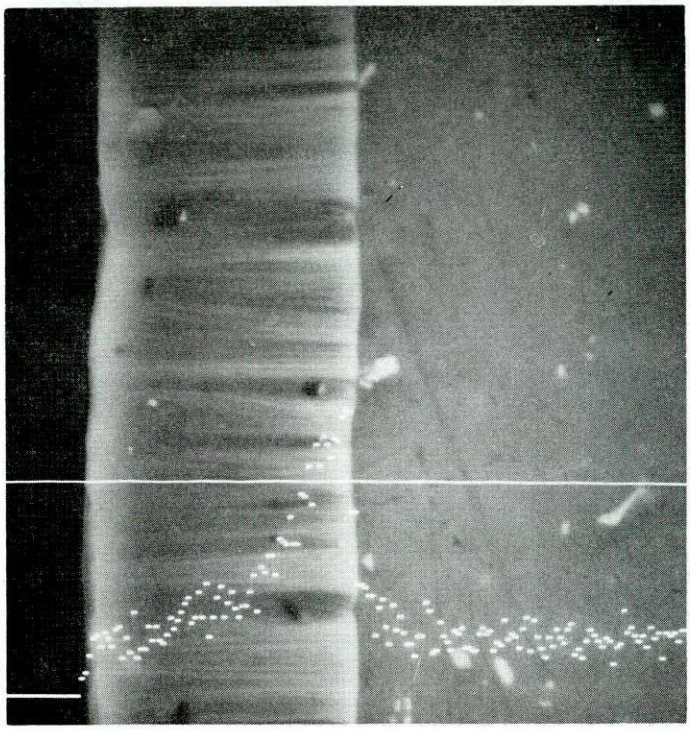

Fig. 11: Tin distribution inside a black film

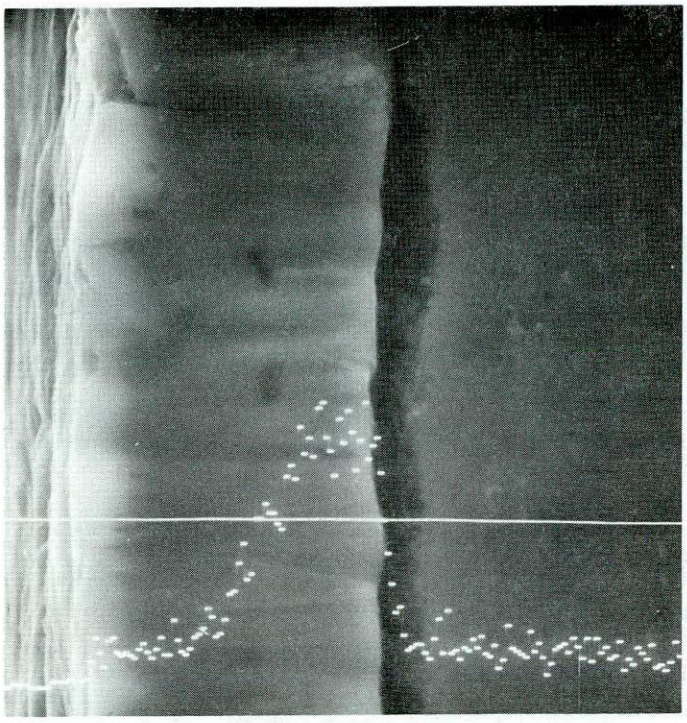

Fig. 12: Cobalt distribution inside a black film

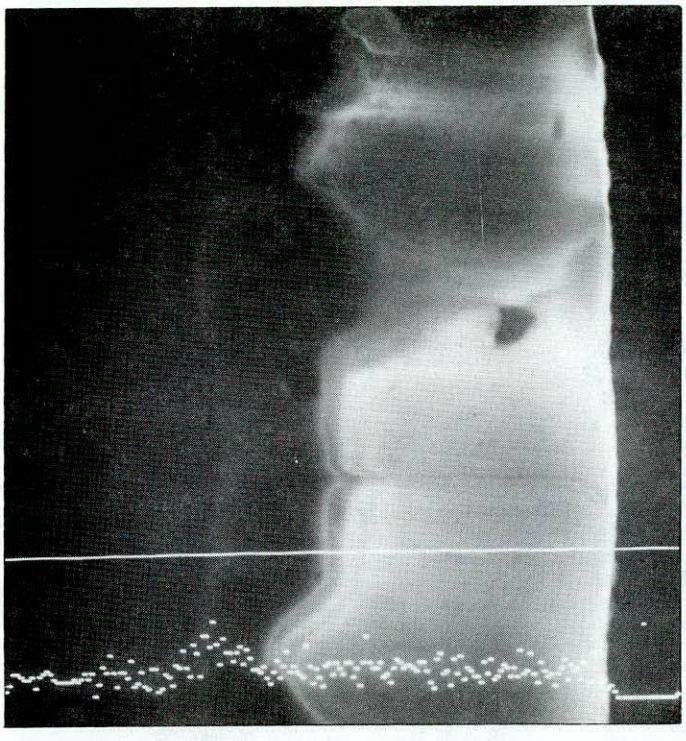

Fig. 13: Nickel distribution inside a dark bronze film
Colored in a mixed Sn/Ni bath at pH = 1

TABLE IV ADMITTANCE VALUES OF DARK TIN FINISHES AS A FUNCTION OF COLORING TIMES

Color	Coloring Conditions		Admittance Y_{20} (μS)
	Voltage (V)	Time (T)	
Dark Bronze	16	4	23
Black	16	8	77
Black	16	9	100
Black	16	10	130
Black	16	15	200

Anodizing: 200 g/L H_2SO_4; 8 g/L AL^{+3}; 15 ASF; 18°C; 19 μm

Coloring Electrolyte: 10 g/L Sn^{+2}; 20 g/L H_2SO_4; 20 g/L additive

Sealing: 3 min/micron in Deionized water.

J-4

Light Metal Finishing I
Session J

Electro-Coloration of Anodized Aluminum: Evolution of these Processes

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ELECTRO-COLORATION OF ANODIZED ALUMINIUM
EVOLUTION OF THESE PROCESSES

MICHEL LEGRAND
SURFACE TREATMENT DEPARTMENT
CEGEDUR PECHINEY

In 1967, when the very first electro-coloration processes appeared on western markets, European anodizers waxed lyrical about these processes.

They were emerging at a time when the construction industry was experiencing a boom, and architects were designing many prestigious buildings.

At that time, the colors available to the users of anodized aluminium for buildings were being obtained :
- either by chemical means for a gold coloration
- or by integral coloration for bronze and black
the shades of bronze being the most commonly-used range.

Under the dynamic impulse of the American aluminium construction industry, some integral coloration processes were perfected - processes including the baths and the procedures involved - but also the processing of alloys to obtain sheets and sections in metallurgic shades enabling integral coloring anodization.

North America quickly became equipped with integral coloring anodizing plants, and much architectural planning was realized.

Non-American aluminium companies had also been busy, and many of them disposed of methods enabling them to obtain integrally colored alumina layers. Equally, a certain number of the important European anodizers had acquired licenses from American firms, resulting in - Germany and Switzerland are cases in point - the acquisition of major integral coloration means.

From 1967 onwards, very few integral coloration anodizing plants were being built in Europe. The expansion of the market was almost totally limited to the field of electro-coloration. Then, over the years, this process has gradually taken over the position once occupied by methods using integral coloration, and it would be fair to say that, nowadays, integral coloration has in Europe all but disappeared.

In North America, the same evolution is taking place, hoping to replace integral coloration by electro-coloration systems.

Let us now examine the origins of these electro-coloration processes, and then we shall discuss their advantages over those involving integral coloration ; finally, we shall examine the technology of a process of electro-coloration in use throughout the world.

Although electro-coloration made its European debut in 1967, researchers and industrialists had discovered the principles of the process some thirty years previously.

In fact, the Italian patent N° 339232 submitted by Vittorio Caboni on the 10th of february 1936, accurately describes the principles of the process such as it is being used today.

He discusses the use of copper salt, nickel or silver, as well as the use of continuous or alternating currents. He even quotes the possibility of carrying out both anodization and electro-coloration at a single sitting.

A few years later, Dr. Gerhard Elssner and a German company that still deals today with surface treatments,* made several requests for patents allowing them to perfect V. Caboni's invention.

The request for a patent made in Germany on the 13th of april 1940 demonstrates that this company had experimented in the use of copper salts, with alternating currents in order to obtain colors nowadays well-known from the copper range, going from pink to black, with all the shades of more or less dark red in between.

In the course of these experiments, the rectifying effect of the alumina layer had been properly identified and a drawing enclosed with the patent illustrates how this effect favours the metal deposit.

The problems being experienced at that time and in subsequent years doubtless explain why approximately 30 years have elapsed between V. Carboni's invention and the industrial application of electro-coloration processes.

Finally, it is with Dr. Asada's patent that electro-coloration processes emerged from the Dark Ages and began to be used in an industrial capacity.

This period marks the beginning of a flurry of activity in the shape of research in this domain, encouraged by the strong position of the construction market that required bronze or black coloration, having grown accustomed to those by the integral coloration processing.

This research activity is also stimulated by the anodizers themselves, who feel the need to have at their disposal methods of coloration easier to implement than the integral coloration one.

This research has resulted in a considerable number of patents being taken up by numerous companies, and an important number of processes now on the market.

*LANGBEIN-PFANHAUSER WERKE AKTIENGESELLSCHAFT

Research has above all concentrated upon :

- the baths used ...
  for this, all metals able to be deposited by electrolysis have been tested and discussed ; then the dosage and mixing of metallic salts is examined. Similarly, the bath content, in products favourable to the stability of the bath constituents, eveness of color and ease of color reproduction, have all been considerably improved.
- application of voltage ...
  the most widely-used is still the alternating current. But certain processes use continuous current, since anodized aluminium is cathodic. Some authors, taking into account the fact that the alumina layer had a rectifying effect on the alternating current, have exaggerated this imbalance by using non-sinusoidal alternating currents in which one of the polarities is more accentuated than the other. Other authors have in effect varied the frequency of the alternating currents.
  The aim of all these variables is of course to control the color uniformity, as well as the throwing power.

Why choose electro-coloration rather than integral coloration

1) For energy saving, hence reduction in working costs

This data was collected in an anodizing workshop that had initially worked with integral coloration, then with electro-coloration methods.

	Integral coloration	Electro-coloration
PRODUCT :	COMMERCIAL DARK BRONZE	
anodization power	0.6 KwH/ft^2	0.094 KwH/ft^2
cooling "	0.2 "	0.038 "
coloration "	0 "	0.007 "
TOTAL	0.8 KwH/ft^2	0.139 KwH/ft^2
	gain = 0.66 KwH/ft^2	
	representing 82.6 %	
PRODUCT :	INTEGRAL BLACK	CLASS 1 BLACK
anodization power	1.50 KwH/ft^2	0.125 KwH/ft^2
cooling "	0.51 "	0.051 "
coloration "	0 "	0.028 "
TOTAL	2.01 KwH/ft^2	0.204 KwH/ft^2
	gain = 1.81 KwH/ft^2	
	representing 82.6 %	

This reduction in working costs is a considerable one. It results from the high voltage level needed for integral coloration, which in turn requires a considerable cooling system. What is noticeable is that only very low levels of voltage are required for the coloration itself.

2) For a reduction in investment costs

The power of the rectifiers (less important in the electro-coloration systems), together with the reduction in cooling requirements, result in a lower level of investment costs.

3) For a greater ease of alloy treatment

The commonly-used alloys : 6063 in sections
5005 in sheets
are easily treated in electro-coloration systems.

In the case of integral coloration, special alloys are required, at least to obtain the darker shades, and these alloys are harder to manufacture and are more costly.

Furthermore, using those alloys means a reduction in metal stock, whereas with electro-coloration the same semis can have a colorless or colored anodization.

In this way the user can obtain his semis from various processing sources.

The metallurgic constraints imposed on semis no longer exist, and this is a definite plus.

The practical point of view - that of the anodizer

Let us now consider electro-coloration from a practical viewpoint, from the anodizer's angle.

What should he do to obtain satisfactory results ?

. We are used to saying : if the anodizer makes a colorless alumina layer of an overall high quality, then his result will be a regular high-quality coloration.

  A colorless high-quality alumina layer can be obtained by paying attention to the following points :

  - the quality of the electrical contact between the sections and racks - the clamps are a satisfactory means of obtaining this result, but any other method ensuring a good electrical contact can be used.
  - sufficient area for current supply
  - stability of the anodizing bath temperature
  - control of current density during anodization so as to be able to control the anodizing thickness
  - adherance to simple rules of separation of pieces to be treated.

It is worthwhile pointing out that we have observed anodizers solely involved in colorless treatments who have improved their quality and revenue price performance levels by sticking to the simple rules.

. Once the colorless anodizing is complete, a rinsing in controlled conditions must be carried out, conditions that are dependent on the coloration process used.
. The coloration itself can then be made : and the voltage is applied for a pre-arranged time
  for instance : 3 to 5 minutes for a dark bronze) according to
  13 to 18 minutes for black) the process used.

Whatever the electrical complications of certain processes, they all use automatic voltage control systems. The operator must then select the color and/or the corresponding time, and then switch on the electricity generator.

Then all that remains for the operator to do is to check the results of the coloration.

If, for whatever reason, it is necessary to insist a little on the color obtained, all that needs to be done is to re-start the coloration cycle to obtain a slightly darker shade.

Most processes allow for this adjustment.

. The electricity generator used for the coloration is conceived for a given process.

The most common processes use alternating currents - in this case, the central part of the generator is a step-down voltage transformer, so as to obtain a maximum current density of 25 to 30 volts on the tank. A regulatory and a voltage programmer device complete the apparatus.

Other processes use continuous current or modified alternating currents. In this case, the apparatus is more complex to manufacture, to program and even to use.

. The coloring tank has no special features. It is fitted with electrodes, and a wide range of fittings are available for this purpose :

- certain processes use inert electrodes : graphite, stainless steel
- others use consumable electrodes whose metal corresponds with the elements of the solution
- the geometric forms vary a great deal : flat sheets, bent large-surface sheets, vertical strips, wire, cylindrical bars.

The only thing that matters is the result of the coloration.

. The bath is a vital factor in the coloration results obtained. Each process holds the secret of its bath ingredients.

What is vital is to possess the means of making permanent checks to see that the bath content is as it should be, and this is done by systematic analysis.

In certain plants, where accidental pollution from other baths may be a problem, precautionary measures should be adopted (the use of lids for example). Usually, in normally designed plants equipped with the necessary rinsing tanks, there should be no pollution problem.

How to choose an electro-coloration process

In conclusion, after having summarized the developments of the coloration of anodized aluminium processes that led to the use of electro-coloration processes, and after having examined their practical features, I would like to give some indications as to the criteria that should apply when choosing a process :

- The quality and durability of the colorations are good, thanks to the very principles of the processes. The fact that these processes have been in existence for several years, combined with the architectural realizations, are an excellent test of their durability.
- It would be important to ensure that the process(es) envisaged can be satisfactorily applied to the products to be treated, as well as giving the different shades of color desired.
- Next to be dealt with are the problems raised by investment costs and working costs, in other words the overall cost price to include specific amortizations.

  Certain processes are accessible subsequent to a license purchase, others use commercial chemical products ; and some require the payment of royalties proportional to the treatments carried out.

- All have one thing in common - the need to purchase the necessary equipment : tank and electrodes of course, but above all the generator. This last point can make a considerable difference when it comes to investments. The processes most elaborate in terms of electricity will often require far more burdensome equipment than those processes giving equally good results and functioning with much simpler equipment.

- The overall approach to the cost price, proven by experience, shows that often the most economic working solution consists in purchasing a process, free from eventual payment of royalties, and with the option of using commercial chemical products.

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WE HOPE THAT THIS CONTRIBUTION WILL HELP ANODIZERS TO MAKE A GOOD CHOICE FOR THE EVOLUTION OF THEIR PRODUCTION.

K-1

Non-Electrolytic Deposition Processes Session K

Continuous Cable Processing by The Physical Vapor Deposition Technique

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CONTINUOUS CABLE PROCESSING BY THE PHYSICAL VAPOR DEPOSITION TECHNIQUE

By G. J. Hale

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ABSTRACT

A continuous cable processor (CCP) has been designed, built and tested to deposit aluminum or copper on 70-mm-wide polyimide film by the physical vapor deposition process. Thickness uniformity of the deposited film can be better than 2 percent. Various equipment difficulties resulted in deposited films with the thickness uniformities of ±1.4 to ±12.9 percent. Deposit thicknesses up to 30 μm could be achieved in a single deposition. The present CCP equipment has design limitations that prevent films with a 4-μm coating thickness from being deposited more than 10 m in length in one continuous operation. Future activity will incorporate many new design features to achieve film lengths more than 10 m with thickness uniformities of ±2 percent or less.

*Operated for the U.S. Department of Energy by The Bendix Corporation, Kansas City Division, under Contract Number DE-AC04-76-DP00613.

INTRODUCTION

Vacuum deposited aluminum and copper are frequent choices for conductor metallization of integrated circuits, front-surface mirrors, corrosion resistant coatings, and flexible circuit conductors. The use of metallized plastics for various flexible circuits is evident throughout the electronics industry. Commercial suppliers of flexible circuit materials often use vacuum deposited aluminum or copper to acquire a conductive surface on a plastic film such as a polyimide. However, the deposited metal conductor is seldom over 0.5 μm thick.

This paper discusses a method of depositing aluminum and copper on 70-mm-wide polyimide film by the physical vapor deposition technique. This system is a prototype cable processor designed, built, and evaluated for depositing the metal films with a thickness up to 30 μm and a thickness uniformity of ±2 percent or less.

EXPERIMENTAL

Deposition Equipment

The deposition equipment which makes up the continuous cable processor (CCP) consists of a base vacuum system, a microprocessor deposition rate controller, a specially designed cable processing unit, and other associated vacuum processing equipment items (Figure 1).

Base Vacuum System

The base vacuum system is a standard high vacuum pumping station which includes a 152 mm oil diffusion pump with liquid nitrogen baffling, high vacuum gauging, twin electron beam (EB) vapor sources, and a 14 kW EB power supply.

Two EB gun sources are located 25.4 cm center-to-center to minimize magnetic beam interference. These EB sources feature 40 cm^3 water-cooled, hopper-type crucibles. Water cooling of the copper crucibles creates a shell of solid evaporant at the copper/ evaporant interface, producing a natural barrier against possible cross-contamination from the crucible.

Crucible inserts are useful adjuncts to electron beam evaporation. They increase the evaporation rate of the material being deposited. Surface sealed graphite crucible inserts were used throughout this activity to deposit copper. This resulted in a lower deposition temperature because of the reduced power required to deposit the copper. No crucible insert was used to deposit pure aluminum. Satisfactory

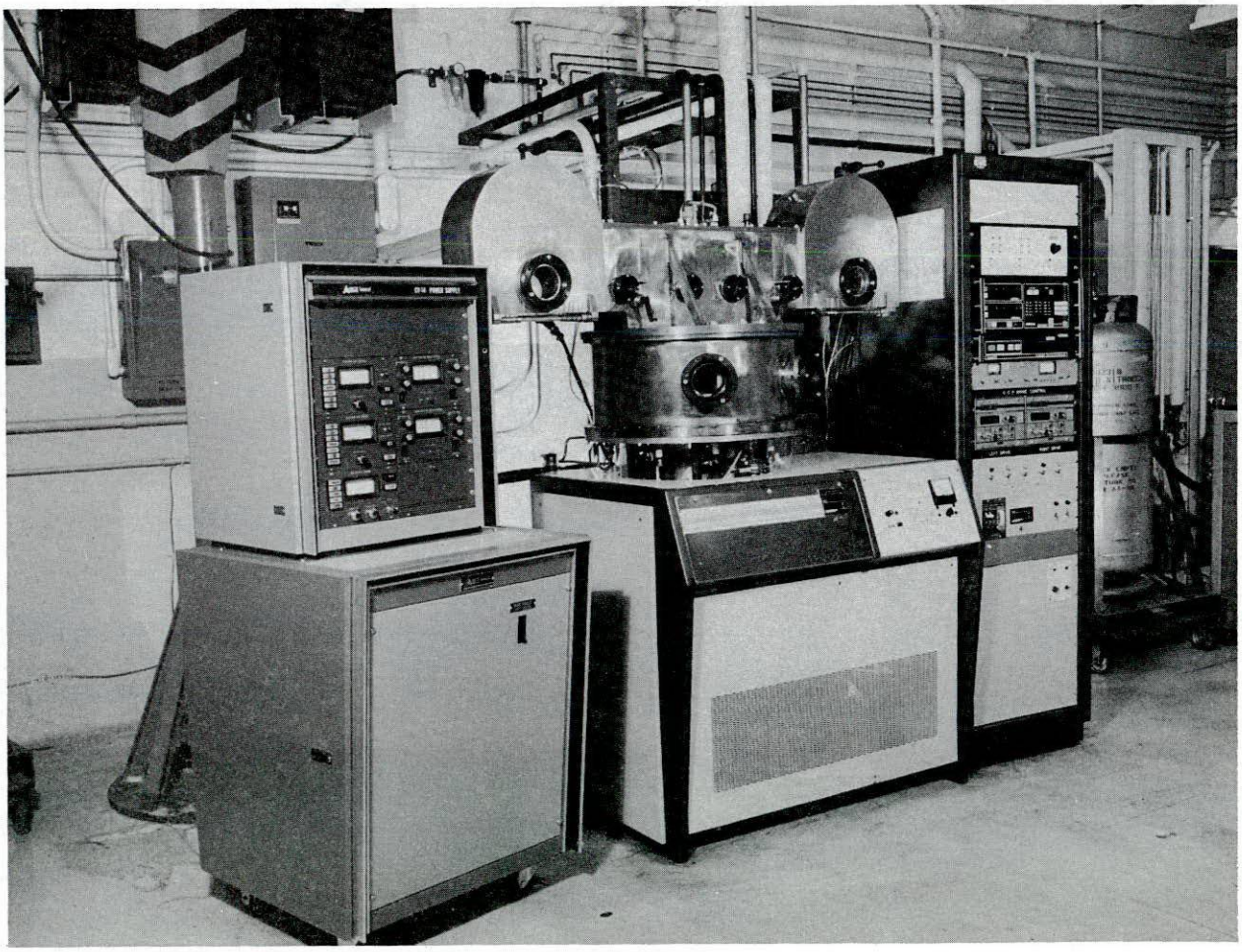


Figure 1. Continuous Cable Processor

deposition rates and process temperatures were achieved without the use of a crucible insert. Figure 2 illustrates the twin EB gun source arrangement.

The twin EB gun vapor sources are powered by a 14 kW power supply. It provides for simultaneous operation of these two EB gun sources. The deposition rate of the material being deposited is controlled by the amount of power being supplied to each of the two EB vapor sources. The power control is achieved by two independent vapor source sensors. These sensors measure the amount of material being evaporated inside the chamber, and a control signal is sent from the sensor power unit to the EB power supply. Figure 3 illustrates the closed-loop control for the EB gun sources through the use of

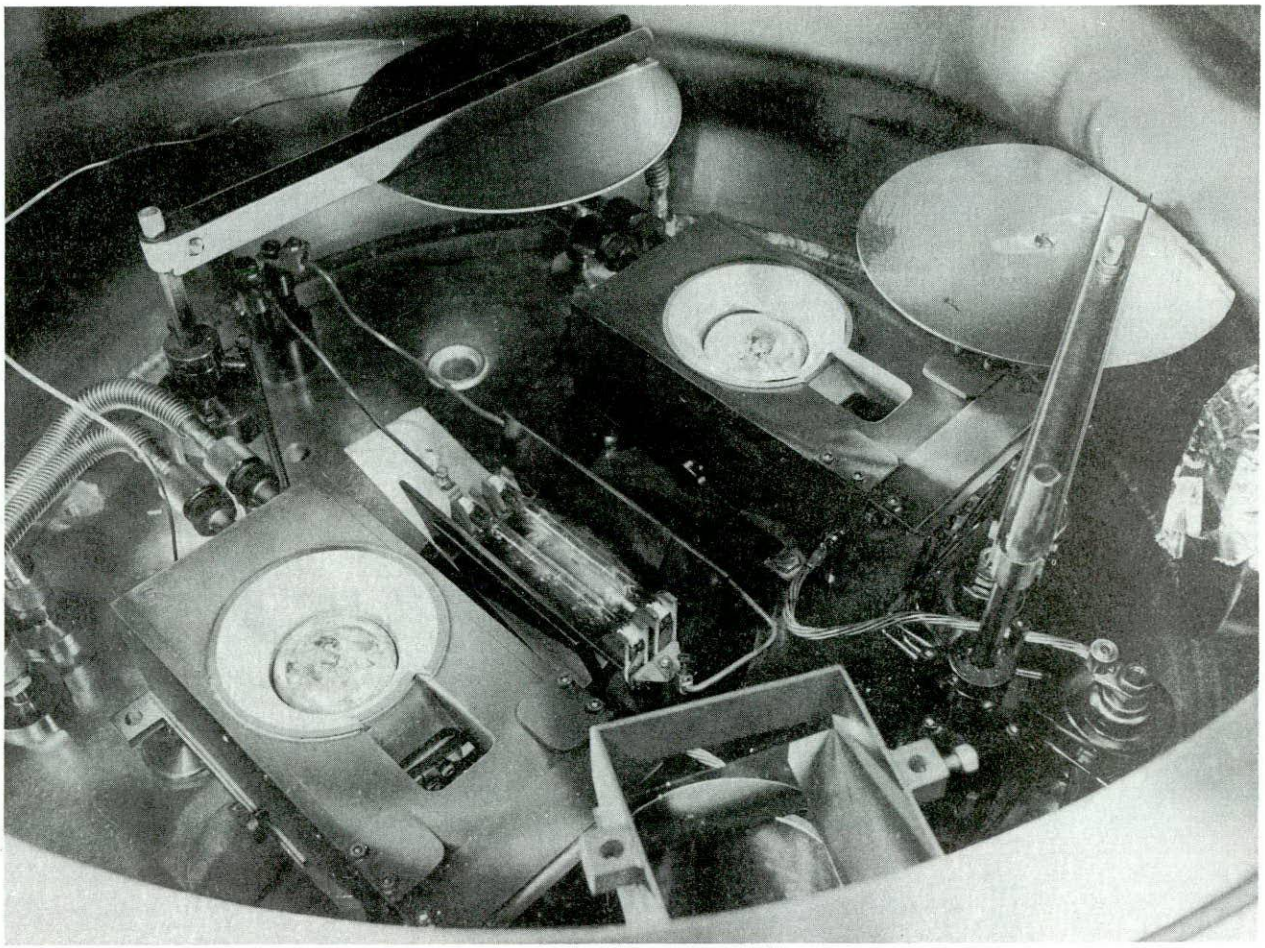


Figure 2. Twin Electron Beam Gun Vapor Source

an electron impact emission spectrometer for deposition rate control.

Deposition Rate Controller

The deposition rate controller (electron impact emission spectrometer) is one of the major equipment items that provides the capability to deposit controlled thickness uniformity films. It is the means by which a long length of polyimide film can be deposited with a highly uniform metal layer. It must provide a control capability for long deposition times. Conventional film-thickness and deposition-rate controlling devices such as quartz crystal microbalances do not have the capability to control over long deposition times and withstand the deposited metal accumulations.

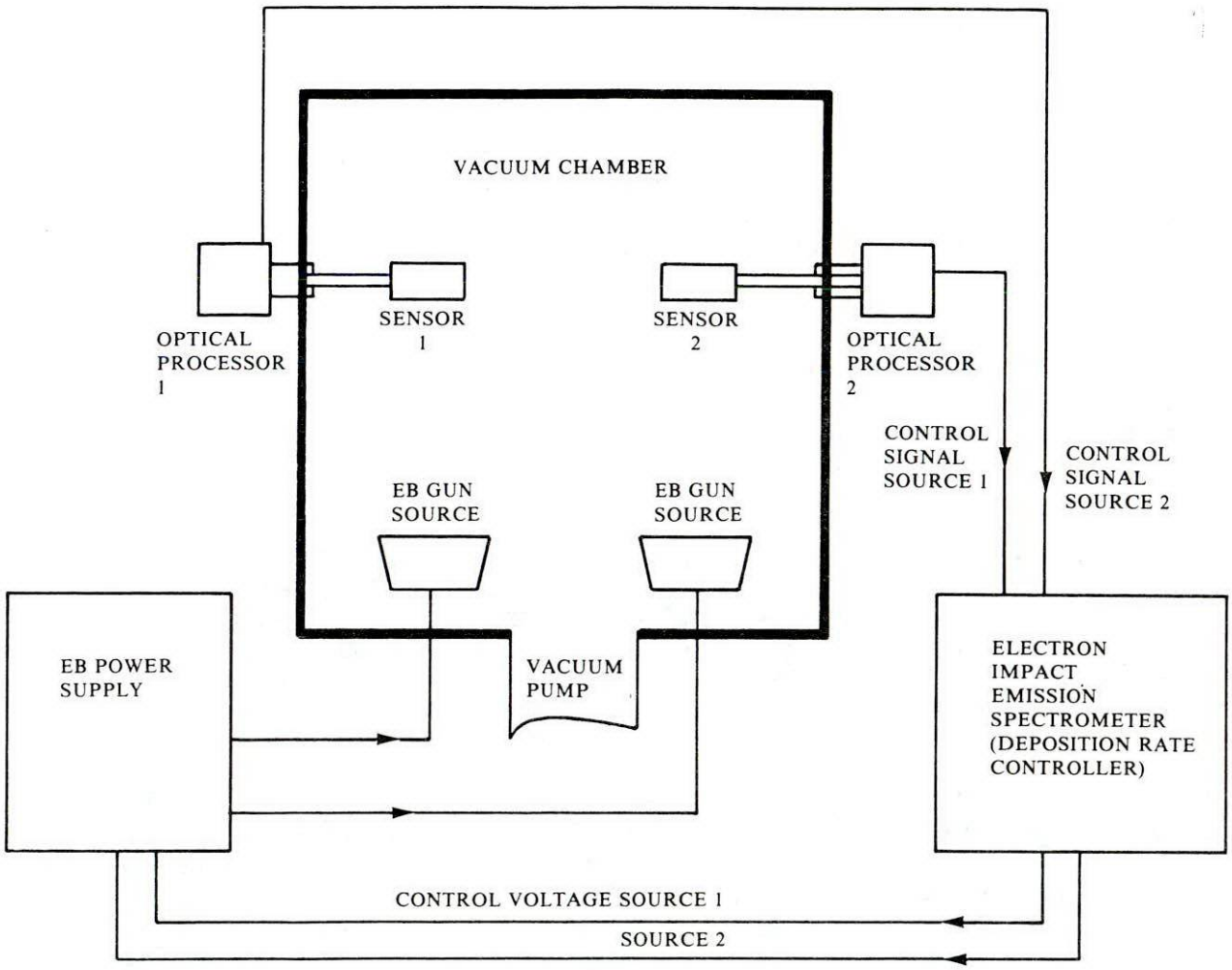


Figure 3. Closed Loop Deposition Rate Control

The operation of the electron impact emission spectrometer as a deposition controller uses the following basic approach. The evaporant is allowed to pass through an excitation region where it is cross bombarded by an electron beam. The collision process excites a fraction of the atoms or molecules, resulting in optical emission. The wavelengths of the emitted radiation are characteristics of the atomic or molecular species being evaporated. The emitted radiation (photons) is transmitted to a narrow-band optical filter, and the intensity of the selected emission line is measured by a photomultiplier where the signal is converted to a current-voltage signal. This I-V signal is then sent to the microprocessor which provides a control voltage to the EB gun power supply. When operated in the closed-loop mode, this signal automatically

adjusts the EB power supply so that the deposition rate matches a preset value.

Cable Processing Unit

The cable processing unit is a specially designed vacuum chamber. Constructed of 300-series stainless steel, it consists of two major components. The lower section is a 61-cm diameter, 30-cm-high vapor source chamber, which houses the vapor sources, source shutters, heater assembly and viewports. The upper section contains the film processing mechanism and the close-loop rate control sensors. The 70-mm film is loaded on a reel (Figure 4), with a capacity of approximately 150 m of 127-μm-thick film. The film is fed through a spring-loaded sprocket, across a water-cooled platen (Figure 5), through another sprocket, and onto a second reel.

The film is punched to American National Standard ANSI-PH1.20-1970, Type II to match the drive sprockets, and is driven by a digital servo system. This digital servo system contains a high resolution pulse generator for input to a high response DC servo motor. The servo motor provides input, through a 4 to 1 gear reduction system, to the sprocket for driving the 70-mm film for deposition. This drive system provides a highly repeatable speed control.

Speed of the film is adjustable from 3.6 to 40 cm/min. The speed of the film is displayed directly on a digital meter separate from the servo-drive system. In addition, the total number of meters of film is displayed with an automatic film drive termination. If 20 m of film is to be deposited, 20 m can be programmed into the film accumulation system, and it will stop the film when this unit has been reached. Furthermore, the film speed and accumulation system, in conjunction with the servo-drive systems, allows for the automatic processing of the film in either direction by the use of two servo-drive sprocket systems, i.e., the speed indicator and the film accumulator are functional in both directions.

The accumulator meter also provides the capability to count up as well as down. This allows one to process a given amount of film, then reverse the film to return to the original starting point or any other position along the processed film. This provides capability for multiple pass deposition and for processing the film for high vacuum bakeout.

Substrate

The substrate is made from polyimide (Kapton) with a thickness of 50.8 μm. The film is 70-mm wide and the length is "as-desired." The 70-mm polyimide film is punched to American

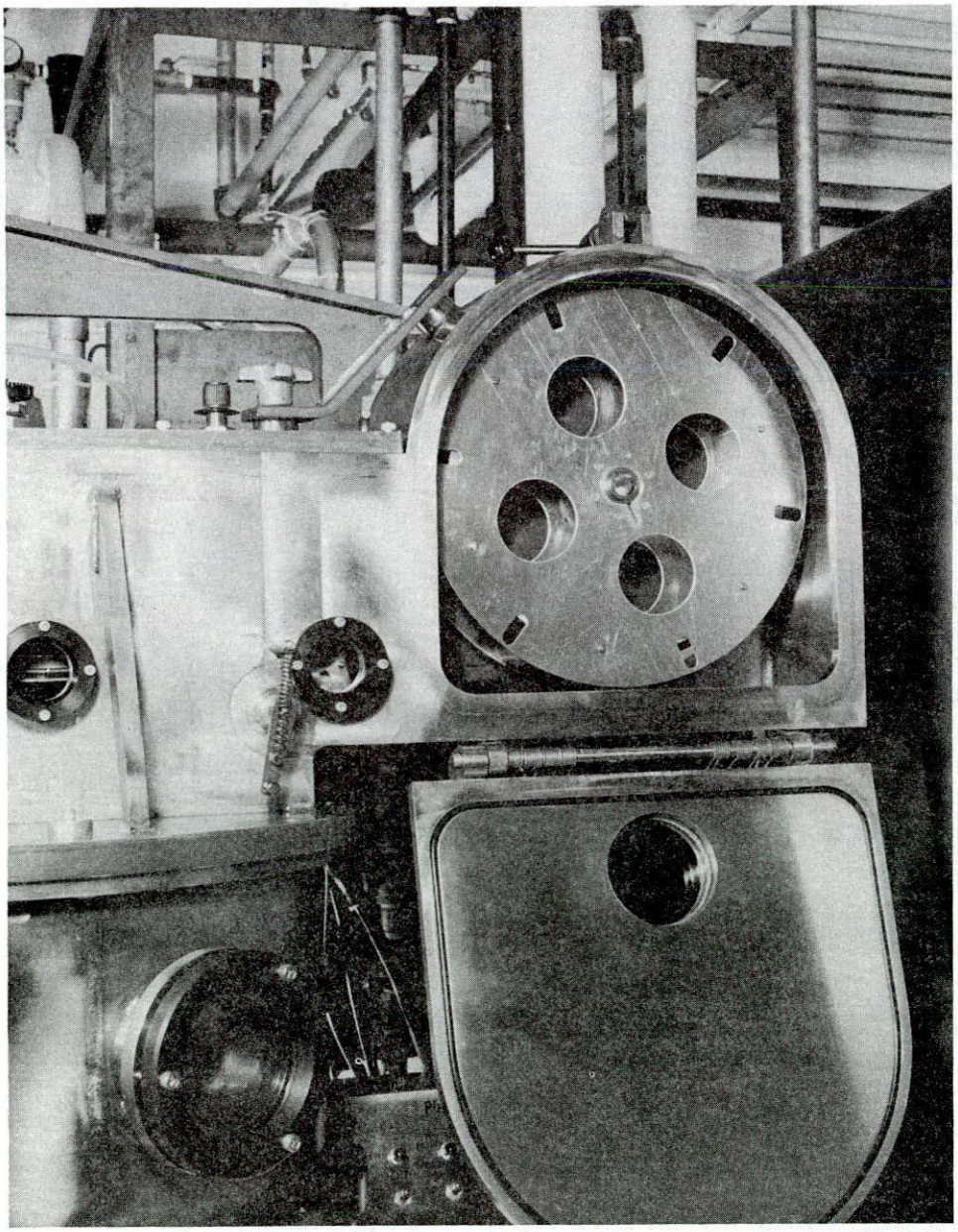


Figure 4. Cable Processing Unit Film Reel

National Standard ANSI- PH1.20-1970, Type II. A 150-m roll of 70-mm film is normally procured, cleaned, and loaded on a reel for processing.

Because polyimide substrate material is a source of contamination, it must be thoroughly cleaned and thermally treated before aluminum or copper is deposited. Dirt particles, lint and fingerprints, as well as other contaminants, must be

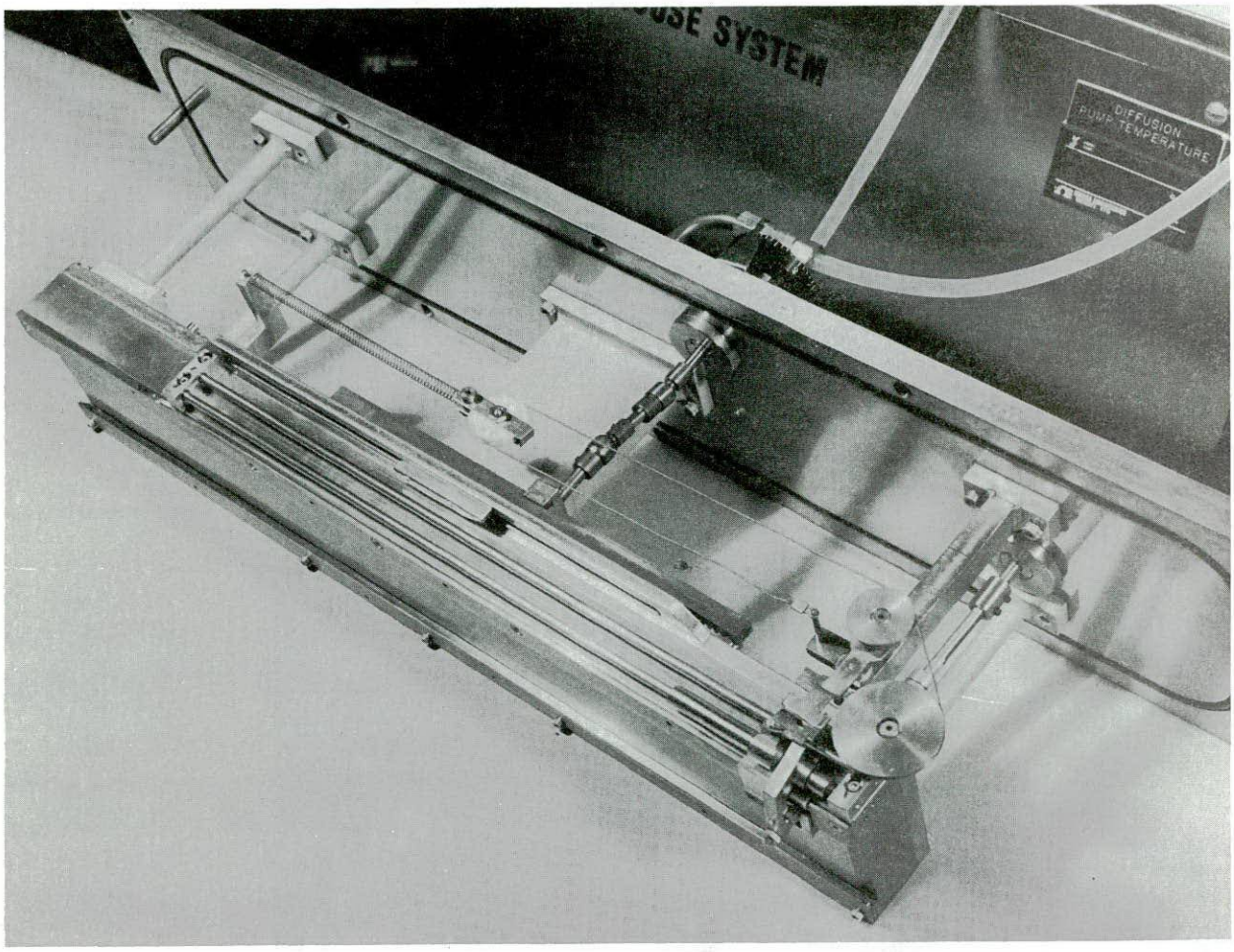


Figure 5. Water-Cooled Film Platen

removed to acquire good quality deposits with acceptable adhesion.

Cleaning is accomplished by a thorough trichloroethylene washing and rinse, followed by an ethyl alcohol rinse and then an immediate blow dry using dry nitrogen. During this cleaning process, the 70-mm film is wound on a processing reel. The loaded reel is then placed in a vacuum oven and baked at 150°C under vacuum at 1.33×10^{-4} Pa for a minimum of 2 hours. The selection of 150°C was based on a mass spectrometric analysis of polyimide exposed to various temperatures and conditions. These data indicated that a 2-hour bake-out between 140 and 150°C removed most of the water and air from the organic substrate.

Process and Parameter Characterization

General Process Description

Aluminum (99.999 percent) and copper (99.998 percent) films were deposited under vacuum on the 70-mm polyimide film using a PVD process. Each of the two materials was deposited in a separate project experiment. The capability of depositing aluminum was first examined and then the copper deposition was evaluated. The process procedures were basically the same for these two materials.

The 70-mm polyimide film was processed in a line over the two EB sources (Figure 6). The EB guns were located 25.4 cm apart to minimize magnetic effects on the electron beams. The film was moving at a constant speed controlled by the stepper motor control.

The EB guns were being automatically powered (individually) to supply a pre-programmed rate of deposition. The rate of deposition of each electron beam gun was monitored by individual sensors mounted inside the vacuum chamber. The polyimide film substrate was located 30.5 cm from the two EB guns.

In the process for evaporating copper, each of the guns used a surface-sealed carbon crucible. This reduced the power necessary to maintain the preset rate of deposition by a factor of 8 to 1. However, this reduced the EB gun capacity from 55 to 29 cm^3 and consequently, the total amount of film that can be processed without reloading the source. The aluminum was evaporated without the use of a crucible which allowed for the full volume usage of the EB hearth.

The general deposition processes for aluminum and copper illustrated in Figures 7 and 8 relate the deposition power to the EB sources, vacuum chamber pressure, and relative process time.

The vacuum chamber is typically evacuated to a pressure of 4×10^{-4} Pa before the start of the deposition cycle. During the pump-down time, an optional chamber bake takes place. This enhances the pump down and the cleanliness of the vacuum chamber. When the appropriate vacuum level is reached, the programmed microprocessor is activated. There is a 4.5-min power soak of the vapor source material before the source shutters are ready to open. The film drive mechanism is activated and deposition begins. Deposited film thickness is directly dependent on the speed of the polyimide film and the net rate of deposition from each of the two EB guns. The microprocessor is programmed for deposition time, rate of

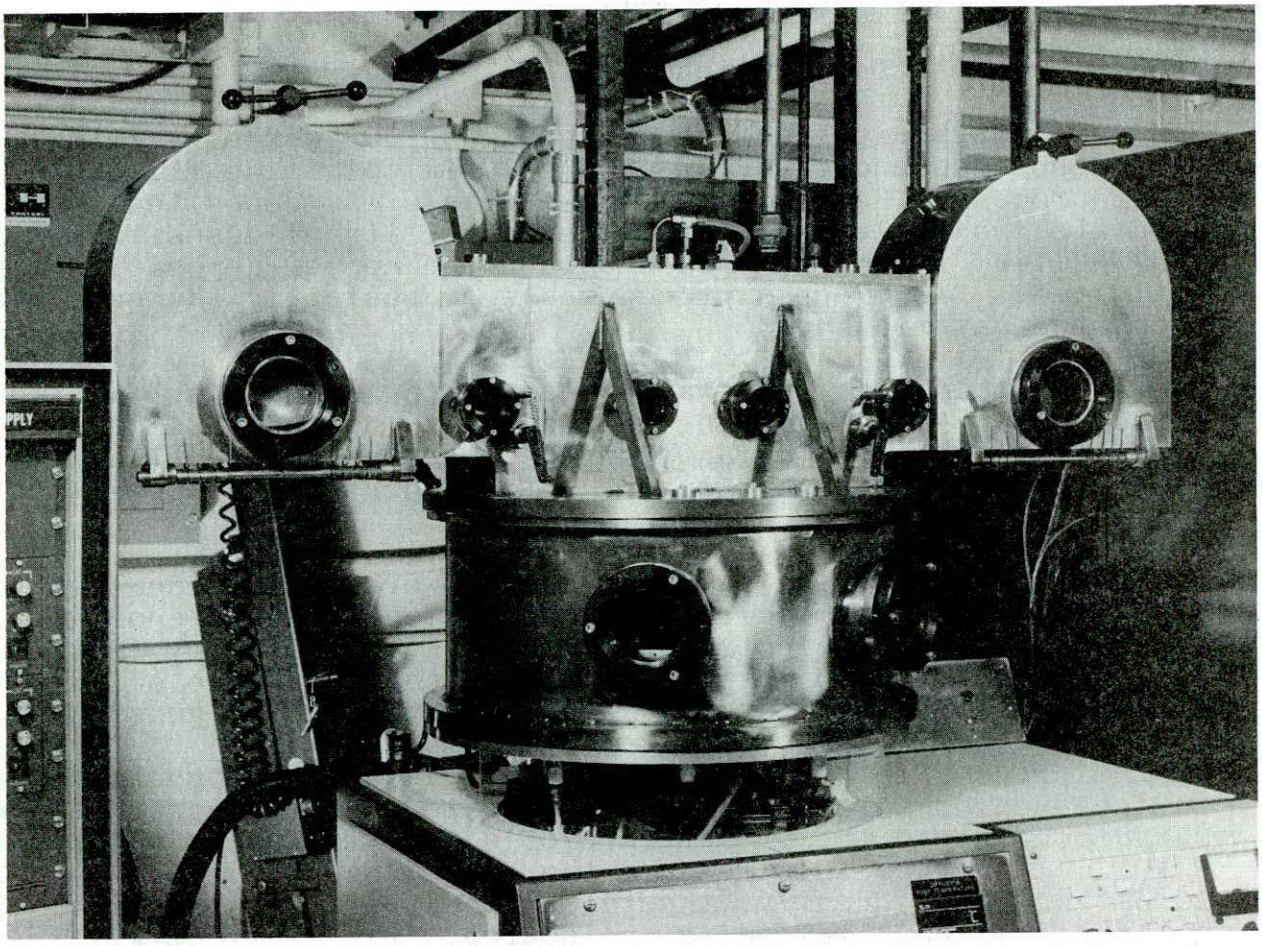


Figure 6. The 70-mm Polyimide Film Over the EB Sources

deposition for each gun, soak power time, and various material and process correction factors. The film drive system is also pre-set for speed and length of the film to be processed.

The one process difference between aluminum and copper can be seen in the process illustration in Figures 7 and 8. When copper is being deposited, the vacuum chamber pressure tends to rise slowly to some level and hold for the remainder of the deposition run. However, with aluminum the pressure rises at the start of deposition and then slowly decreases with processing time. This phenomenon is caused by the reactiveness of aluminum.

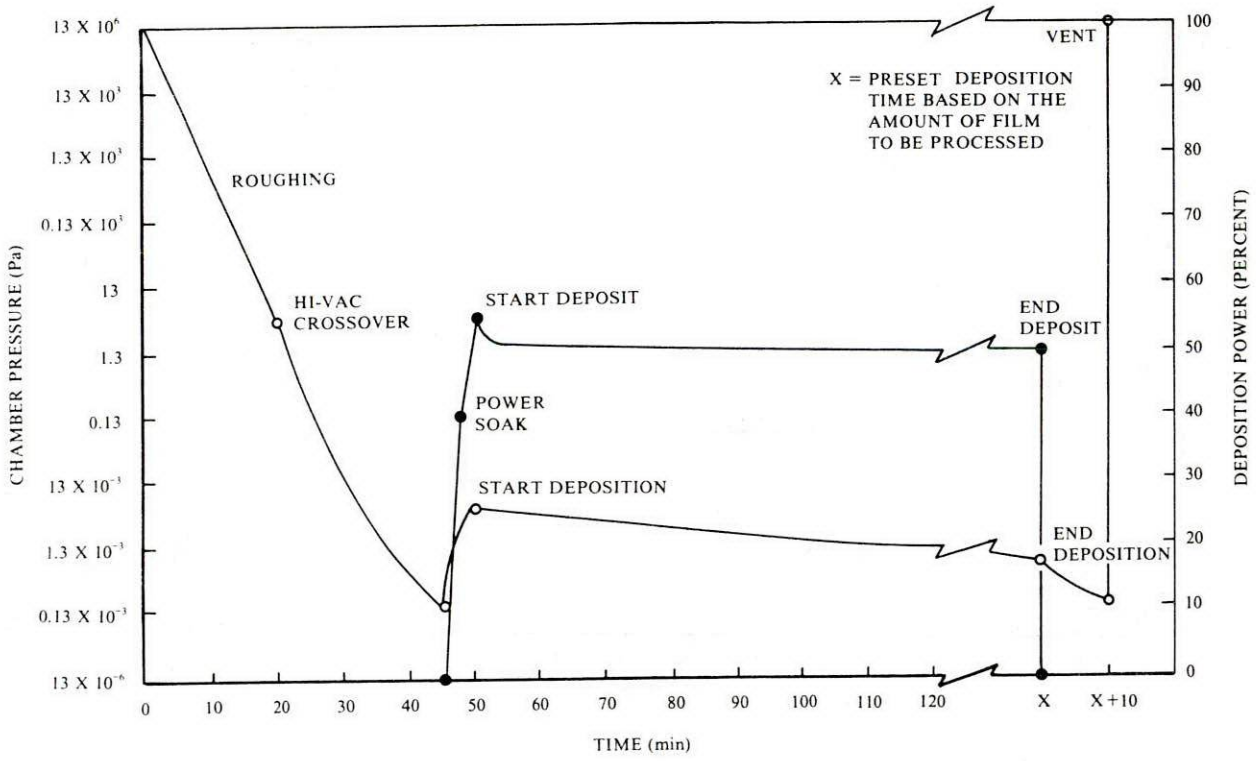


Figure 7. Typical Deposition Process for Aluminum at the Rate of 125 A/s

Aluminum reacts with residual amounts of water and oxygen, gettering the water and oxygen, thus reducing the overall system pressure. However, in the case of copper which does not react as well with residual water and oxygen and has a higher deposition temperature, higher gas content in the vacuum chamber can be expected.

High deposition rates were examined and found to lead to unstable electron beam control, high chamber pressures, and degradation of the polyimide substrate. There are limits of how fast molten metal can be deposited on the plastic substrate which are dependent on the substrate material, the deposit material, and the capabilities of the vacuum system.

Deposition Temperature

The maximum temperature during deposition for the polyimide substrate is an important parameter in the deposition process. It can affect the appearance of the final aluminum and copper deposits primarily by increasing the amount and type of out-

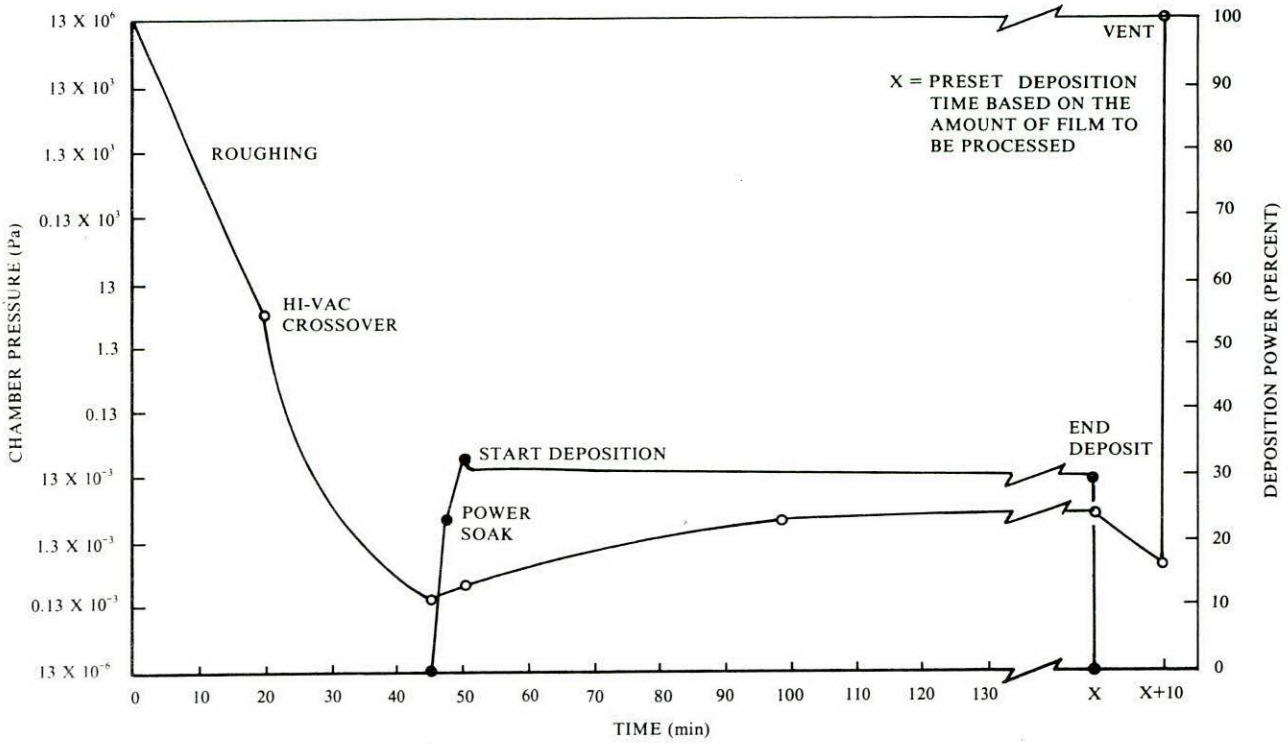


Figure 8. Typical Deposition Process for Copper at the Rate of 125 A/s

gassing species from the chamber fixturing and the substrates. An alumel-chromel thermocouple placed behind the moving polyimide film serves as reference thermocouple to provide deposition temperature data on a run-to-run basis.

The film temperature was monitored during all deposition runs. For a typical 250 A/s deposition rate for aluminum, from two EB sources, at a film speed of 11 cm/min, a temperature of 75°C was recorded. Copper was deposited at a rate of 125 A/s from each of the two EB guns with a film speed of 11 cm/min; a film temperature of 160°C was measured.

Thickness and Uniformity of Deposit

The thickness and uniformity of the various metal deposits were established using the beta-backscattering technique[1-2] by measuring the deposit thickness at a point every 2.5 cm for the entire length of the deposited film. The beta-backscatter measurement system used for this initial development was a hand-operated system which had a significant error factor. Each point measured was recorded and plotted, providing a detailed thickness readout for a given length of deposited

film. The uniformity of a deposited film was established by calculating the coefficient of variation (standard deviation divided by average thickness).

The CCP was calibrated for deposition rate control. Aluminum and copper required independent calibration. The calibration of the rate controller was required to establish a reference point for the deposition rate. Without this calibration, no correlation would be achievable on a run-to-run basis. The rate control calibration involved placing glass slides directly over each of the EB guns on the surface of the 70-mm polyimide film. Five-minute deposition runs were made with the rate control set at a specified rate of deposition. The thickness deposited on the glass slides was measured using a stylus profilometer and the actual rate of deposition was calculated. This rate of deposition was then fed into the rate control unit and the deposition repeated. This calibration procedure was repeated until the actual rate of deposition was the same as the control rate of the rate controller. Once this calibration was complete, deposition of 70-mm polyimide film commenced.

Parameter Characterization

Process parameter characterization was done with both aluminum and copper. A technique of evaluation was established using the Du Pont "Strategy of Experimentation". The experimentation design used was the three-factor Box-Behnken. The three-factor design uses 13 of the 27 points from the full factorial with two extra replicates at the center point, for a total of 15 points (Figure 9). This technique provides a method of mathematically describing the independent variable relationship to various dependent variables. The three-factor independent variables selected were film speed, deposition rate from EB source 1, and deposition rate from EB source 2. The dependent variables were film thickness, film uniformity, process temperature, material load in EB gun 1 and material load in EB gun 2. Once the 15-run experiment was complete, computer analysis of the data provided a "Fit" to the quadratic equation

$$y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3$$

$$+ b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2$$

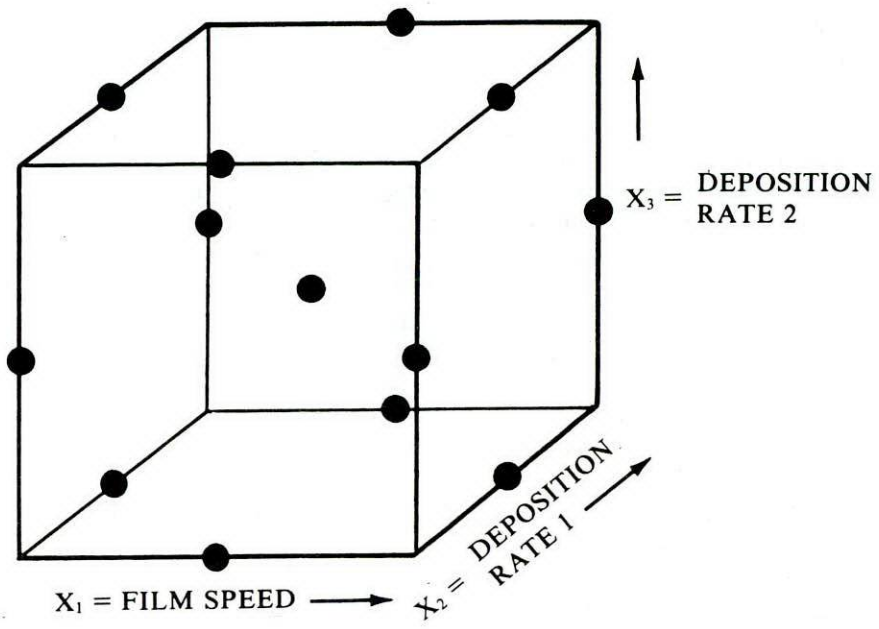


Figure 9. Three-Factor Box-Behnken Design

Statistical Evaluation of Aluminum Deposition

Fifteen runs were made depositing aluminum. Each EB source was loaded with 150 g of aluminum. After each deposition run, the aluminum in each EB gun was weighed and replenished to the 150 g level. Polyimide film 0.127 mm was used throughout the experiment and a total of 1.86 m of film was used on each deposition run. Many problems were encountered during this evaluation, including problems with the film drive and the rate controller. As a result, the reliability of some of the 15 runs was suspect. However, the resulting data and the process parameter equations do provide some insight into the system operations and interdependencies. The resulting data are shown in Table 1.

The equations generated from these data are as follows:

$$\text{Thickness} = Y_{TK} = 41.2422 - 18.7478X_1 + 0.3328X_2$$

$$+ 0.2736X_3 - 0.0334X_1X_2 - 0.0260X_1X_3$$

$$- 0.0001X_2X_3 + 1.6108X_1^2$$

Table 1. Aluminum Deposition Rate

Run	Film Speed (cm/min)	Deposition Rate (Å/s) 1	2	Material Usage (g) 1	2	End Temperature (°C)	Deposition Time (min)	Thickness (kÅ)	Uniformity (Percent)
1	3.6	0	125	0	12.384	74	51.8	39.9	3.85
2	12.7	125	125	3.265	3.601	63	14.7	21.0	3.72
3	25.4	250	125	3.795	1.891	54	7.4	16.9	6.79
4	12.7	125	125	4.137	3.864	65	14.7	26.3	5.92
5	25.4	0	125	0	1.921	67	7.4	9.1	9.26
6	12.7	0	250	0	7.251	98	14.7	24.5	3.46
7	12.7	0	0	0	0	25	0	0	0
8	25.4	125	0	2.193	0	32	7.4	11.3	4.53
9	3.6	125	0	13.344	0	39	51.8	46.7	12.92
10	3.6	250	125	26.653	13.325	90	51.8	124.2	1.87
11	12.7	250	250	7.486	6.518	75	14.7	42.9	4.99
12	12.7	250	0	7.726	0	71	14.7	26.9	3.38
13	3.6	125	250	13.447	21.944	95	51.8	115.0	5.59
14	25.4	125	250	2.269	3.089	57	7.4	20.0	2.73
15	12.7	125	125	4.824	4.609	63	14.7	28.9	2.66

$$\text{Uniformity} = Y_{Unf} = 8.3771 - 1.6088X_1 + 0.1388X_1^2$$

$$\text{Vapor Load}_1 = Y_1 = 6.5336 - 7.7759X_1 + 0.0987X_2 - 0.0251X_1X_2 + 0.2620X_1^2$$

$$\text{Vapor Load}_2 = Y_2 = 6.2923 - 2.6613X_1 + 0.08286X_3 - 0.00823X_1X_3 + 0.2198X_1^2$$

$$\text{Process Temperature} = Y_{Temp} = 18.5228 + 0.8738X_3 - 0.0011X_2X_3 - 0.0307X_1X_3 - 0.0013X_3^2 + 0.0005X_2^2$$

where

X_1 = Film Speed (in./min),

X_2 = Deposition Rate (Å/s) 1, and

X_3 = Deposition Rate (Å/s) 2.

The equations containing X_1 must have X_1 in units of in./min.

Based on these equations, one could expect to deposit 4 μm of aluminum at a rate of 250 Å/s from each EB gun at a film speed of 20.3 cm/min. The EB guns used approximately 0.5 g/min at 250 Å/s deposition rate. The EB gun hearths hold approximately 120 useable g of aluminum which provide 240 min of deposition time at the 250 Å/s deposition rate. This would allow approximately 49 m of 4-μm-thick aluminum/polyimide film to be deposited in one loading of the EB gun hearths.

Statistical Evaluation of Copper Deposition

Fifteen runs were made depositing copper. Each EB source was loaded with 260 g of copper. After each deposition run, the copper in the EB gun was weighed and replenished to the 260-g level. Throughout this experiment, 50.8-μm polyimide film was used. A total of 2 m of film was used on each deposition run. The resulting data are shown in Table 2.

The equations generated from these data are as follows:

$$\text{Thickness} = Y_{TK} = 11.370 - 5.549X_1 + 0.0191X_2 + 0.102X_3 - 0.0106X_1X_3 + 0.444X_1^2$$

$$\text{Uniformity} = Y_{Un} = 5.593 - 0.9847X_1 + 0.0056X_2 - 0.000059X_2X_3 + 0.000959X_1X_3 + 0.0536X_1^2$$

$$\text{Vapor Load 1} = Y_{V1} = 21.897 - 14.175X_1 + 0.458X_2 - 0.0465X_1X_2 + 1.304X_1^2$$

$$\text{Vapor Load 2} = Y_{V2} = 58.732 - 25.505X_1 + 0.786X_3 - 0.0723X_1X_3 + 2.053X_1^2$$

Table 2. Copper Deposition Rate

Run	Film Speed (cm/min)	Deposition Rate (Å/s) 1	2	Material Usage (g) 1	2	End Temperature (°C)	Deposition Time (min)	Thickness (kÅ)	Uniformity (Percent)
1	10.9	0	0	0	0	25	0	0	0
2	10.9	250	0	82.12	0	155	18.4	30.9	2.74
3	10.9	250	250	40.03	98.65	179	18.4	101.9	3.05
4	25.4	125	0	14.94	0	99	7.9	5.2	3.3
5	3.6	0	125	0	133.30	115	56.6	102.4	4.9
6	10.9	125	125	15.52	45.20	158	18.4	54.3	5.0
7	25.4	0	125	0	19.17	145	7.9	15.4	2.1
8	25.4	125	250	6.51	28.23	143	7.9	38.5	1.5
9	10.9	125	125	17.44	40.78	158	18.4	48.9	1.5
10	25.4	250	125	17.59	19.87	121	7.9	31.0	1.4
11	3.6	250	125	136.06	121.40	201	56.6	233.6	2.8
12	10.9	125	125	16.35	38.49	158	18.4	41.1	1.5
13	10.9	0	250	0	101.61	166	18.4	88.2	4.7
14	3.6	125	0	53.33	0	97	56.6	37.3	7.21
15	3.6	125	250	25.62	195.85	193	31	339.0	2.2

$$\text{Process Temperature} = Y_{Temp} = 66.375 + 0.223X_2 + 1.203X_3 - 0.028X_1X_3 - 0.0293X_1X_2 - 0.00244X_3^2$$

where

X_1 = Film Speed (in./min),

X_2 = Deposition Rate 1, and

X_3 = Deposition Rate 2.

The units of X_1 must be in./min for all of the above equations.

Based on these equations, one could expect to deposit 4 μm of copper at a rate of 150 Å/s per EB gun at a film speed of 14.7 cm/min. The EB hearths hold approximately 180 usable g of copper with a consumption rate of approximately 3 g/min. This provides a net deposition time of 60 min. At a speed of

14.7 cm/min, a total of 8.8 m of film could be processed before reloading.

Throughout the deposition runs for aluminum and for copper, the equations were indicating control problems with the film drive mechanism and EB gun source 2. This coincides with the observations of the deposition runs.

As a result of these problems, modifications were made to the film drive and adjustments were made in the EB control. These changes helped to minimize those problems.

Some of the other films deposited revealed a continuing problem that may not be rectifiable with the present prototype cable processor; i.e., the deposited film thickness tends to increase slightly with the film length. This results in an abnormally high nonuniformity in the deposit film, which can be seen in the general data Tables 1 and 2.

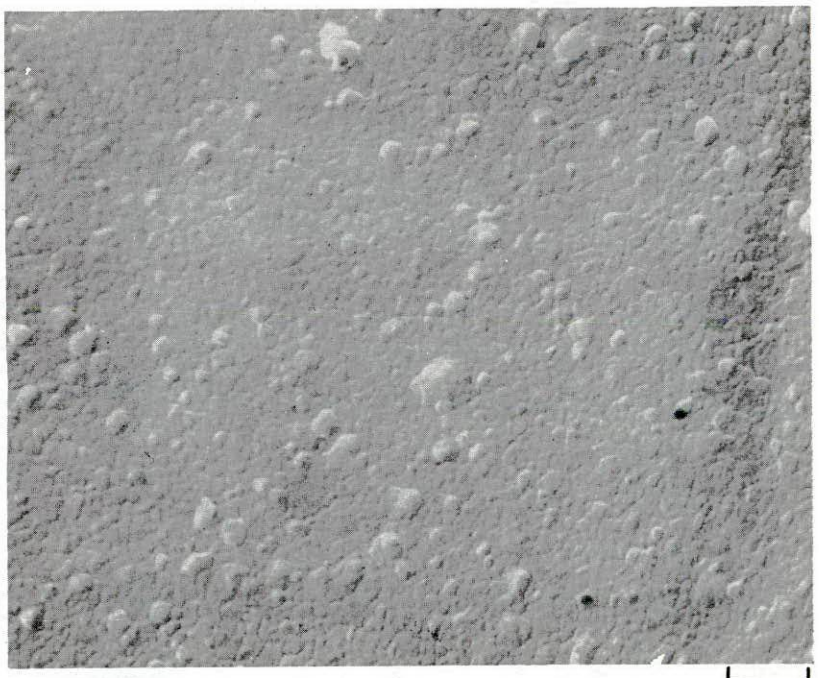
Deposit Characterization

Microstructural Analysis of Deposit

Typical surfaces of the aluminum deposit are shown in the scanning electron micrographs (SEM) (Figure 10). The periodic hillocks (white abnormalities in Figure 10a) on the aluminum film's surface are localized nucleation sites typical of thick PVD aluminum deposits.[3-5]

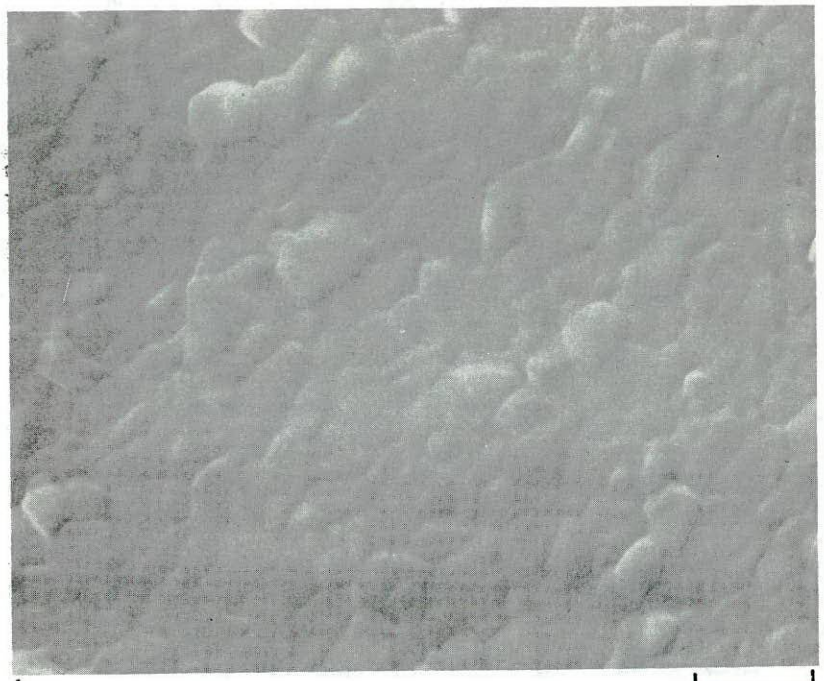
Defects typically originate from fingerprints, dirt, lint and fibers that collect on the polyimide surface prior to loading the substrate into the vacuum chamber. The initial surface conditions of the polyimide substrate, including scratches and pits in the polyimide, definitely determine the density of these defects in the deposit. Typical defects are illustrated in Figures 11 and 12. Figure 11 shows cold worked nodules that developed from the polyimide surface. These nodules represent preferential growth from a contaminate such as a dirt particle. Figure 12 shows surface damage created when a hard particle was rolled across the film.

The deposited copper surface is typified by Figure 13. The general surface has an extremely fine surface texture which is very reflective. Defects in the deposited material are represented by Figure 14. The defects are polyimide-surface originated. Figure 14b shows a depression area where a large nodule had fallen out during the deposition process, as evidenced by the copper that was subsequently deposited into the depression area.



a.

1 μm



b.

5 μm

Figure 10. Aluminum Film, 4 μm Thick
45° Tilt

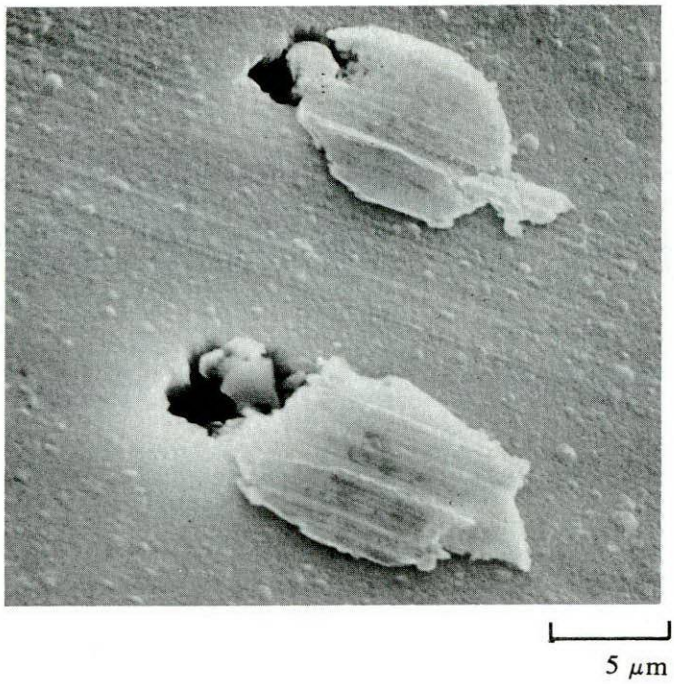


Figure 11. Cold Worked Surface Defect Nodules Aluminum Film, 4 μm Thick 45° Tilt

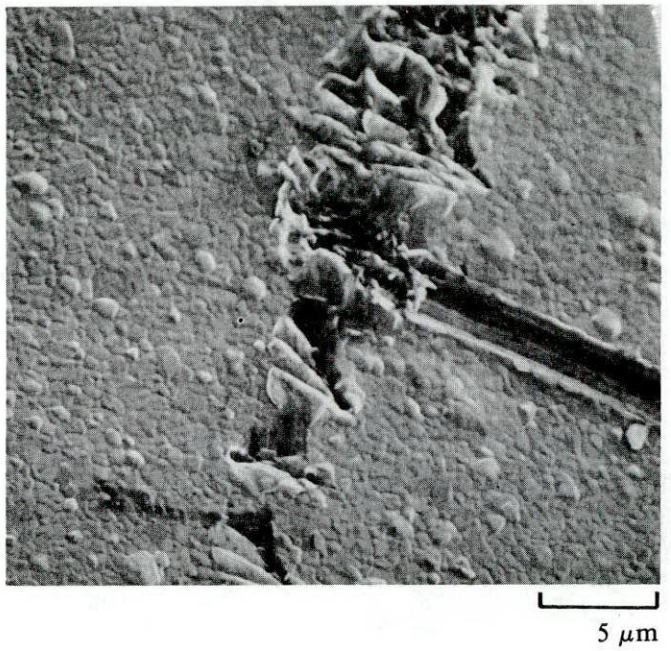


Figure 12. Aluminum Film 4 μm Thick With Surface Damage, 45° Tilt

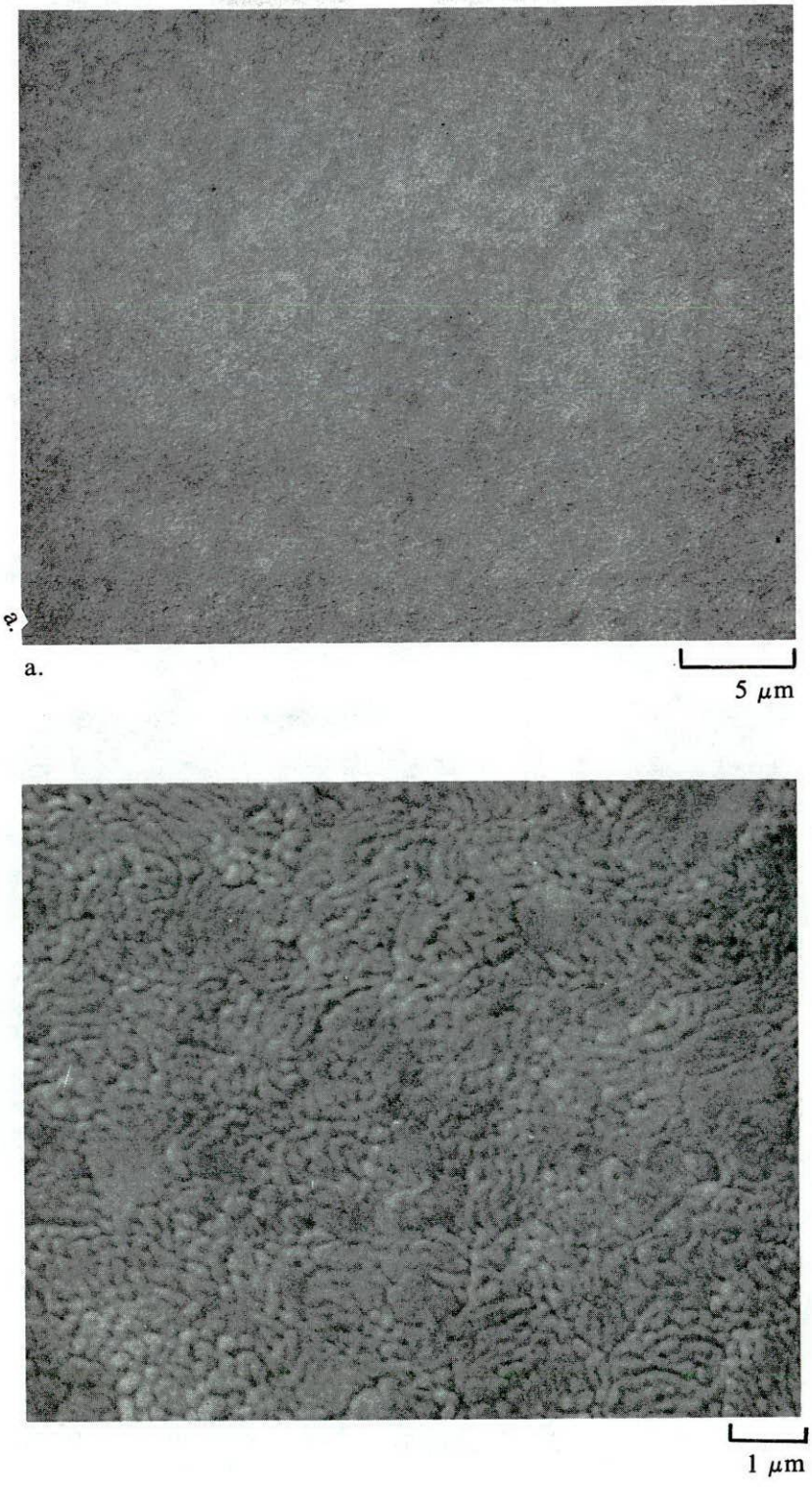
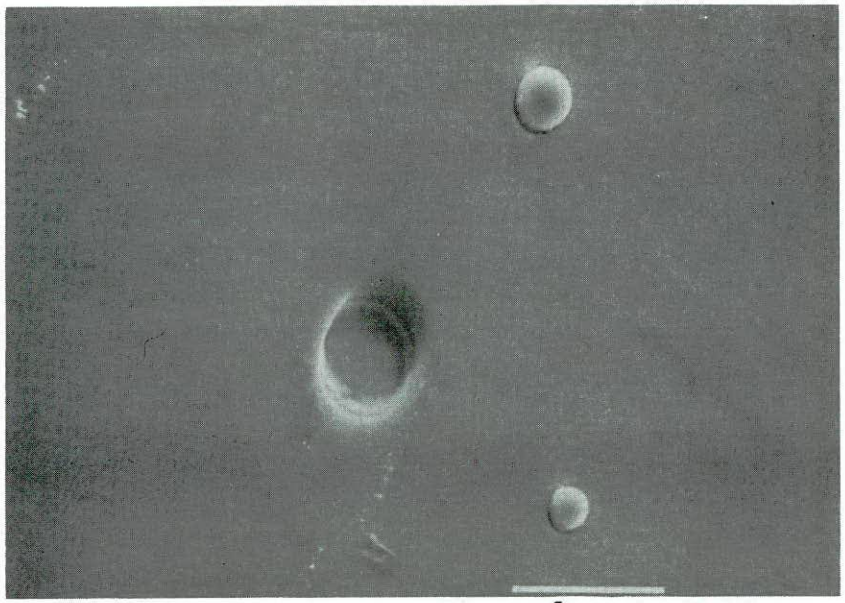


Figure 13. Copper Surface, 4 μm Thick, 45° Tilt



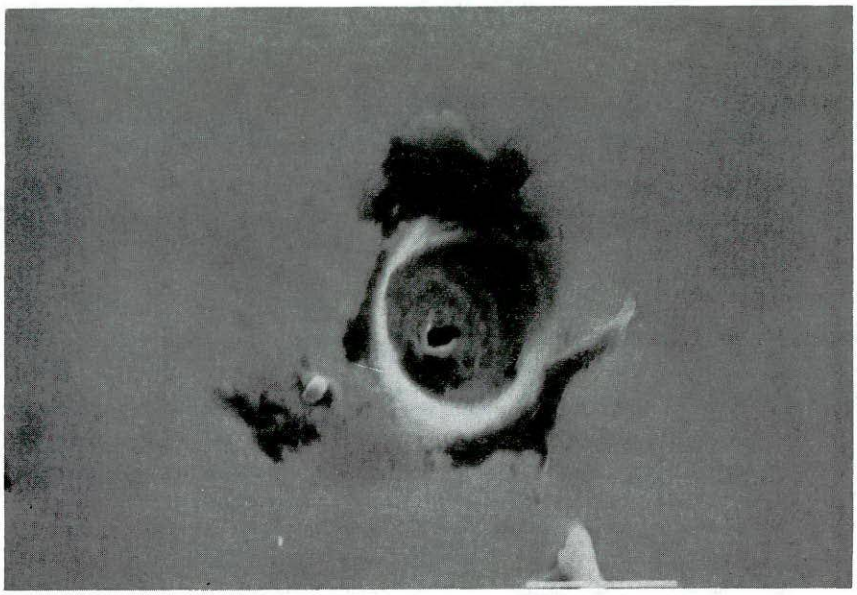


Figure 14. Surface Defect in Copper Film, 4 μm Thick, 45° Tilt

Resistivity

The resistance of the vacuum-deposited aluminum and copper on polyimide film was measured using a four-point in-line probe system. This resistance and the film thickness measured with the beta-backscatter technique were used to calculate the resistivity of the deposited film.

The theoretical room temperature resistivity of pure aluminum thicker than 1 μm is 2.71 μΩ·cm.[6,7] The room temperature resistivity of pure copper is 1.724 μΩ·cm.[8] The reported values for resistivity of these two metals is dependent on many effects: grain size, deposition rates, substrate conditions, forming environment and errors inherent in the resistance and thickness measurements.

Three samples of aluminum and copper on polyimide were evaluated using the four-point probe system. Thirty measurements were made on each of the two materials. The resulting average resistivity for aluminum was 2.987 μΩ·cm and the average resistivity for copper was 1.729 μΩ·cm. The resulting aluminum resistivity deviated slightly from the theoretical because of the pratical pressure effects from water and oxygen.[9,10] For all practical purposes, the measured copper resistivity was the same as the reported theoretical value.

Density

The density of the aluminum film was examined using a trioptic measuring machine consisting of a light sectioning microscope, a contact interferometer, and an analytical balance. Optical flats were weighed and then coated with aluminum. The average density of the deposits was 2.68 g/cm^3 with an uncertainty of ±4 percent. The theoretical density of aluminum is 2.70 g/cm^3 at 20°C.[8] These data indicate that the thick aluminum films are within 1 percent of the theoretical density. This difference in density between theoretical and PVD material could have easily resulted from the measurement uncertainties of the technique and the equipment used.

The density of the copper was determined by performing a precision area measurement and weight measurement on a sample of copper/ polyimide. The copper was then removed in a nitric acid solution. The remaining polyimide was weighed to establish the final weight value. Special care was taken to assure constant moisture and temperature for all weight and area measurements. The resulting density of the copper was 8.64 g/cm^3 with an unknown uncertainty. Theoretical density is 8.9 g/cm^3.[8] As a result of the values obtained for the density of these two materials, it cannot be conclusively stated that the deposited films are less than full density;

more precise measurement techniques and more sophisticated analytical techniques would be required. This is especially true for the technique used to establish the density of the copper.

Adhesion

Adhesion tests of vacuum-deposited films have been shown to be rather subjective and dependent upon the testing method and the individual performing the tests. The pre-deposit cleaning and the vacuum thermal treating procedures used throughout this work have provided aluminum and copper films with good adhesion. In the initial work it was found that improper cleaning techniques were being used that resulted in poor adhesion. However, since that time precautions have been taken to improve the polyimide cleaning.

A direct pull test using a commercial testing unit was used in an attempt to establish a quantitative measure of the adhesion of the aluminum and copper deposits. A small metal stud was bonded to the metal film using a high strength epoxy. The specimen was pulled and analyzed for fracture strength and location.

The results of the adhesion testing did not indicate any particular relationship among deposit thickness, temperature of deposition, material of deposition and the achieved adhesion values. The test values varied because of the slight deformity of the polyimide film and therefore, could not be correlated. The failure region was invariably in the polyimide. Polyimide material was pulled with the metal film, indicating the adhesion of the metal film to the polyimide was above the strength of the polyimide.

Crystal Orientation

Several deposits were analyzed with a pole figure device[11] using Cu-Kα radiation. The aluminum deposits had a crystallographic orientation with a strong [111] fiber texture. Vacuum deposited face-centered cubic (FCC) metals often exhibit a [111] fiber texture.[12] The copper was evaluated and found to have slightly different orientations in the longitudinal and transverse directions. Table 3 shows the various peak intensities in relation to the [111] peak for both the longitudinal and transverse directions of the 70 mm copper/polyimide.

The lattice parameter derived from this information also was slightly different for the two directions of the copper on polyimide film.

Table 3. Peak Intensities

Peak	Longitudinal Direction	Transverse Direction
[111]	1	1
[200]	0.18	0.15
[222]	0.02	0.04
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[420]	<0.01	<0.01

		Lattice Parameter
Longitudinal	=	3.6146 Å
Transverse	=	3.6118 Å
Theoretical Handbook Value[8]	=	3.6150 Å

The copper deposit was highly strained in both directions, as evidenced by the lack of resolution of the $K\alpha_1$-$K\alpha_2$ doublets of the low index planes. This strain was made up of a combination elastic (stressed grains) and plastic (high dislocation density) components. Based on the fact that the measured lattice parameter was significantly less than the theoretical, it can be concluded that the copper was in compression in the transverse direction. The stress state could not be determined since the deviation was less than the experimental error.

RESULTS

A continuous cable processor has been designed, built, and tested to deposit aluminum or copper by the PVD process on 70-mm polyimide film. The system is capable of depositing aluminum and copper up to 30 μm thick in a single pass. Deposits thicker than 30 μm are possible with refinement. Aluminum films 4 μm thick can be deposited at a rate of 250 A/s from each of the two EB gun sources at a film speed of 20.3 cm/min. A 4-μm copper film can be deposited at a rate of 125 A/s per EB gun, at a film speed of 14.7 cm/min. During copper deposition the polyimide film reaches a temperature of 160°C. The temperature of the film during aluminum deposition is 75°C.

The deposit uniformity over long lengths of film ranges from ±1.4 to ±12.9 percent. The variation in the uniformity is due to equipment instabilities and limitations. With appropriate design changes, a uniformity of ±2 percent can be expected. The deposited aluminum film surfaces are generally reflective with a whitish cast due to periodic surface hillocks on the aluminum surface. The copper deposit is very bright and reflective, and has an extremely fine surface texture.

Future work will include redesigning the continuous cable processor to minimize the equipment limitations in the present CCP system. The areas of redesign will include an improved film drive system, new rod-fed EB gun sources and relocation of the deposition rate sensors. The present film drive system has resulted in many deposited films with nonuniform deposits; this area must be improved if high uniformity deposits are to be achieved.

The present EB gun vapor sources were used initially because of cost and vacuum equipment size limitations. As a result, the deposited films have a characteristic nonuniformity associated with the bulk loaded source hopper. As the evaporation material depletes in the vapor source hopper, the metal vapor density changes. This change results in an increasingly thick deposit as the film is processed. This is particularly noticeable with long deposition runs where a majority of the metal is evaporated out of the vapor source hopper.

To overcome this effect, a rod-fed EB gun source could be used. This would provide a stable, constant level of material in the EB gun. To further increase the stability of the metal vapor density, relocation of the deposition rate sensors is required.

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K-2

Non-Electrolytic Deposition Processes Session K

Vacuum Processes for Hard Surface Film Deposition

Ted Van Vorous
Van Vorous Consultants
Boulder, CO

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K-2

Non-Electrolytic Deposition Processes Session K

Vacuum Processes for Hard Surface Film Deposition

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Van Vorous Consultants
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VACUUM PROCESSES FOR HARD SURFACE FILM DEPOSITION

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Coating of cutting and forming tools with titanium nitride to improve their useful life is not a new technology. Chemical vapor deposition has been used for this purpose for many years and is still the dominant process. Physical vapor deposition (PVD) processes are a second logical method that needed to be considered. In both instances the processes were needed to reduce tool wear, extend life and improve cutting or wear characteristics. The PVD processes also have the capability of use with better materials than titanium nitride in some instances.

Evaluation of technical requirements for hard surface coating by PVD methods showed the following essential criteria. First, the process needed to be limited in temperature rise when tool steels were coated to avoid loss of strength. Second, the process must have a high coating material energy to obtain very high film adherence. As an alternate, a medium energy process and pre-cleaning by sputter cleaning could be used. Thirdly, the process should be adaptable to better materials than titanium nitride if at all possible. Last, the process should provide high deposition rates so that they would be economical substitutes for CVD processes.

Physical vapor deposition processes have been considered as an alternate to CVD for many years, but major investigation of feasibility only started in the 1960s. This included work by Bunshah, et al, on the reactive ion plating process; White on an ion source modification of reactive ion plating; Van Vorous, Karstendiek and others on the triode sputtering process and numerous United States and Russian workers investigating the controlled arc process. All of these processes were found to be technically feasible or at least worthy of additional work, but none became commercially viable during the 1960s.

During the 1970s, planar magnetron sputtering became an important high rate process and was used to apply hard surface films to cutting tools. Both small and large systems built in the United States and Germany were provided for commercial use. Most notable were systems using closely coupled, opposed, magnetron cathodes in large in-line designs built by Leybold in Germany.

The White process was put into use commercially for tool coating. A pulsed gas reactive magnetron sputtering process developed by William D. Sproul was put into use at Borg Warner Corporation for automotive applications. Modifications of the Bunshah process using improved electron beam gun sources was put into commercial use at several locations for tooling and aircraft applications.

Some of the most notable new work was development by three groups of similar magnetically confirmed arc sources for reactive ion plating. This work was done in Russia, East Germany and the United States. The Russian process was licensed in the United States to the Multi-Arc Corporation and has become a major commercial success. Numerous systems are being provided for tool coating and other process applications are being investigated by Multi-Arc. The United States developed process is still in the development phase so commercial equipment is not yet available.

At present the most commercially viable processes are the magnetically controlled arc and opposed planar magnetron sputtering methods. Other methods are finding some use, but many have been limited to depositing titanium nitride as a gold "look-alike" film on watch cases. These PVD processes have already shown their ability to be used in thinner films with the same life improvement obtained with CVD films. They also allow use of materials such as hafnium nitride to achieve better film properties. The 1980s should see major use of PVD processes, with some added refinements, as a substitute for CVD technology.

K-3

Non-Electrolytic Deposition Processes Session K

Magnetron Sputtering

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MAGNETRON SPUTTERING

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Introduction

It should be explained at the outset that the author doesn't know a lot about electroplating; only a little, in a general sense. He has been invited to be a member of the Vacuum Coating Committee of the AES as a result of his involvement in systems engineering projects with vacuum coating processes, most recently involving magnetron sputtering technology. There are those who might consider he doesn't know a lot about magnetron sputtering either, but then not many do. In comparison to electroplating as a mature industry with a long and colorful history, magnetron sputtering is a very recent process of interest for surface finishing. The depth of understanding of sputtering processes is somewhat a function of the relatively recent interest.

Because of growing interest in vacuum coating technology in general, not just magnetron sputtering, the AES has seen fit to establish the Vacuum Coating Committee to provide a better understanding of vacuum coating for AES members. This paper is one result.

Magnetron Sputtering Illustrated

Magnetron sputtering is but one of many processes for coating one material as a surface on a substrate of another material, that can be performed in a vacuum or a partial vacuum. The most well known of these processes is evaporation of a material by heat in a vacuum and condensation on the substrate. Evaporation as a technique has historically had some limitations, notably the difficulty in controlling the structure and thickness of the resulting film, and the difficulty of coating with alloys. The constituent metals in an alloy will always evaporate at different temperatures, so the resulting condensed film will not represent the alloy closely. Co-evaporation techniques from separate sources are possible, but very difficult to establish and control. Sputtering, on the other hand, has offered the ability to deposit materials with much more precise thickness control, structure control, and control of constituents in the film. Control, obviously, is the key word when comparing sputtering and evaporation techniques. Even with the advantage of control, however, sputtering techniques have had until recently, an ever more

serious drawback - rate. Magnetron sputtering has largely solved the rate problem, and sputtered films can now, in many instances, be deposited at rates comparable to evaporation and plating techniques.

Sputtering is often explained as a physical process very different from electroplating. It helps, in my view, to relate the two processes by their commonalities, rather than by their differences.

Figure I is a simplistic diagram of an electroplating process. The material supplied to the process to form a film or coating on the substrate is suspended in an aqueous solution and made (+) anodic relative to a common D.C. power source; the other side (-) of which is connected to the substrate, suspended in the same solution. The anode material is dissolved in the solution, resulting in metallic ions, positively charged (anions), in the medium. These anions are attracted to the substrate by the negative electrical potential; and, upon arrival, are supplied with an electron to become neutral atoms, and form a plated film on the substrate. An important requirement is that the material to be plated is electrically conductive, or the process ceases.

Figure II is a simplistic diagram of a magnetron sputtering process. A sputtering cathode is interfaced to a vacuum enclosure with the material to be sputtered (supplied) inside the enclosure. The cathode material is connected to the negative side of a high voltage D.C. plasma power supply, the other side of which is grounded to the chamber, and to earth ground. A non-reactive working gas is admitted to the vacuum chamber at a very low pressure, roughly one half millionth of an atmosphere. Electrons from the cathode surface (or elsewhere) strike the argon atoms, creating argon ions (AR^+) that are strongly attracted to the cathode surface. The impingement of the ions on this surface erodes metal atoms (neutrals) from the surface, which, because of their kinetic energy (a result of the arriving kinetic energy of the argon ions) "fly out" into the chamber, and adhere to whatever is in the way. The substrate is placed in the way, and becomes coated with the material.

There are a number of common aspects, listed in Fig. III. Both of these processes require an energy supply, an enclosure, a process medium, and a generally similar geometric arrangement of the substrate and the material source. They are really quite similar ways of accomplishing a quite similar purpose.

Figure IV illustrates magnetron sputtering in somewhat more detail. Another name for magnetron sputtering is "magnetically enhanced" sputtering. A magnetic field is imposed over the surface of the cathode material. Electrons relate to the magnetic field by spiralling around the lines of

force. If the lines of force penetrate the cathode surface in two places, (or other means are used that aren't discussed here), an efficient "electron trap" is formed. The electrons are reflected at both ends electrostatically, and continue to be trapped in the field. A very energetic electron cloud can be maintained close to the surface, and, in the presence of a gas, a very dense and contained plasma can be formed (and controlled) because of the ionizing efficiency of the electron cloud.

The general result is that much higher than usual deposition rates can be achieved. Argon pressures can be lowered because of the ionizing efficiency of the trap, and there will be fewer collisions between the coating material atoms and gas neutrals in the medium. Also, one of the difficulties generally encountered in sputtering, heating of the substrate by secondary electrons, is brought under better control. It was really this last advantage that fueled the development of magnetically enhanced sputtering.

Why Should Electroplaters Be Interested?

There is one overriding reason why electroplaters and equipment and material suppliers to the electroplating industry should be interested in sputtering technology: $. You may have noticed that the electroplating industry as a whole is not in a growth mode. Automotive brightwork, as one example, is down by less brightwork per car, and by fewer cars produced.

You may also have noticed that attempts by sputtering technology to replace electroplating in automotive brightwork and some other decorative areas have not been particularly successful. You can be sure, however, that the attempts to do so are not over. The sputtering people haven't quit. They've learned a lot, and sputtering is a profitable and growing process. There is a very good reason. The few attempts that have been made to make inroads in areas that are traditionally electroplating were not motivated by the companies with some expertise in sputtering, they were fueled by the customers of the electroplating industry that are burdened with the rising costs of wastewater treatment and waste disposal, and all the other costs of environmental safety and liability. Your traditional customers are looking for alternatives, and they will find them. Magnetron sputtering is a real alternative in many areas.

The point here is that there is no real reason why there has to be a dichotomy. In one sense vacuum coating processes are just another way of applying an expensive surface to a relatively inexpensive substrate structure; and are no more different from "state-of-the-art" electroplating processes

than some of the newer electroplating technology is from its counterpart of twenty years ago. To remain competative and profitable as a supplier to the surface finishing industry, there is a good case to be made for becoming more familiar with vacuum coating techniques in general and sputtering technology in particular. The AES has begun to make this effort through the establishment of a vacuum coating committee; and much more can be done through training programs, joint ventures, possibly acquisitions, industry funded research etc.

Sputtering & Electroplating - Characteristics

The subtitle is sputtering and electroplating intentionally; rather than sputtering vs. electroplating. There are advantages to electroplating techniques in many areas that sputtering may never match - thick bulk film properties is one. But there are advantages in sputtering that electroplating can't match as well - such as the ability to coat with ceramics and other non-conductive materials. An "and" approach can't help but be beneficial in the consideration of coating technology as a whole. And, if it's done, could result in new approaches incorporating the best from both technologies.

The following is a list of important points to be considered when comparing sputtering and electroplating, from the author's viewpoint, and is included separately as Figure V.

1. Environmental Impact -

Sputtering as a process for applying one material to the surface of another is environmentally "clean". There are no chemicals used, hence no chemical disposal to be considered. Water is used only as a coolant where applied energy is degraded to heat, and is never in contact with the process. There is no waste water, and no need for expensive treatment facilities. There are no requirements for waste treatment and sludge disposal.

This factor alone has to loom very large when considering any finishing process.

It must also be remembered that in many sputtering applications, particularly decorative, there are certain requirements for polymer basecoats and topcoats that are not environmentally "clean", because the polymer materials and solvents are a waste problem.

2. Energy & Other Utility Requirements

It is very difficult to make a general comparison of energy costs in particular between sputtering processes and

and electroplating processes. Claims (and expectations) have been made in the past that sputtering as an alternative to electroplating has a lower energy cost. This may be true if we choose to compare the cost of operating an automatic sputtering plant for depositing a few hundred angstroms ($1A^{o} = 10^{-10}$ meter) of chrome alloy on PVC parts. If we look at the energy cost of curing the necessary basecoat to prepare the surface for the sputtered layer and the topcoat to protect the very sensitive film, the energy cost comparison can be quite different.

A typical sputtering plant capable of 800 square feet per hour of sputtered chrome alloy film for automotive trim will require 200 amps at 480V at productive capacity; or about 100kw of electrical energy. Base and topcoats can require 30 minute cures at 100°C. A planned facility for sputtercoating magnetic films on mylar for floppy disks for computer memory applications will require 1 megawatt. These are NOT super ecomonical from an energy standpoint.

Sputtering processes require cooling water for the cathodes that operate at high voltages and currents, and the cathodes would melt if not cooled. Conveyor drives, pneumatic systems, sometimes hydraulics, and vacuum pump motor drives are also required. The sputtering cathodes themselves are typically the biggest energy and utility appetite, representing 50% to 75% of the total for a sputtering plant.

3. Capital Equipment Costs

There is no doubt by now that capital equipment costs for sputtering are considerably higher than for electroplating facilities of comparable capacity. It can't reliably be said how much higher, but a factor of 1.5 to 2.0 would not be unreasonable to suppose. Part of the reason for this is the medium for the process. It is less expensive to build a tank to hold a solution, even with the liner, than it is to build a vacuum chamber that has to have diabolically low leak rate even for hydrogen or helium. Another part is that the companies that specialize in vacuum equipment are so called "high-technology." This means that they have very high R&D costs to amortize. The controls and instrumentation for vacuum plant are more numerous and more sophisticated than for electroplating.

Also, most vacuum plant operations are "special engineering" projects with high one-time costs, while more standard equipment can generally be adapted in electroplating.

Balancing these high amortization costs for vacuum processes in many instances is the requirement for waste water treatment facilities, facilities for sludge treatment, and the requirement to ship wastes to perhaps special dump sites,

for plating plants.

Again, only a careful analysis of overall equipment costs can help to make a decision in any specific comparison.

4. Direct and Indirect Material Costs

The direct material costs for sputtering processes vary widely just as they do in electroplating. There is a big difference, for instance, between sputtering aluminum and platinum in direct material cost.

It is probably true that sputtering cathodes are in general quite a bit more expensive than equal quantities of plating anodes. Cathodes for sputtering have to be compatible with the vacuum environments used; and typical applications for sputtering require highly refined and pure materials. It is also true, however, that sputtering has broad application where very thin coatings will do, and a cathode can go a long way if the thickness required is a few hundred Angstroms.

A high purity sputtering cathode a few inches in diameter and one half inch thick can cost a few hundred to several thousand dollars; but may coat 10,000 parts or more.

Be prepared in every case to derive the material cost per part for reasonable comparison purposes.

A typical sputtering plant uses argon as a working gas at a cost of a few dollars per week, and requires some high quality synthetic fluids for some of the vacuum pumps. These are the only indirect materials. The indirect material costs in electroplating are by comparison very high for the maintenance and replacement of chemicals for the various cleaning, plating, and treating solutions.

5. Application

It is quite true that sputtering as a technology has a considerably broader range of material application than does electroplating. Non-conductive ceramic materials, such as SiO_2 (quartz) and Al_2O_3 can be sputter coated quite routinely. This, of course, is not a valid comparison, since these materials can't be plated. The consideration of the range of materials that can be applied by sputtering, however, comes in the consideration of the more sophisticated, primarily functional, applications where several alternating layers of different materials have to be applied. This is often true in the semiconductor industry, which is why sputtering has a high success rate in that industry.

Another example is in the manufacture of thin-film

magnetic memory disks for memory drives in computers. Most of the required thin films can be electroplated, but many (not all) manufacturers are finding that wear resistant, non-conductive top coats, such as Al_2O_3 are desirable. Some of these manufacturers are deciding that if one of the films has to be sputtered, they had just as well sputter them all, rather than have both sputtering and electroplating processes in house.

Another area in the broad subject of application is "cleanliness". There are many chemicals involved in an electroplating process, and they are all in intimate proximity to the process. In general, anything in intimate proximity becomes part of the process. Sputtering processes can be super-clean from the standpoint of material purity and contaminants in the resulting films. This is a function of the process medium.

Plating can produce thick films with bulk material properties. Sputtering, in general, does not. If bulk properties are required (i.e. thick films) plating will have an advantage.

6. Control

It is often said, usually by physicists, that physical processes are inherently more susceptible to control than are chemical processes. If this is true, then extremely tight material and thickness characteristics could be more easily repeated by sputtering processes than by electroplating. It is certainly true that, with the proper instrumentation and computer type control, that sputtered films can be controlled to extremely tight tolerances. I don't know about electroplating. It is also true that the control is very expensive, and not worth it unless the tight tolerances and repeatability are really required. In many functional areas, such as semiconductors, thin film disks, solar cells etc., the tight tolerances are mandatory, and the cost of the controls is justified by the cost of the product.

7. Available Manpower

One area often overlooked in the consideration of type process and plant to invest in, is whether or not the facility can be operated once purchased. The availability of process engineers and technicians to deal with electroplating facilities is certainly higher than with vacuum plant facilities in general, and sputtering facilities in particular. The lack of people trained in the operation and maintanance of vacuum equipment is a real and growing problem as the demand for such facilities grows. An investment in equipment to do vacuum processing has to be made with the underatanding that the operators and technicians will have to come from somewhere. Serious manufacturers of vacuum equipment are beginning to face this problem out of necessity, offering training facilities,

and making efforts to do system design to lower the level of experience and expertise required. The provision of operators, technicians, and process people is a tangible cost consideration for vacuum processing.

Thin Film Winchester Disks

There is a particular development in the computer industry that is getting very "hot" right now, in which sputtering or electroplating, or both, have an opportunity to establish very profitable new business. The development is fueled by the insatiable appetite of end users of all kinds of computers for more and more memory storage capacity in small volume at low cost.

There are two kinds of computer memory; "semi-conductor" memory storage, in which the bits are stored on semi-conductor chips (integrated circuits); and moving, or dynamic, storage devices, for which the bits of information are stored on, and retrieved from, the surface of moving tapes, drums, or disks. The first type, semi-conductor memory, is generally "on-board" the computer mainframe, and used for executive programming and processing. It is part of the Central Processing Unit, or CPU. This kind of memory is roughly ten times as expensive per bit as dynamic memory, but is super permanent and reliable. The dynamic storage devices are used as peripherals, off-line, for compiling data, filing, etc., and generally to feed information to, and retrieve information from the CPU.

Figure VI is a diagram of a "personal" computer, indicating the on-board semiconductor and the peripheral dynamic memory, with capacity range that is typical. Capacity of the peripheral memory is 10 to 50 times that of the onboard memory. As shown in the figure, the peripheral memory can be digital tape, floppy disk drive, or hard disk drive. Our interest, concerning both electroplating and sputtering, is hard disk memory drives.

By far the most popular, because of density and cost, is memory storage in magnetic films. And the conventional means of producing such films, whether on tape, drums, or disks, is a thin film of iron oxide particles suspended in an epoxy binder.

Figure VII is a cross-section of a hard, or rigid, disk, indicating the particulate films, the substrate, and a lubricating layer that is applied to the outside surface. The recording density for such a film; the number of bits per inch that can be packed onto the disk; is an inverse function of the thickness of the film.

The very interesting thing to us is the fact that manufacturers of such recording films have now reached the upper limit of recording density, because they can't make the films any thinner; and the end users are demanding higher and higher

recording density.

The way to get increased recording density is to deposit continuous metal alloy films, usually cobalt-nickel, with high (and repeatable) coercivity. Plating and sputtering are both reasonable ways to produce such films, and useful films have been demonstrated by both processes.

Figure VIII shows a cross-section of a rigid disk with a thin cobalt-nickel recording film. There are two other films shown. One is a "thick" film, usually called a substrate layer, which many researchers find they need to apply to the substrate before the recording layer. The purpose is to cover up defects in the aluminum substrate and level the surface as a preparative step. (Much the same purpose as in copper-nickel-chrome plating.) The other is a "hard" protective topcoat to protect the recording layer from "head" crashes and corrosion.

The dilemma for planners is this: The substrate layer is too thick to be done economically by sputtering, and sputtering replicates the surface anyway, having no leveling effect. The topcoat layer, on the other hand, is a material that can't be plated. The amortization of the required capital equipment is a really significant part of the cost of making the new films; and if both plating and sputtering equipment have to be purchased and operated, the new films might not be competitive.

Does one find a way of eliminating the substrate layer, allowing sputtering of all the films? Or does one find a way of changing or eliminating the topcoat, allowing investment just in plating equipment? Or, finally, does one both plate and sputter? The answers are certainly not in yet. There are plans by various manufacturers to go all three ways.

To define things a little more, and a point that surprises more than a few people, is that the peripheral memory storage for a computer of any size, is a large percentage of the cost of the computer system. The off-line memory unit is typically from 30% to 60% of the dollar value of the system. So we aren't looking at a small fraction of the computer market, we are looking at roughly one-half of a multi-billion dollar industry, poised to take a dramatic new tack.

Three or four years ago, hard disks were 14" and 8" diameters. Today, 5¼" disks are bigger in volume than the larger disks, and manufacturers are introducing hard disk (Winchester) drives with four 5¼" disks capable of storing 50 + megabytes. Next year will see 3.9" and 3.5" disk drives. Industry analysts are predicting 30% to 50% growth rates for the smaller sizes over the next several years because of application in small computers, office equipment, cash registers, control systems, and other devices.

Figure IX is a summary of some of these statements leading to the conclusion that there is a real opportunity for equipment and material suppliers in both the plating and sputtering industry over at least the next several years.

Finally, it must be said that there is a lot more to this story than what is presented here. The coming revolution involves drive and head design, vertical recording media, research into magneto-optical and optical techniques, and much, much more. The author has tried to winnow the problem down to the topics of interest to electroplaters and vacuum equipment and material suppliers, and to present it in a very general way.

FIGURE I

SIMPLE DIAGRAM OF ELECTROPLATING PROCESS

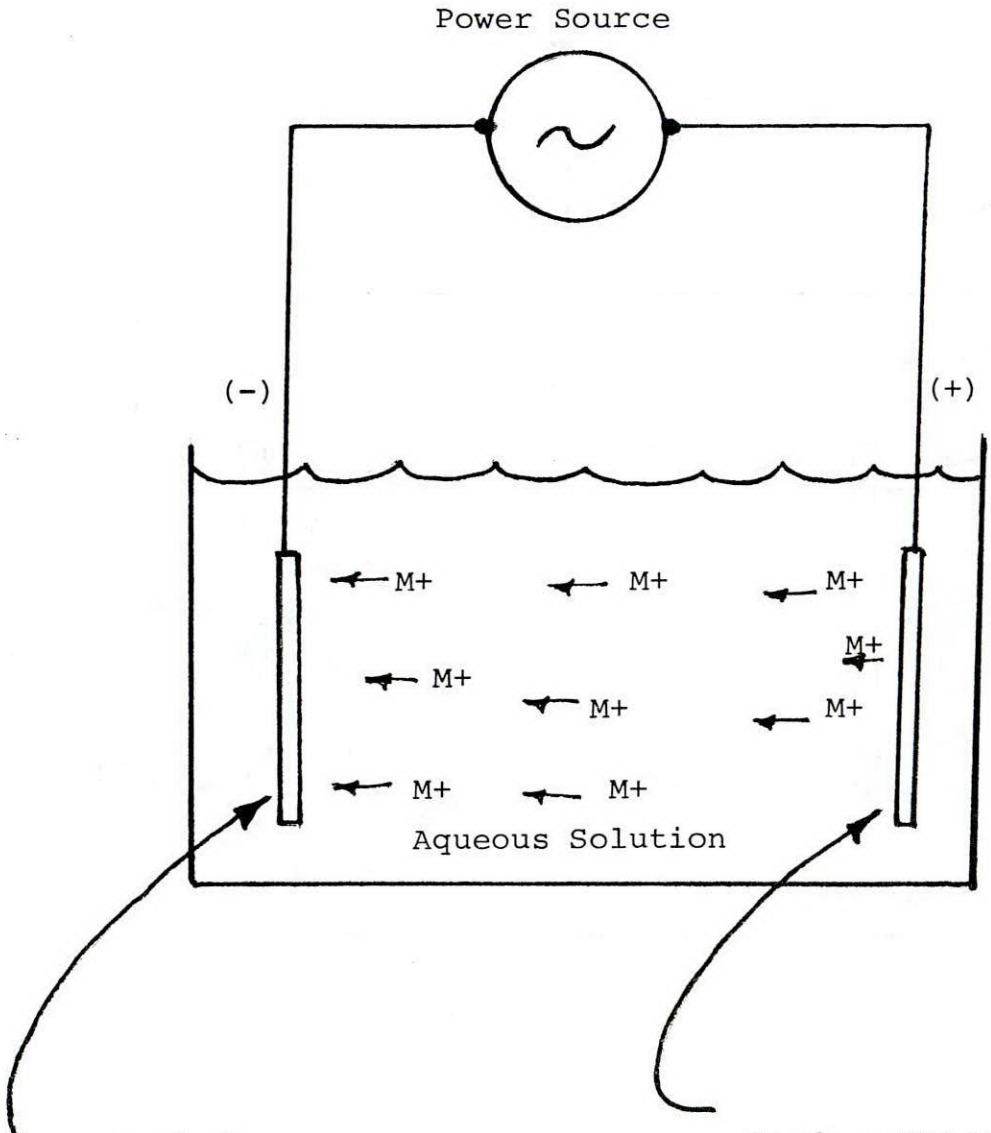


FIGURE II

SIMPLE DIAGRAM OF SPUTTERING PROCESS

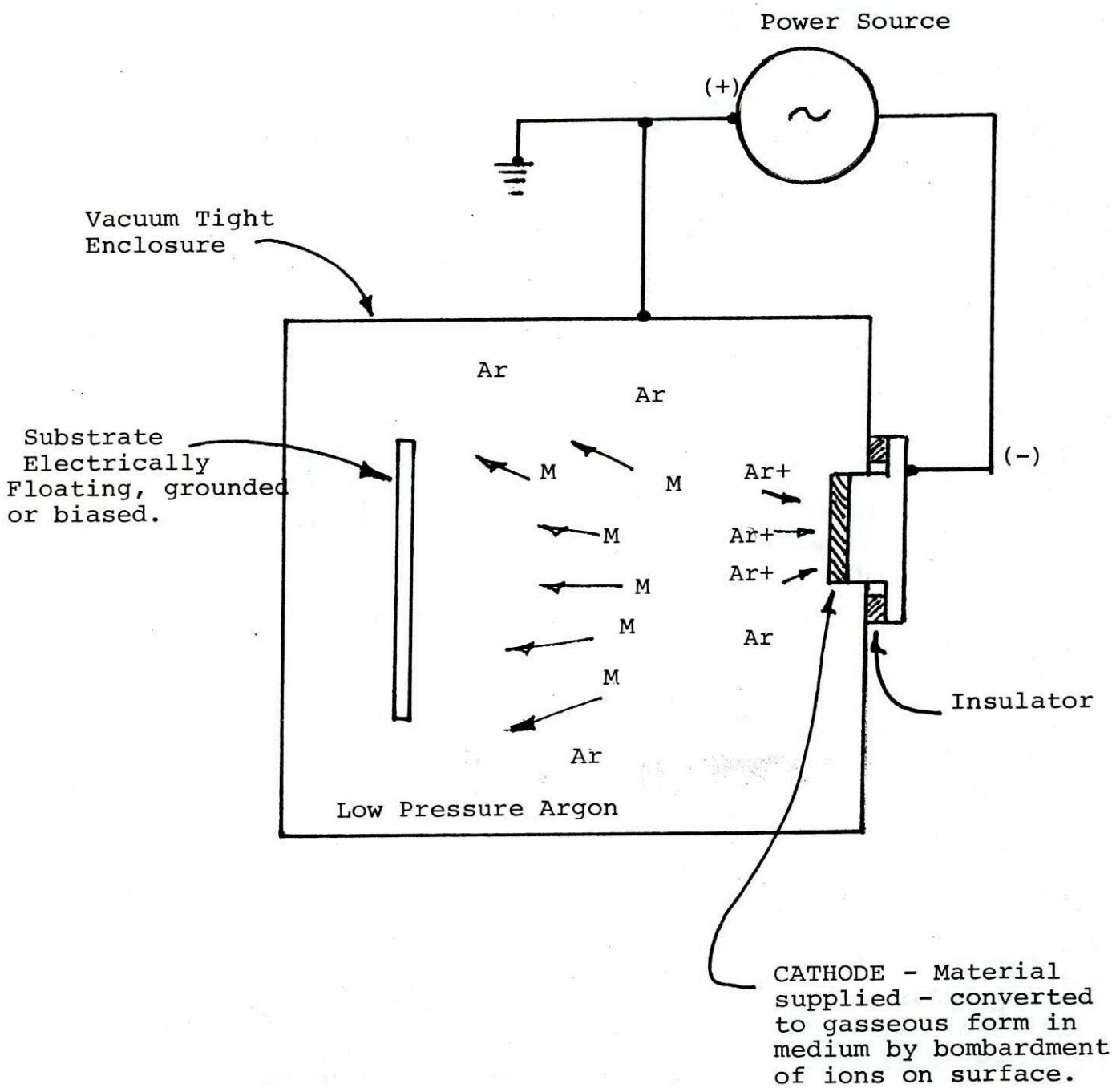


FIGURE III

COMMON ASPECTS

1. PROCESS ENCLOSURE

   A. Plating - Solution Tank
   B. Sputtering - Vacuum Chamber

2. ELECTRICAL SUPPLY

   A. Plating - Low Voltage D.C.
   B. Sputtering - High Voltage D.C.

3. PROCESS MEDIUM

   A. Plating - agueous chemical solution
   B. Sputtering - Low pressure argon gas

4. Both require that the substrate and the material source be suspended in the medium within the enclosure.

5. In both cases, the coating material is transported through, and influenced by, the medium.

FIGURE IV

MAGNETRON - MAGNETICALLY ENHANCED - SPUTTERING

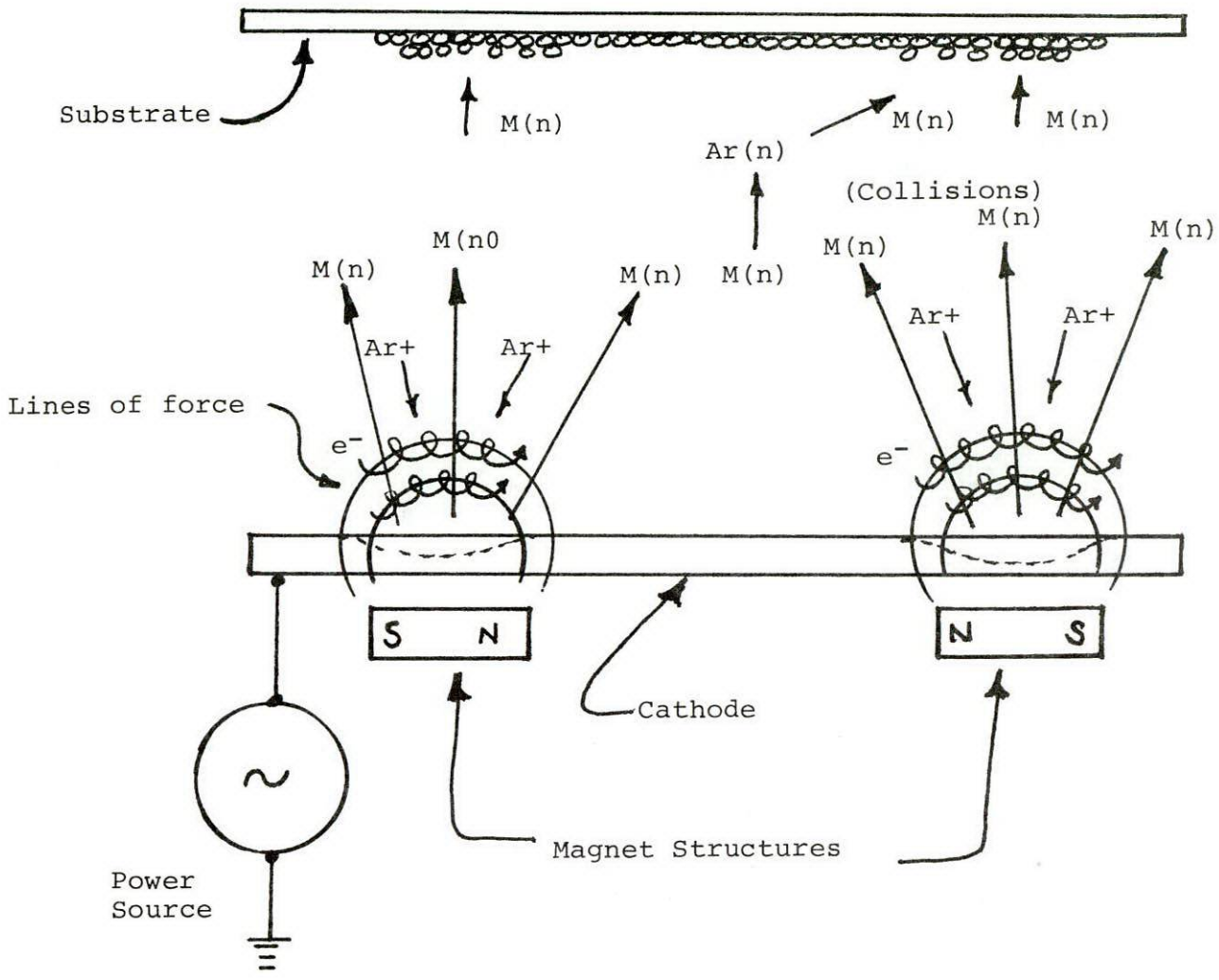


FIGURE V

SPUTTERING & ELECTROPLATING

1. ENVIRONMENTAL IMPACT

   ** Generally in favor of vacuum processing

2. ENERGY & OTHER UTILITY REQUIREMENTS

   ** Probably a trade off - No free lunch

3. CAPITAL EQUIPMENT COSTS

   ** Higher for vacuum processing when waste treatment and disposal not a factor

4. DIRECT & INDIRECT MATERIAL COSTS

   ** Direct generally higher for sputtering
   ** Indirect higher for electroplating

5. APPLICATION

   ** Broader range for sputtering
   ** Sputtering may have advantages in multi-layer and super-clean applications
   ** Sputtering can't produce bulk properties

6. CONTROL

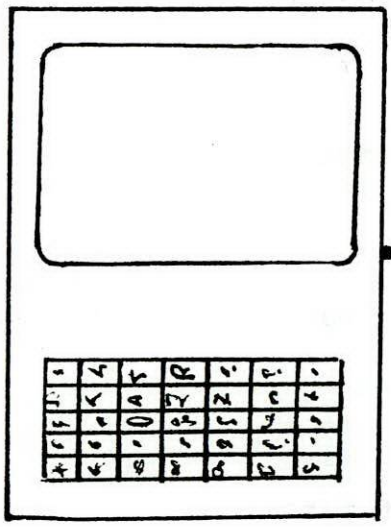
   ** Extremely tight specs & repeatability favor sputtering
   ** Sputtering controls more expensive

7. AVAILABLE MANPOWER

   ** More available for electroplating
   ** Sputtering requires investment in training

FIGURE VI

TYPICAL PERSONAL COMPUTER



CABLE

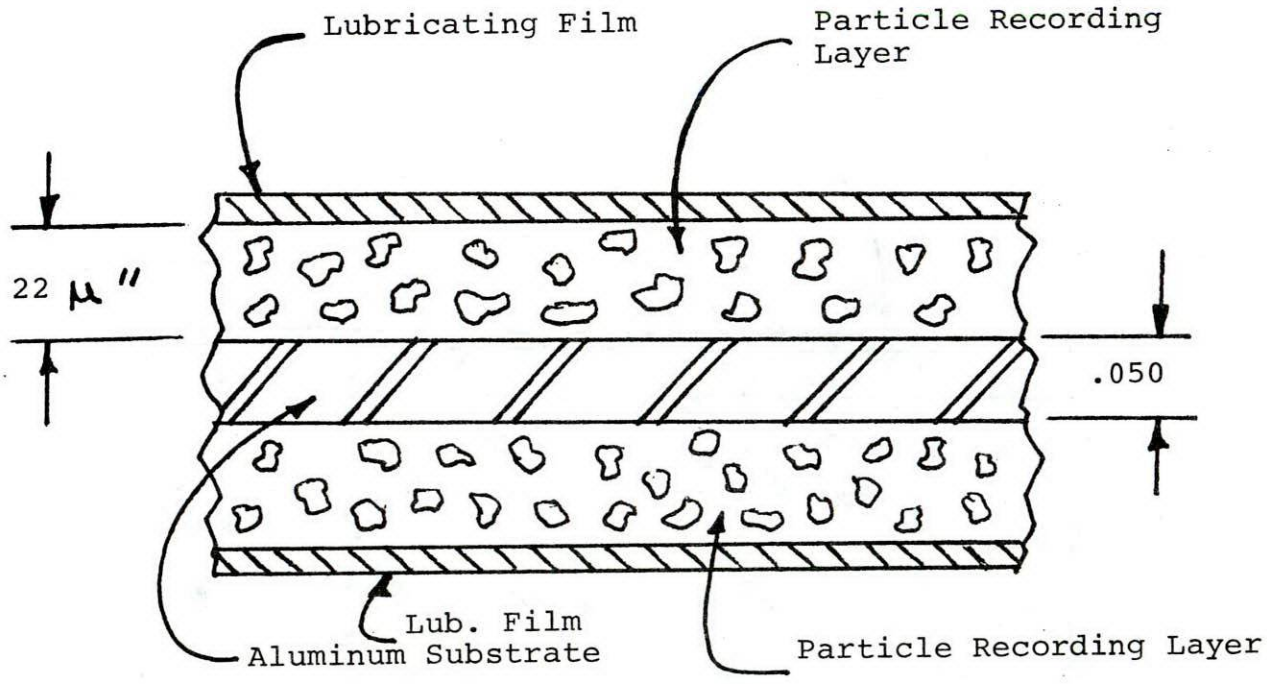
Tape, floppy disk, or hard disk memory drive

CPU - with display, keyboard I/O, and on-board semiconductor memory.
Capacity Range:
64,000 - 256,000 bytes

Off-Line Memory
Capacity Range:
500,000 - 5,000,000 bytes

FIGURE VII

CROSS - SECTION OF RIGID DISK WITH CONVENTIONAL PARTICAL PROCESS



Recording film is applied to both sides of disk.

Recording density is an inverse function of film thickness: becoming greater with thinner films.

$22\ \mu$ in. $= \sim 5600A^{o}$
$1A^{o} = 10^{-10}$ meter

FIGURE VIII

CROSS - SECTION OF RIGID DISK WITH THIN COBALT/NICKEL RECORDING FILM

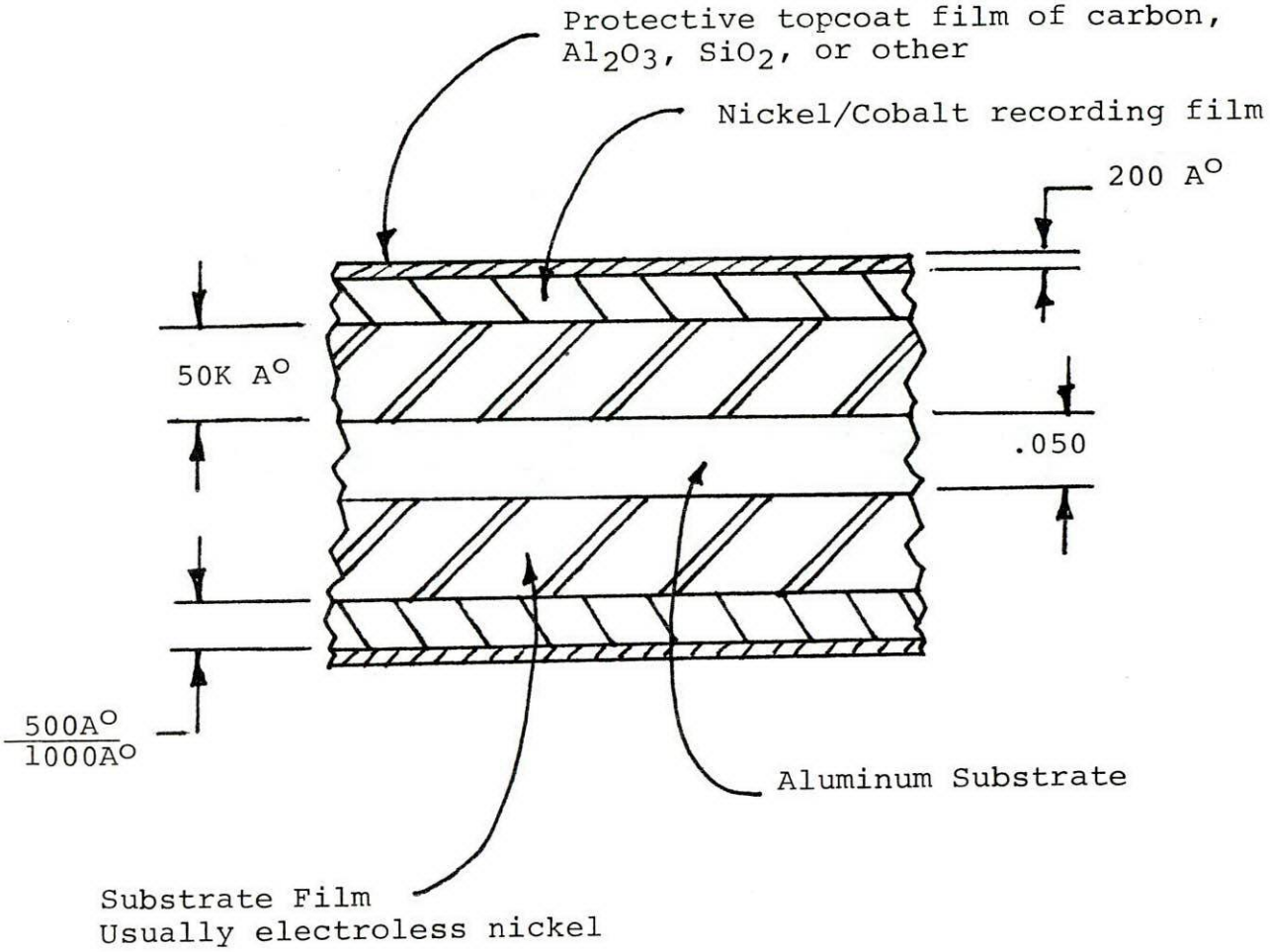


FIGURE IX

** THE CONVENTIONAL IRON-OXIDE PARTICULATE PROCESS CANNOT YIELD HIGHER RECORDING DENSITIES

** PRODUCT DESIGNERS AND END USERS DEMAND, AND ARE READY TO PAY FOR, HIGHER DISK STORAGE DENSITIES TO PRODUCE HIGH MEMORY CAPACITIES IN SMALL VOLUMES.

** PROCESSES HAVE BEEN DEMONSTRATED, BY BOTH PLATING AND SPUTTERING, THAT INCREASE STORAGE CAPACITY BY AS MUCH AS THREE TO FIVE TIMES. SOME MANUFACTURERS ARE PRODUCING PILOT QUANTITIES OF DISCS, BOTH PLATED AND SPUTTERED.

** THE KEY TO SUCCESS IS RELIABLE, HIGH YIELD PROCESS AND EQUIPMENT TO MEET THE DEMANDING PRODUCT SPECIFICATIONS, AND METHOD IS FAR FROM SETTLED.

** THE CHANGE WILL RESULT IN CONSIDERABLE REWARD FOR THOSE WHO MEET THE CHALLENGE.

K-4

Non-Electrolytic Deposition Processes Session K

Thermal Outgassing Behavior of Electrodeposited Black Chromium

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THERMAL OUTGASSING BEHAVIOR OF ELECTRODEPOSITED BLACK CHROMIUM

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Abstract

The outgassing characteristics of electrodeposited black chromium were determined because of interest in using this coating in vacuum applications. Data obtained for a variety of conditions led to the conclusion that this coating is acceptable for use in optical transport networks and plasma physics experiments. The outgassing rate for an unbaked coating was 3×10^{-10} Torr liters/sec/cm^2.

Introduction

Electrodeposited black chromium is of interest in several areas of activity. In the solar energy field the coating serves predominantely as a collector[1,2]. In plasma physics experiments and optical transport systems it is used as an anti-reflective coating. For these latter applications, the coating is used in vacuum chambers and in these situations outgassing characteristics must be known to establish pumping speed requirements. Many gases are observed in the initial degassing of vacuum systems. Water vapor is almost always predominant with carbon monoxide, carbon dioxide, nitrogen, oxygen, and many hydrocarbons present. These primarily come from the surfaces within the system and may be essentially removed by the outgassing process. Although there are data available on the outgassing characteristics of a variety of materials including aluminum[3,4], aluminum anodizes[5], copper[3,6], nickel base alloys[7,8], and stainless steels[3,4,6,9-13], there are no data in the literature on black chromium. Therefore, the purpose of the work reported in this paper is to provide such data.

Sample Preparation

The samples used for this work were 304 stainless steel, 2.5 cm x 30.5 cm x 0.725 mm thick. They were cleaned, acid pickled, given a Wood's nickel strike and then plated with proprietary black chromium (Dupont Econo-Chrome BK). Thickness of the chromium deposit was approximately 2200Å. Complete details on the plating process are given in Table 1.

TABLE 1
Procedure for Plating Black Chromium
on 304 Stainless Steel

1. Vapor degrease
2. Electroclean in hot alkaline solution, 15 seconds cathodic, then 30 seconds anodic
3. Rinse
4. HCl acid dip (10% wgt.)
5. Rinse
6. Wood's nickel strike at 215 A/m^2 for two minutes
7. Rinse
8. Black chromium plate at 2150 A/m^2 for 1.5 minutes in Dupont Econo-Chrome BK.
9. Rinse and dry
10. Wrap parts in aluminum foil.

Outgassing Apparatus and Procedure

The outgassing was conducted by the throughput method using AVS* Standard 9.1[5], in which $Q = \Delta PC/A$ where: Q is the outgassing rate in Torr liters/sec/cm^2, ΔP is the differential pressure across the aperture in Torr, C is the conductance of the aperture in liters/second, and A is the surface area of the sample in square centimeters.

Figure 1 is a schematic of the outgassing system used for this study. Shown is a chamber of known surface area with an ion gage, and an aperture with an ion gage on the side away from the chamber. This arrangement allowed for measuring ΔP across the aperture. A bypass pumping network of higher conductance than the aperture permitted using the gas analyzer in two modes of operation. In one mode the chamber was at a higher pressure. In this mode the gas analyzer was used on the low pressure side of the aperture. In the second mode the chamber was at lower pressure. In this mode the analyzer was used on the chamber itself, thereby increasing the sensitivity of the analyzer. The system was all-metal-sealed above a liquid nitrogen high vacuum trap. This allowed a high temperature bake, which decreased the background gases evolving from the system. A turbomolecular pump backed by a mechanical pump accomplished this purpose. Figure 2 is a photograph of the system. Note the close coupling of the gaging with the aperture in between, and the close coupling of the sample chamber to the pumping medium. This was done to minimize the error introduced by conductance limitations other than the aperture itself. Figure 3 is a schematic of the data acquisition system. A LSI-11 computer was used in conjunction with a gas analyzer. The computer controlled the gas analyzer while the signal from the analyzer was fed back to the computer. At this point there were three options: (1) observing a video terminal as the data was produced, or (2) X-Y plotting the data as it was produced, or (3) automatically storing the data on a disc as it was produced. In this study we used the latter option because it allowed us to take data faster. It also made it practical to take data continuously over an extended period of time.

American Vacuum Society

OUTGASSING SYSTEM

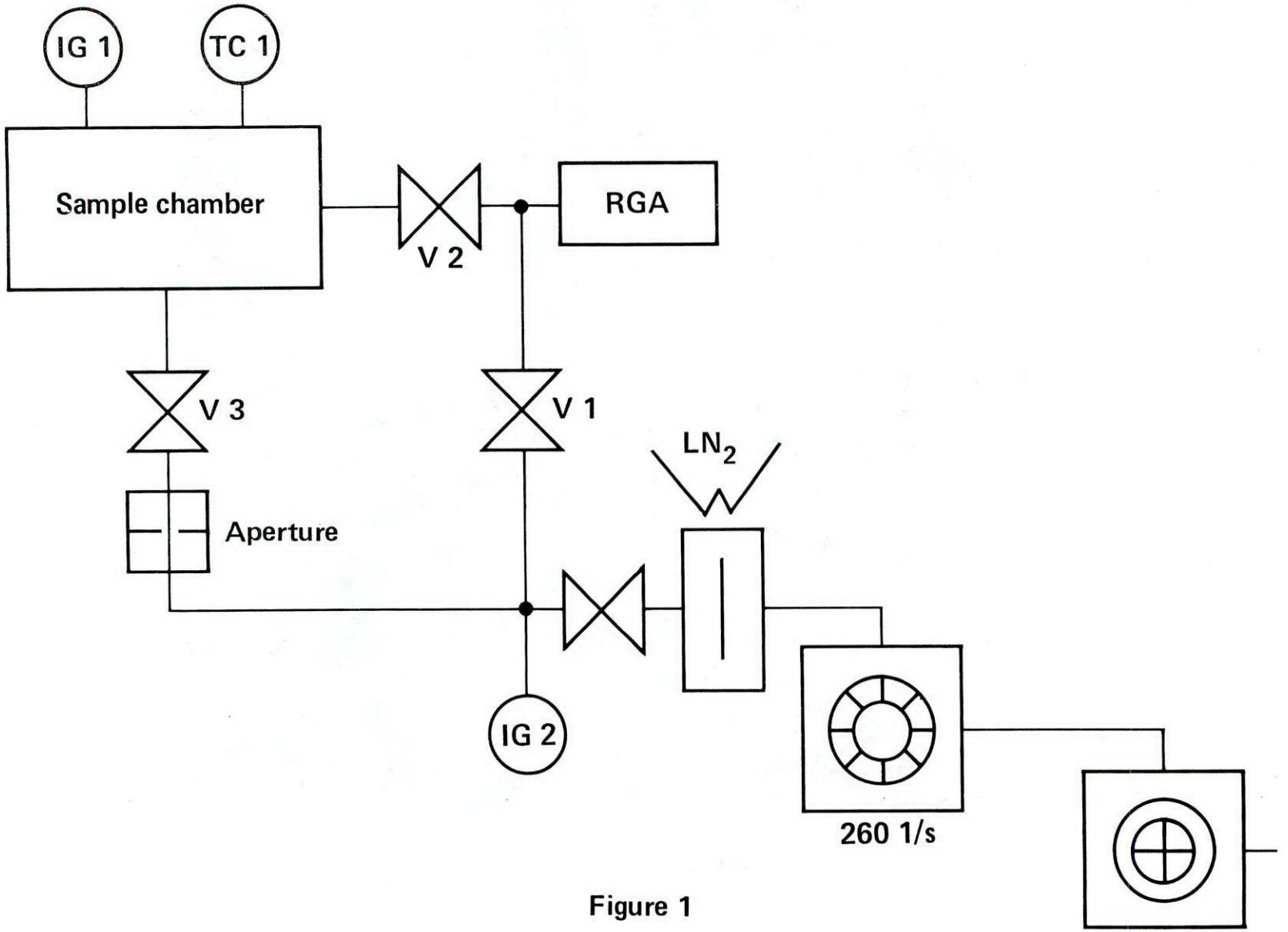


Figure 1

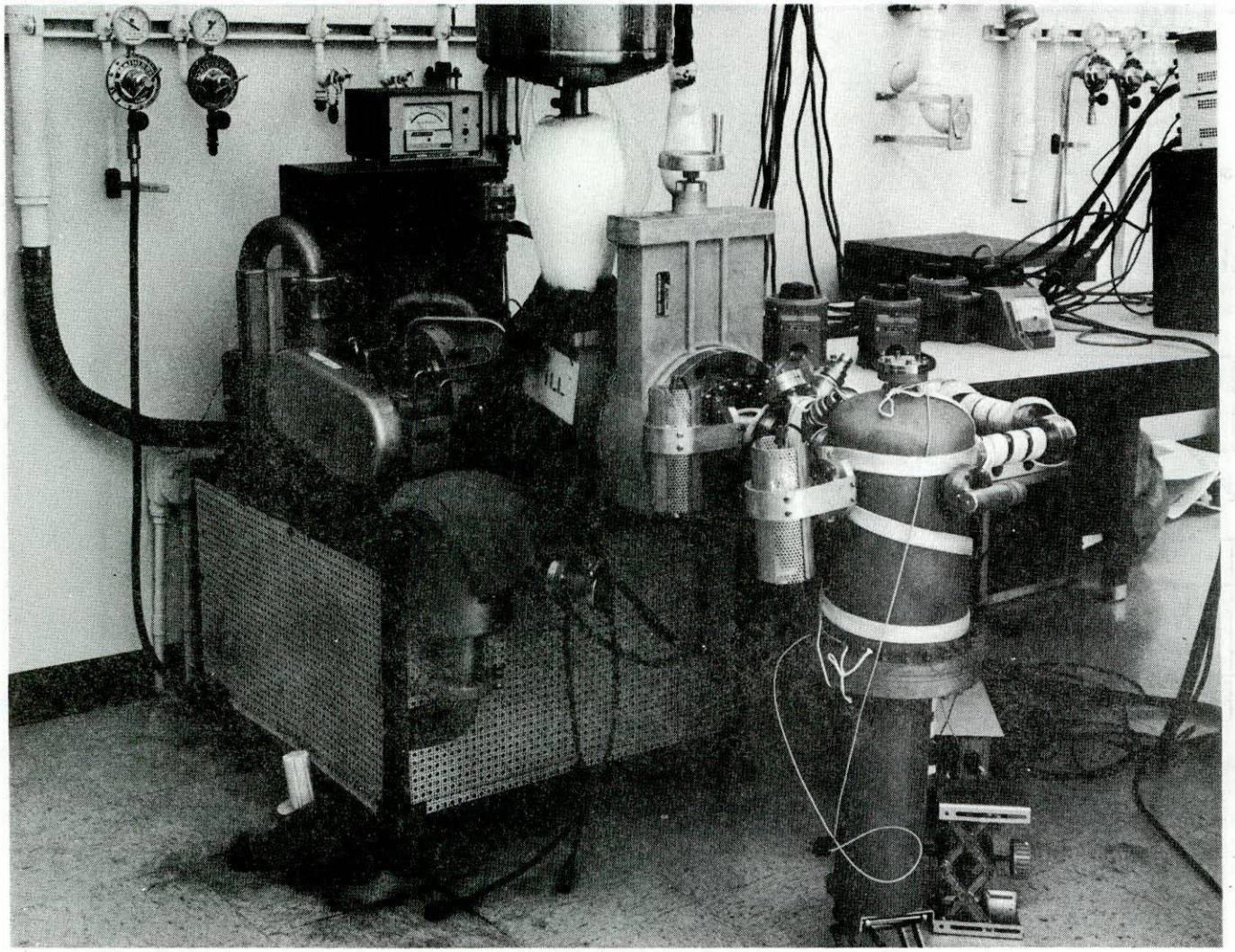
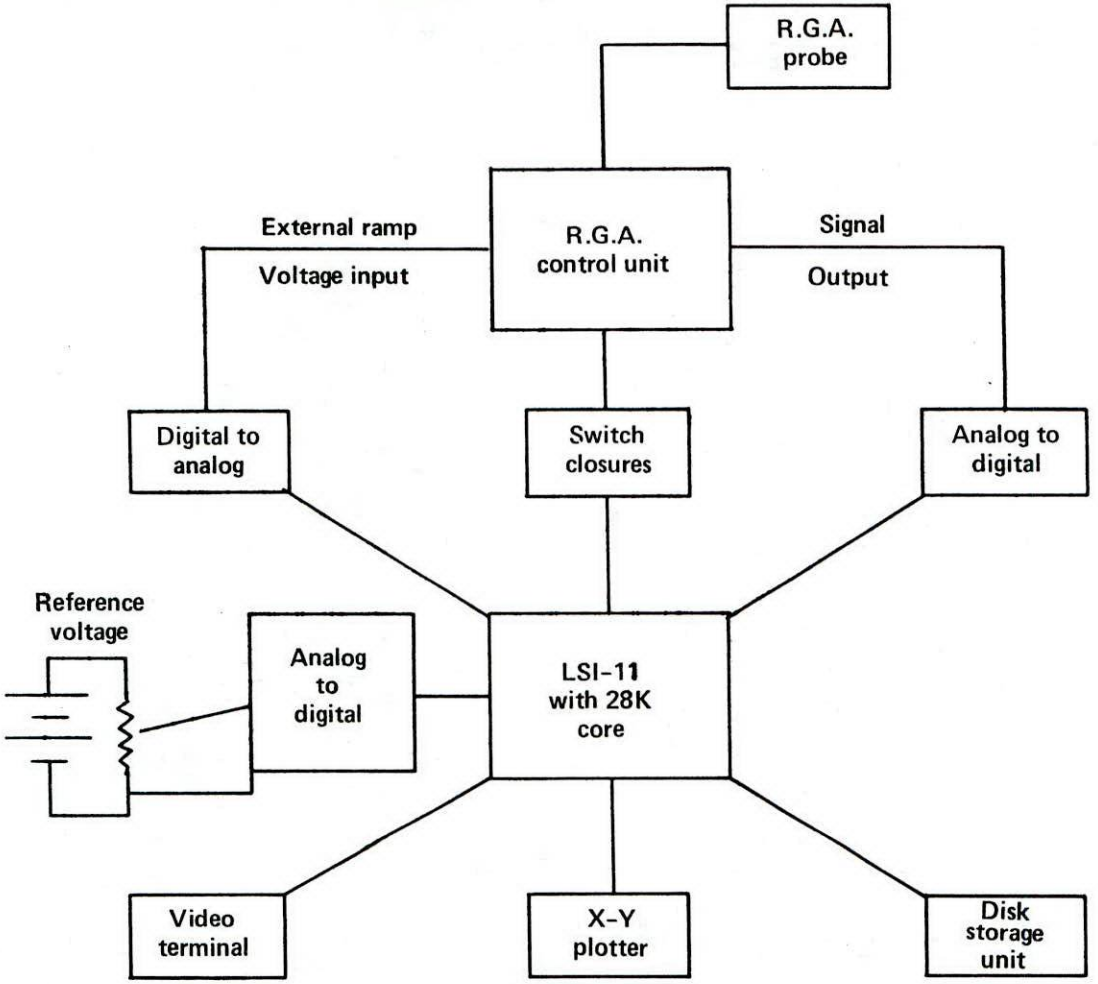


Figure 2



Data Acquisition System

Figure 3

Outgassing was studied under three conditions: (1) at ambient temperature, (2) at 350°C, and (3) at ambient temperature after the 350°C bake. The samples were divided into two sets. The first set (#1) was studied under all three conditions while the second set (#2) was studied at ambient temperature only.

Results

Results are presented in Figures 4-10 and Table 2. They reveal that the outgassing characteristics of black chromium are such that the coating is acceptable for use in vacuum applications. An outgassing rate of 3×10^{-10} Torr liters/sec/cm^2 was obtained for the unbaked coatings.

Figure 4 shows an RGA scan of the empty chamber, at ambient temperature after the 350°C bake. This was done to establish the background prior to the outgassing study. The pressure at this point was 2×10^{-9} Torr with an outgassing rate of 3.8×10^{-12} Torr liters/sec/cm^2. The major constituent was carbon monoxide (mass 28) with a little bit of water (mass 18) and some carbon dioxide. Figure 5 shows an RGA scan of sample set 1 at ambient temperature after 100 hours of vacuum exposure. The pressure was 3×10^{-7} Torr. The outgassing rate was 3×10^{-9} Torr liters/sec/cm^2. The major constituent was water (mass 18). Also present were hydrogen (mass 1 & 2), oxygen (mass 16 & 32), carbon monoxide (mass 28) and carbon dioxide (mass 44). Figure 6 shows an RGA scan of sample set #1 at 350°C. The scan was taken after 100 hours at this temperature. The pressure was 3.8×10^{-7} Torr. The outgassing rate was 1×10^{-8} Torr liters/sec/cm^2. The major constituent was still water (mass 18). Hydrogen (mass 1 & 2) had more than doubled. Carbon (mass 12) was now evident. Carbon monoxide and carbon dioxide had risen slightly. Figure 7 shows an RGA scan of sample set #1 after cooling and being maintained in vacuum for an additional 80 hours. The pressure was 6×10^{-9} Torr. The outgassing rate was 9×10^{-11} Torr liters/sec/cm^2. The major consituent was carbon monoxide (mass 28). The amount of carbon monoxide (mass 28) was greatly reduced. Figure 8 shows an RGA scan of sample set #2 at ambient temperature after four hours under vacuum. The RGA was on the pump side of the aperture because the chamber was operating in the higher pressure regime. The pressure was 4×10^{-7} Torr. The outgassing rate was 8×10^{-9} Torr liters/sec/cm^2. The major constituent was water (mass 18), hydrogen (mass 1 & 2), carbon (mass 12), oxygen (mass 16 & 32), carbon monoxide (mass 28), and carbon dioxide (mass 44) were also present. Figure 9 shows an RGA scan of sample set #2 at ambient temperature after 100 hours under vacuum. The pressure was 2×10^{-7} Torr. The outgassing rate was 2×10^{-9} Torr liters/sec/cm^2. The major consituent was water (mass 18) in approximately the same quantity as in sample set #1. Also present were hydrogen (mass 1 & 2), oxygen (mass 16 & 32), carbon monoxide (mass 28), and carbon dioxide (mass 44). Figure 10 shows an RGA scan of sample set #2 at ambient temperature, after 250 hours under vacuum. The outgassing rate was 3×10^{-10} Torr liters/sec/cm^2. The major constituent was still water, but the quantity was 100 times lower than in the previous scan. The sample was at equilibrium outgassing rate.

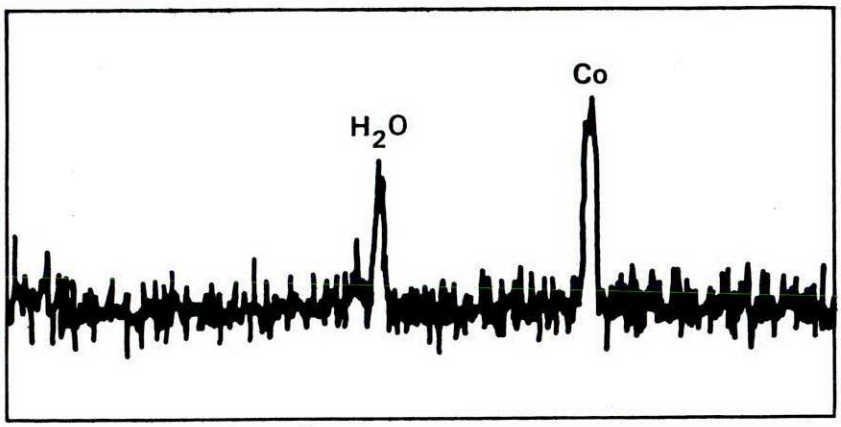


Figure 4

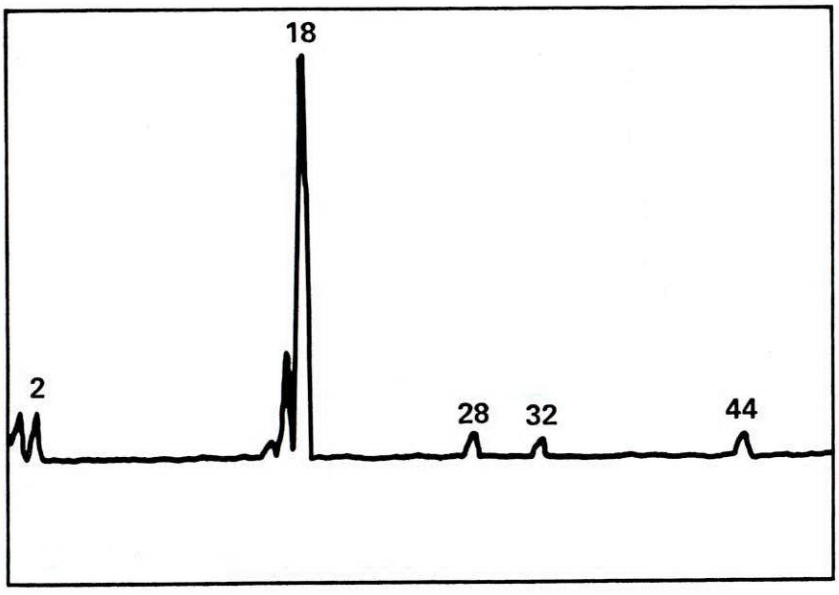


Figure 5

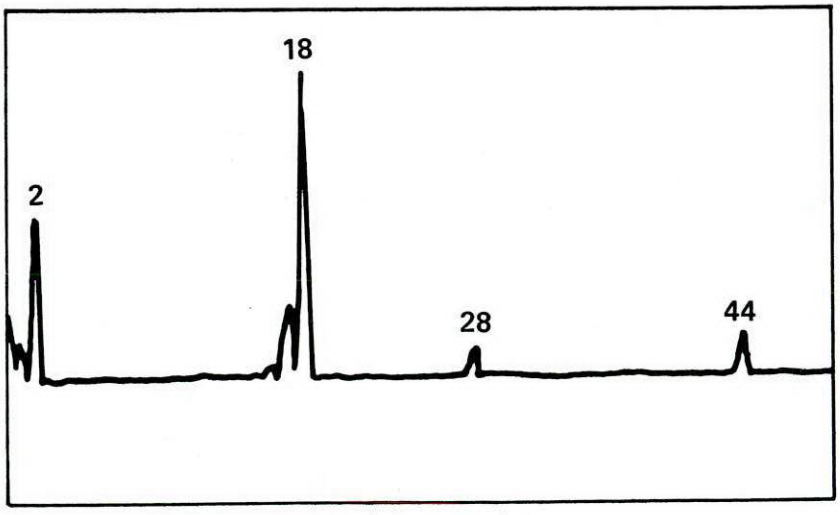


Figure 6

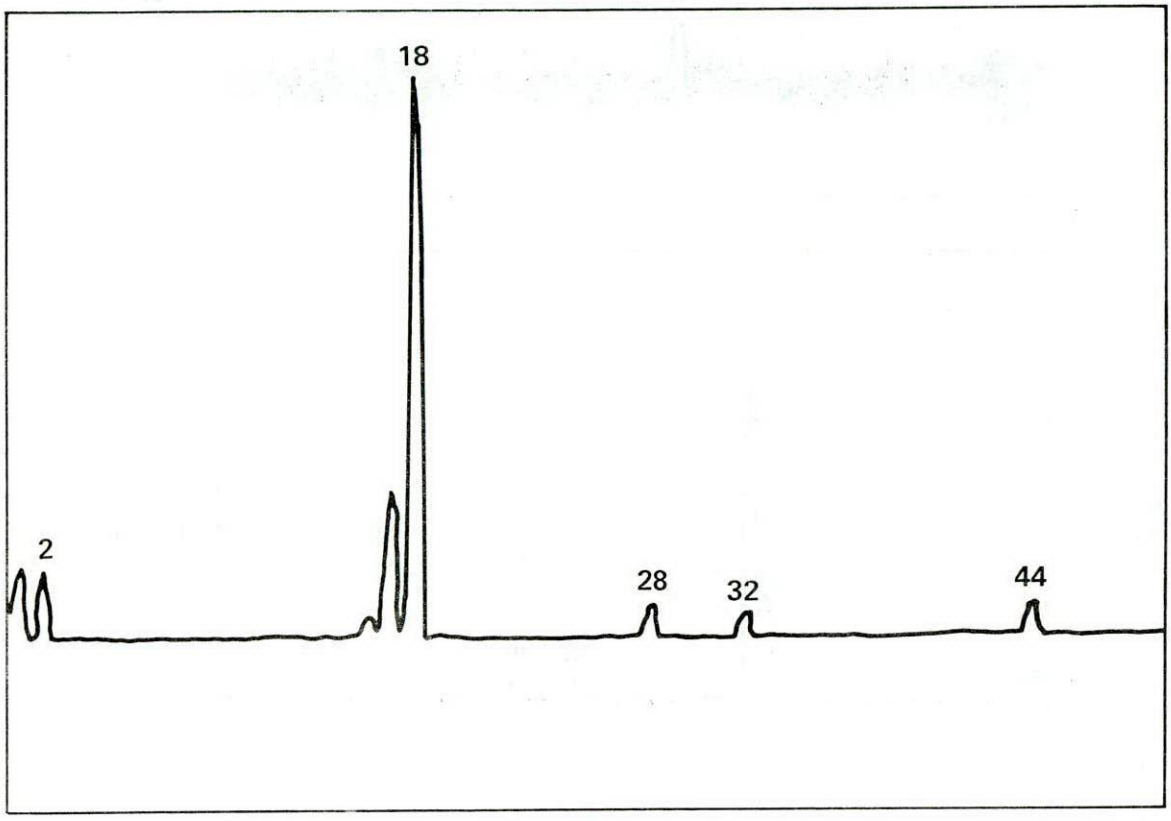


Figure 7

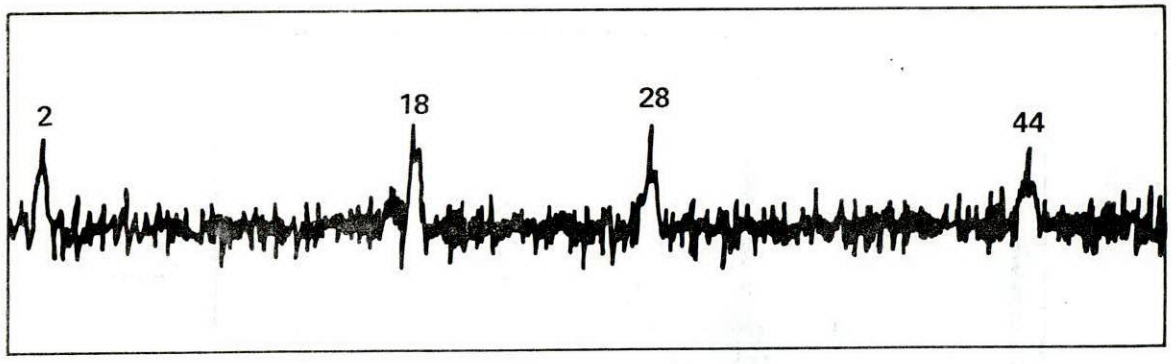


Figure 8

Atomic mass unit

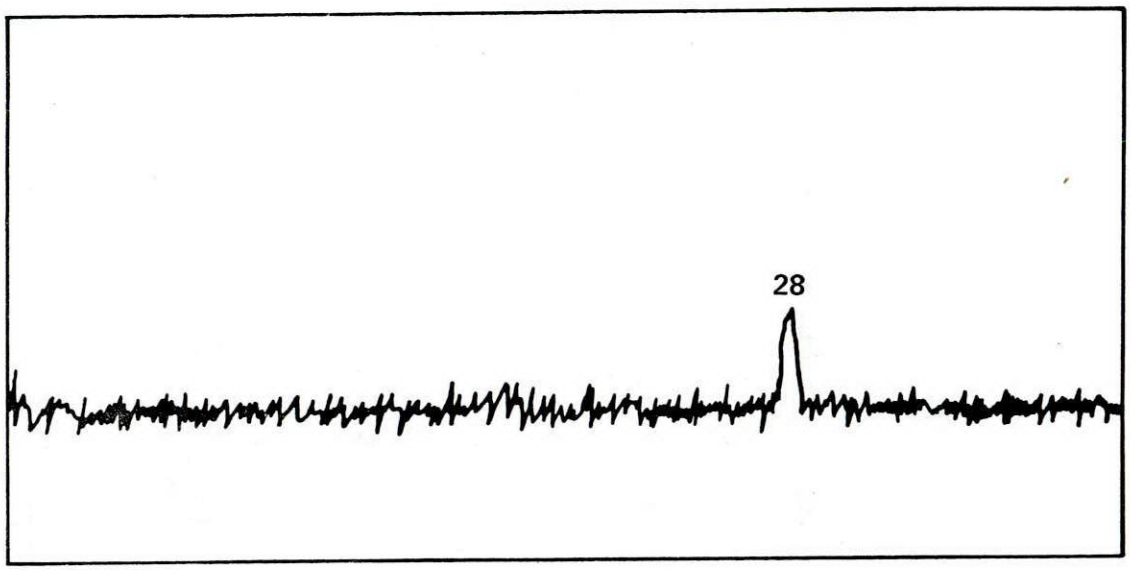


Figure 9

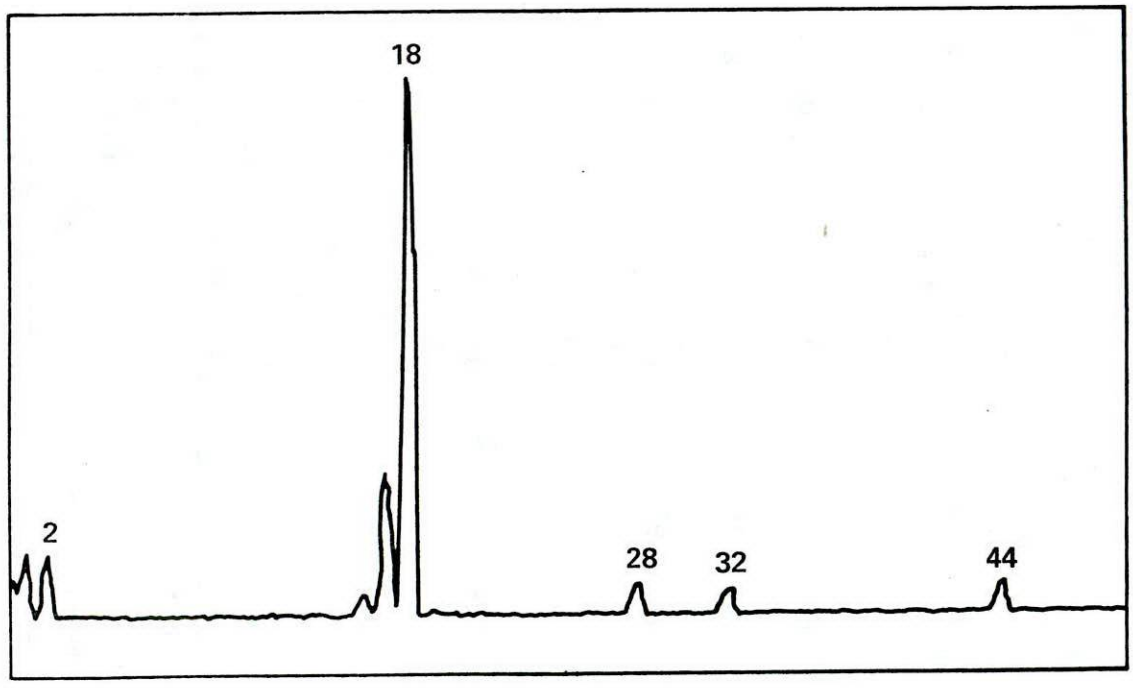


Figure 10

TABLE 2
Outgassing Data for Electroposited Black Chromium

Conditions	Fig.	Pressure (Torr)	Outgassing Rate (Torr Liters/sec/cm^2	Outgassing Constituents Amplitude $\times 10^{-10}$						
				H_2	C	O_2	H_2O	CO or N_2	O_2	CO_2
AMU →				2	12	16	18	28	32	44
Empty chamber – No coating – Ambient temp – After 350°C bake	4	2×10^{-9}	3.8×10^{-12}	0.3			0.5	1.0		0.4
Black Cr – Ambient temp – After 100 hrs. of vacuum exposure	5	3×10^{-7}	3×10^{-9}	85		54	420	60	57	62
Black Cr – At 350°C after 100 hours at temp.	6	3.8×10^{-7}	1×10^{-8}	190	40		320	67		79
Black Cr – Above sample after cooling and remaining in vacuum for 80 hrs.	7	6×10^{-9}	9×10^{-11}	1.0			1.5	6.0		1.4
Black Cr – Ambient temp. after 4 hours in vacuum	8	4×10^{-7}	8×10^{-9}	34	14	25	240	61	43	80
Black Cr – Ambient temp. after 100 hours in vacuum	9	2×10^{-7}	2.8×10^{-9}	78		50	389	61	50	51
Black Cr – Ambient temp. after 250 hours in vacuum	10	3×10^{-9}	3×10^{-10}	4.6			4.9	4.7		3.6

Conclusion

This study indicates that the outgassing characteristics of black chromium allows its use in vacuum applications. The outgassing rate was 3 x 10^{-10} Torr liters/sec/cm^2 unbaked and 9 x 10^{-11} Torr liters/sec/cm^2 for baked samples. This is acceptable for use in optical transport networks and plasma physics experiments. Although the difference between baked and unbaked samples appears extremely small, one must consider that when dealing with surface areas of millions of square centimeters, this difference greatly influences the pump speed required to achieve a given pressure.

Acknowledgement

"Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-ENG-48."

We wish to thank J. Gallagher for his participation in processing the test samples through the black chrome process sequence.

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L-1

Light Metal Finishing II
Session L

Alkaline Corrosion of Anodized Aluminum: Cause and Cure

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ALKALINE CORROSION OF ANODIZED ALUMINUM: CAUSE AND CURE

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FMC Corporation is a large supplier of detergent components to formulator-compounders of various types of cleaners. In an investigation of the effect of carwash detergents on painted surfaces and automotive aluminum trim, we found that some carwash products caused discoloration of bright anodized aluminum trim parts. Representatives of car manufacturers, aluminum producers, aluminum fabricators and suppliers of carwash detergents were aware of the problem. The phenomenon was commonly called aluminum "blush" or aluminum "buttermilking". The discoloration shows up as an unsightly white film and, once formed, it cannot be removed. We decided to investigate the problem further when we learned that the mechanism of attack was not fully understood and that there were no guidelines for preventing its occurrence.

An aluminum producer defined blush as "the partial dissolving of the amphoteric anodic coating by acid materials below pH 4 and alkaline materials above pH 10". Note that the anodic coating, not the aluminum metal is dissolved. In our research, we found this description approximately fits one of the three types of anodized aluminum corrosion we observed. We called it alkaline attack. The other two types are sodium chloride blush and chelate related blush. The concept of chelate related blush is new and unexpected. Each type of corrosive attack is different in appearance and will be described more fully.

Figure 1 provides an estimate of the growth in the use of aluminum in, and on, cars. Currently an average of over 125 pounds of aluminum per car is used and projections are that this will more than double during the 1980's. Weight reduction to improve fuel efficiency is an important strategy of car makers in order to meet government requirements on their fleet average. Aluminum and other light weight materials are being used for both internal and external applications.

This paper deals with the external use of bright-anodized aluminum trim and components such as side body mouldings, window trim, mirror frames, wheel covers and bumpers. However, we believe that the type of corrosion under discussion applies to all applications where anodized aluminum is contacted by alkaline cleaners such as appliance trim, patio furniture, and handrails etc. in commercial buildings.

When these anodized aluminum pieces are processed by an aluminum finisher, the porous anodic film is sealed in a manner that protects it and the substrate aluminum from penetration by moisture and other sources of corrosion. In the case of bright dipped and anodized aluminum, the mirror like finish will be protected for many years when the sealing step is effectively done. Our work involves the use of bright anodized aluminum sealed in a hot water bath containing small quantities of nickel acetate. We believe that nickel ions enter the open pores in the hexagonal cells and attach

to other metal ions that form the anodic film structure and that the anodic film (aluminum oxide) is converted to aluminum hydrate thus swelling and closing off the pore openings. Figure 2 shows the idealized structure of the cells and pores of the anodic film.

To deal with the aluminum blush problem we developed a small lab scale test to evaluate what components or characteristics of alkaline cleaners would cause blush. Figure 3 shows our test apparatus which consists of a constant temperature bath with a test tube containing a piece of anodized aluminum trim immersed in a test solution. In this static immersion test method, at a temperature of 120°F, blush would develop in four hours (or less) with some commercial carwash detergents (used at 0.25%) or not at all with other products regardless of the length of time the aluminum sample remained immersed. The aluminum samples used in these tests were obtained from job shop anodizers and represented 5XXX series trim alloy and 7XXX series bumper alloy. The carwash detergents were also commercially used products.

We found three distinctly different types of anodized aluminum blush. The first, "Alkaline Attack" attacks and dissolves the anodic film when the solution pH is greater than 10. In this form of corrosion, hydroxyl ions in the test solution penetrate the protective film and roughen the underlying aluminum metal surface. A dense white discoloration develops. We also observed that a typical aluminum hydroxide precipitate formed in the test solution. With further tests we determined that this type of corrosion can be prevented by inhibiting the active alkalinity of the cleaning product through the addition of a specific quantity of silica to the product.

When the cleaning product contains a silica (SiO_2) to active alkalinity (Na_2O) ratio of 0.8 or greater, we found that alkaline attack would not occur even at a pH of 12.3. We have recommended an SiO_2/Na_2O ratio of 1.0 to formulators of detergent which contact anodized aluminum trim.

The second type of aluminum blush found was termed sodium chloride corrosion. This occurs when sodium chloride is used as an inexpensive filler in detergents. In this case the oxide film is also dissolved but in more localized areas and clusters of pits can be seen in the aluminum metal. Some white discoloration is also seen. We were unable to develop a procedure for preventing this type of corrosion except to advise compounders to avoid the use of sodium chloride in detergents which will be used on anodized aluminum.

The third type of blush corrosion was called chelate related blush. Chelating chemicals such as complex phosphates are an essential ingredient in cleaning compounds. Their purpose is to build or support the cleaning efficiency of the surfactant through sequestration (or chelation) of water hardness ions. Components of the detergent with metal ion complexing capabilities function by re-opening the sealed pores in the oxide film and complexing, or chelating, the nickel used in the sealing process. A white deposit is formed and spreads laterally across the barrier layer of the pores. The anodic film isn't completely penetrated so there is no corrosive attack of the underlying aluminum metal. We used our scanning electron

microscope and elemental mapping for nickel to determine the mechanism involved in this type of attack.

With organic chelators present in the test solution, we noted a significant decrease in nickel ion concentration in, and on, the anodic film surface where blush occurred. On non-blushed test specimens, the elemental nickel mapping showed little or no change in the pattern or occurrence of nickel in the anodic film.

The time required to develop a blushed condition was dependent on the aluminum alloy being used and the binding strength of the chelator present in the detergent. Figure 5 shows the time it takes for various organic and inorganic chelators to produce chelate related blush. To avoid the potential for confusing two types of blush, these data were obtained in uninhibited test solutions having a pH of 9.8. The organic chelators re-open the pores and complex the nickel ions much faster than do the inorganic phosphates. They also attack the film in all areas whereas the phosphates only cause blush in areas where the anodic film's geometry has been distorted due to bending or otherwise stressing the metal surface. Figure 6 further illustrates these comments. The figure shows an end view of window trim and the areas where blush tends to occur, that is, it occurs on the bends and adjacent to places where the metal was cut. Blush doesn't occur on the inner surfaces of the trim piece even though the anodic film is less thick than the film on the outer surfaces. Our opinion is that this is due to compressive distortion of the film which helps the film resist penetration of corrosive materials. Figure 6 also has electron microscope views of chelate blushed and unblushed anodized surfaces. Scanning electron microscope scans for nickel revealed no nickel in or near these holes but nickel was found uniformly over the unblushed region of the anodic film. The figure points out blushed areas where fabrication has caused metal distortion and the attack is due to inorganic chelate related blush. When the stronger, organic, chelators come in contact with anodized aluminum, blush tends to occur on all areas, not just those where the anodic film has been distorted.

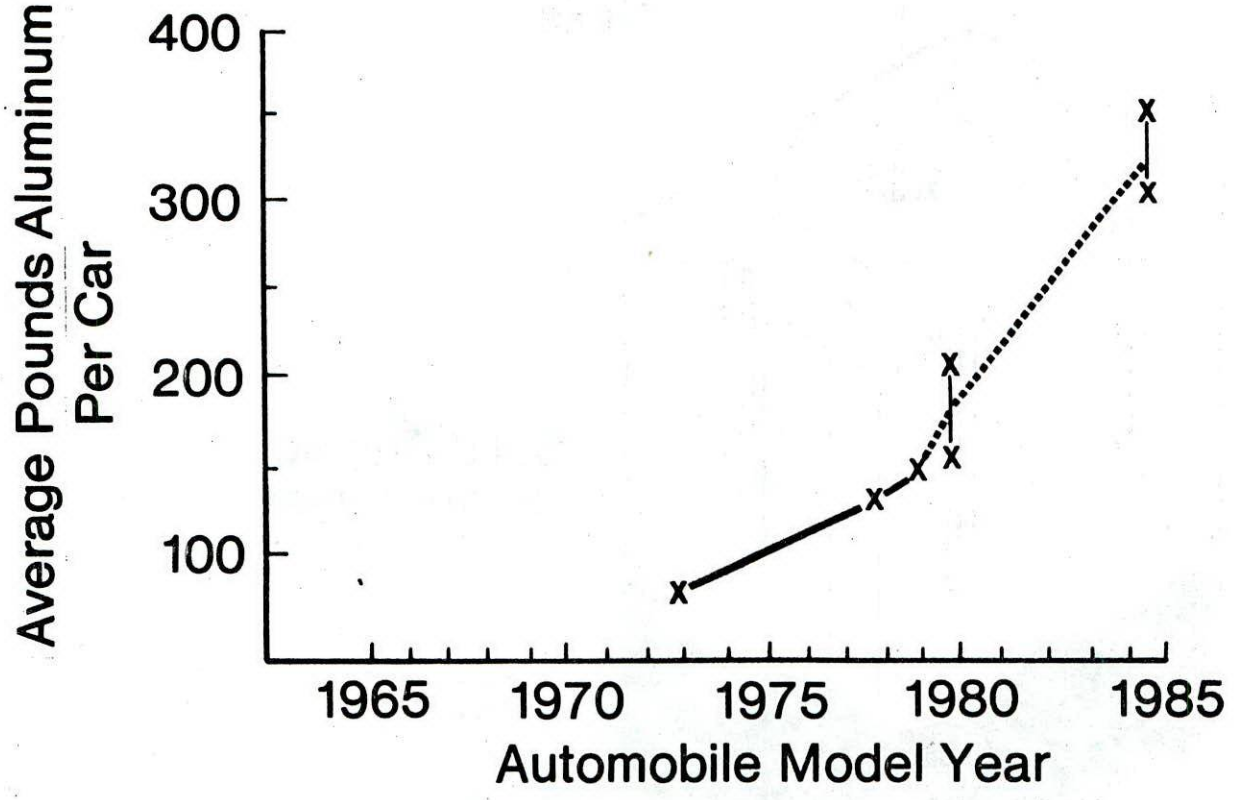
This type of blush is prevented through the use of a silica inhibitor added in certain definite proportions to the chelator contained in the alkaline cleaning product. The 7XXX, zinc containing bumper, alloy is more reactive than the 5XXX, magnesium containing, alloy so more silica inhibitor is required. When the organic chelators such as NTA, EDTA or citrates are present in the cleaning product, about four times as much silica inhibitor is needed than is required when the chelate is an inorganic phosphate. The minimum effective level of inhibition for 5XXX series alloys is 20 parts of silica per 1000 parts of inorganic phosphate; the highest level needed is 160 parts of silica per 1000 parts of organic chelator. Further tests showed that these inhibitor use levels completely eliminated chelate related blush.

In this study we have provided an explanation of the mechanisms which lead to three types of blush corrosion of anodized aluminum. A simple laboratory test method was developed which reliably predicts blush tendency. The

capability of the electron microscope for examining surface defects and developing information on the causes of those defects was demonstrated. The understanding of blush corrosion and how to avoid its occurence was significantly advanced.

Hopefully dissemination of this knowledge will lead to increased use of bright-anodized aluminum.

Figure 1.
Automotive Aluminum Usage



Sources: Aluminum Association, 1977 Aluminum Statistical Review
Aluminum Association, Use of Aluminum in Automobiles—Effect on the Energy Dilemma, Publication T12

Figure 2.
Anodizing

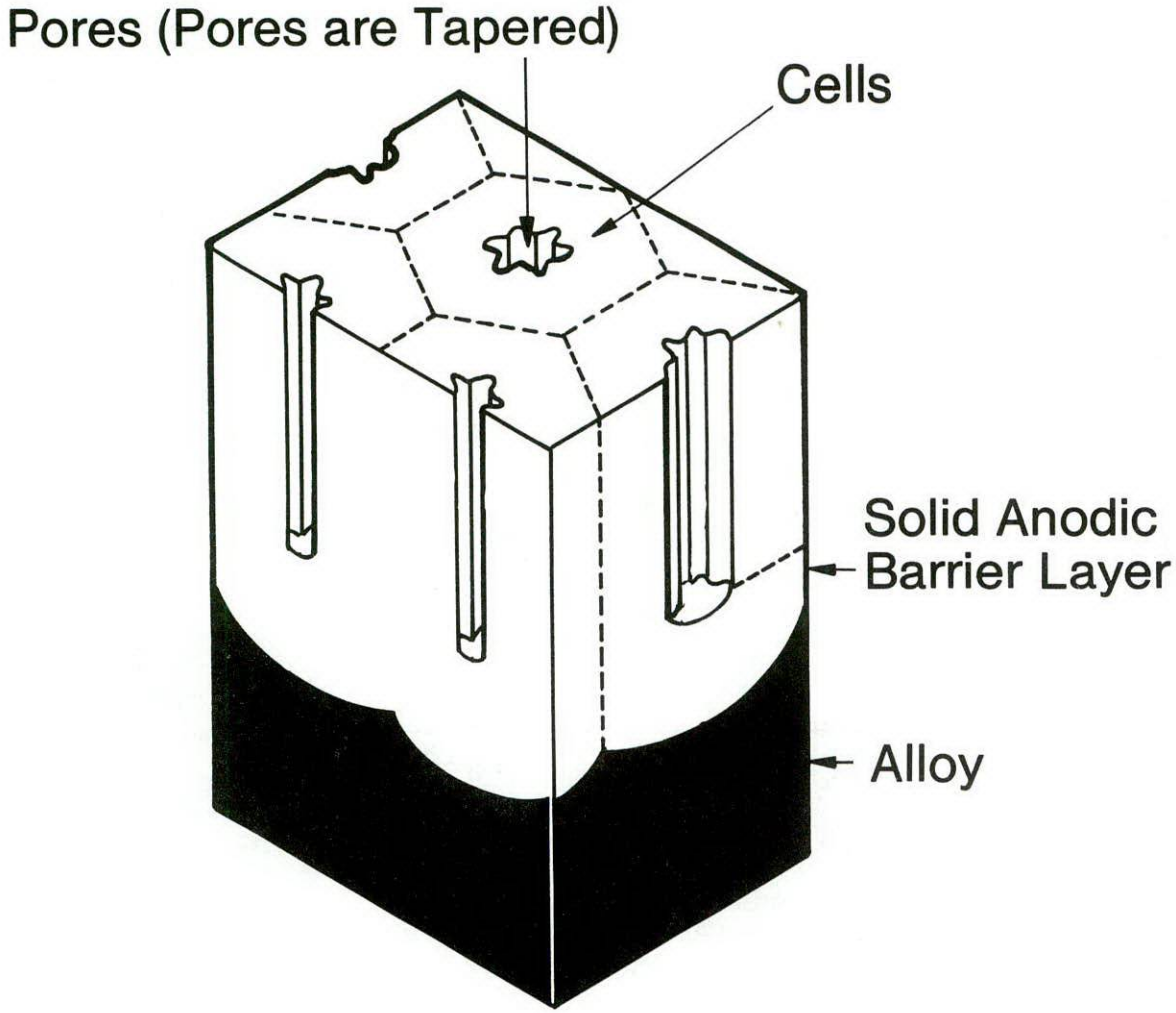


Figure 3.
Blush Test Apparatus

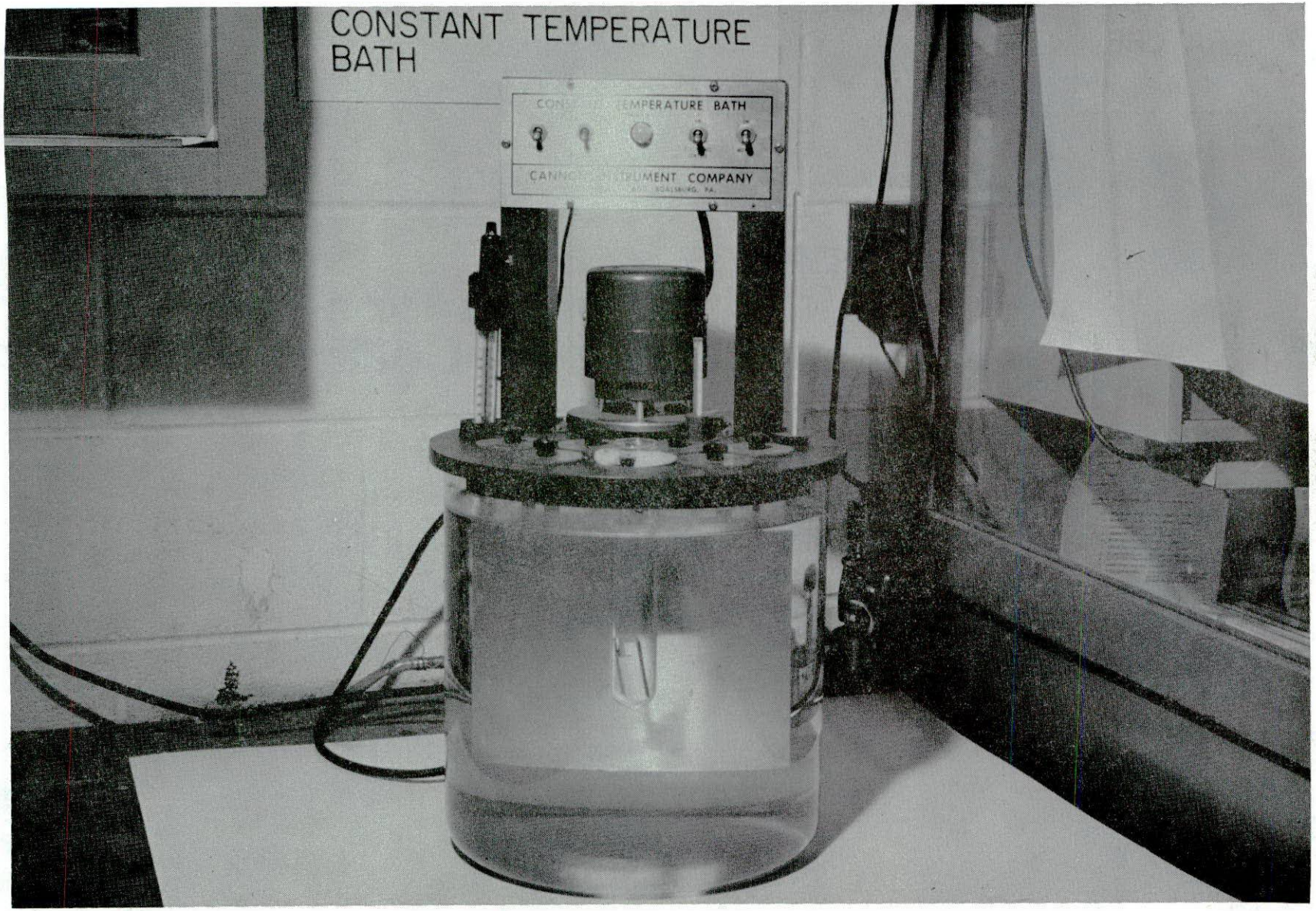


Figure 4.
FMC Studies
Have Identified Three Types of Attack on the Anodic Coating

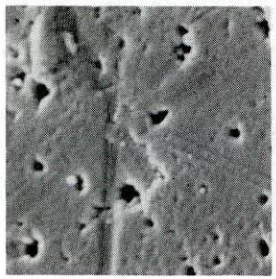
- ALKALINE ATTACK
- SODIUM CHLORIDE CORROSION
- CHELATE RELATED BLUSH

Figure 5.
Rate of Chelate Attack on Anodized Aluminum Automobile Trim (5252 Alloy)

Chelate	Time to First Visible Blush, min[1]	Site of Attack
EDTA	7	All Surfaces
NTA	13	All Surfaces
Citrate	35	All Surfaces
TSPP	42	Stress Sites
STPP	70	Stress Sites
Glassy Phosphate	80	Stress Sites

[1]Test Conditions: 0.25% Solution
150 ppm Water
pH 9.8
Temp. 120°F

Figure 6.
End View of Trim-piece Showing Sites of Poly-Phosphate "Blush"



Blush

Top Surface

Blush

Blush

Blush

No Blush

Blush (in Direction of Shear)



No Blush

Bottom Surface

L-2

Light Metal Finishing II
Session L

How to Prevent Pitting on Color Anodized Parts when Using Titanium Anodizing Racks

Fred Henschel
Vulcanium Corp.
Northbrook, IL

HOW TO PREVENT PITTING ON COLOR ANODIZED PARTS WHEN USING TITANIUM ANODIZING RACKS

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3045 Commercial Avenue
Northbrook, Illinois 60062

Many anodizers do not use titanium racks because they have encountered pitting on dyed parts and some on clear parts. On clear parts the pitting only appears after sealing. It is only natural for anyone to find the simplest, quickest and most expedient solution to a problem which, in this instance, is to use aluminum racks. Yes, aluminum racks add to the contamination of the anodizing bath...

Yes, aluminum racks must be stripped every trip through the line.

Yes, aluminum racks are quickly consumed and must continually be replaced. However, this solution precludes all of the cost-saving advantages of Titanium racks.

The purpose of this discussion is to show you that pitting problems in color anodizing are completely controllable without any costly, specialized equipment or changes in your regular procedure. And, you can use Titanium racks to full advantage.

A Lesson Learned At Sea

Unfortunately nobody has bothered to inform the anodizer that the pitting he is experiencing is caused by "galvanic action" or "galvanic corrosion," an extirely controllable problem. Mariners have had to deal with the problem for over a hundred years when utilizing more than one metal below the waterline of boats and ships. For example, a steel-hulled ship with bronze propeller. Thus, to learn something about this phenomenon let's begin by looking at the definition of galvanic corrosion as stated by the Boating Technical Standard's Body of the American Boat and Yacht Council.

Galvanic corrosion is "the corrosion that occurs at the anode of a galvanic couple, caused by the flow of ions from the anode to the cathode through an electrolyte." Another way of stating it would be that two dissimilar metals, submerged in a liquid which will easily carry a current, can cause the eating away of one of the metals.

Which one? The galvanic table (Figure 1) shows us.

At the top of the list are the most active metals or the most anodic. At the bottom, the least active, or most cathodic. Note that maganesium heads the list followed by zinc and aluminum, whereas titanium is only surpassed as a noble metal by graphite, zirconium, gold and platinum. In galvanic corrosion, the more active metals will become corroded in the presence of a lesser active metal.

Electrolytes Are The Key

Sea water is an excellent electrolyte. Tap water is generally not. However, when tap water contains a great many minerals and particles it can become a fair electrolyte. The addition of chemicals can considerably enhance the electrolytic properties of tap water. Thus, virtually all of your tanks will have current carrying capacities to some degree. But, the only tanks in which parts are

left for any length of time after anodizing are the dye tanks and the seal tanks. These are the ones which can cause the anodizer galvanic corrosion difficulity.

The American Boat and Yacht council also emphatically warns boaters that stray currents, especially from A.C. sources, can also play havoc with galvanically dissimilar metals in sea water (or in our case, in the dye or seal tanks). Stray currents can be present in your tanks, at unacceptabale levels, because of your rectifiers, many of which are located in the vicinity of these tanks. Also, electric immersion heaters, used in many shops for heating these tanks, can contribute to stray current conditions.

Do not underestimate the effect these currents have, for they can be the major factor in creating a galvanic corrosion problem.

The worst condition would have to be in a plastic or fiber glass tank, or in a metal tank lined with plastic or rubber because the electrolyte has no connection to ground as a result of the insulating effects of the tank or liner. Adding insult to injury, our worst case would have an old electric immersion heater, located in an area near a big rectifier, with 140° black dye made with late summer tap water somewhere in Southern California. Believe it or not, we found just such conditions in a Van Nuys, California anodizing operation. Their rectifier is about 18 feet from their black dye tank. They have an old electric immersion heater in a plastic tank.

Here are some test coupons (Figure 2) which we anodized under these conditions, using a titanium rack. These samples are the first of a series we ran in February. They were in the dye tank about 18 minutes. Note the pitting problem.

Later in this report, we will show you other test coupons run through the same system after the galvanic corrosion problem had been eliminated. You will be truly amazed!

The Sacrifical Anode Solution

But first, back to the control of galvanic corrosion in marine applications. Let's see how the mariner's solution can be adapted to an anodizing plant situation.

First, many decades ago "in the olden days," as the younger generation says, zinc blocks were attached to the hulls of metal ships just forward of the screws and rudder. It was found that magnesium, the most active or least noble of all metals, would practically disappear before your eyes when submerged in sea water. So, zinc was the next choice. It lasted and performed well because it was more active or anodic than any of the ship's metals exposed under water and, thus, acted as a sacrificial anode. So long as the zinc was not completely comsumed it protected the most anodic metal of the ship itself. This method is still used today on small ships and boats.

Anodizers can do even better than mariners, for dyes and seals don't attack magnesium the way sea water does. So, with the best sacrificial anode in use, we can expect the best protection for our aluminum parts in those tanks which typically cause pitting problems.

The sacrificial anode is the first major step in solving your pitting problems. Before we discuss how to install your sacrificial anodes, you'll want to help yourself even more by first reducing any

stray current problems which may exist.

Since you aren't about to move tanks or rectifiers, the next best way to eliminate stray current is to ground your tanks with a good copper wire, leading it to some ground other than water pipes, as that would just spread current to all the tanks. If your tank is plastic or rubber lined, drop the wire into the solution. Otherwise, bolt the wire to the tank. It's just that simple. No big expense or need to shut down your production. Ground your tanks to conduit or an electrical box.

Now, it is time to obtain magnesium anodes about the same length as the spline and hook of your longest titanium racks. Vulcanium Corporation supplies square bar anodes complete with hooks to any length required (Figure 3). Before putting these sacrificial anodes in your dye and seal tanks you must first deoxidize the magnesium to remove any oxide coating which might reduce efficiency. This can be done in any nitric acid-based de-oxidizer used in your anodizing line.

After anodizing and before dying and/or sealing, place your sacrificial anodes on the workbar, on either side of the titanium rack or racks being used. A clamp, wire or hook can be used to secure the anodes in place on the workbar. We recommend the use of clamps such as Vulcanium Corporation's Spartan Clamp as it is completely corrosion resistant. If your tank is big and your load consists of many racks, it may be necessary to use more than two sacrificial anodes to protect the centermost racks. Be sure to position the sacrificial anodes as close to your racks as is practical, for the closer to the parts, the more effective your galvanic protection.

Earlier we reviewed examples of test coupons from a worst-case situation involving galvanic corrosion. The samples were liberally pitted, the result of galvanic corrosion in the dye tank. Now, take a look at these (Figure 4) test coupons. The one on the right is from our original test. The one on the left was run on the same anodizing line, the same afternoon, using the same time intervals and the same Titanium anodizing rack. Note the smooth, flawless surface and exceptionally fine quality finish. The difference is truly amazing and due entirely to elimination of galvanic corrosion.

A good deal has been said over the years about the problems encountered when using Titanium anodizing racks, especially on color work. It is hoped that this explanation of controlling galvanic corrosion will encourage you to look at your own production line and adapt the concept of sacrificial anodes to it. Now, you can take advantage of long-lasting Titanium racks. You can do so with confidence. Your parts will turn out perfectly, for you will be protecting them from galvanic corrosion, easily and economically.

c 1982 Vulcanium Corporation

ELECTROMOTIVE OR GALVANIC SERIES FOR METALS

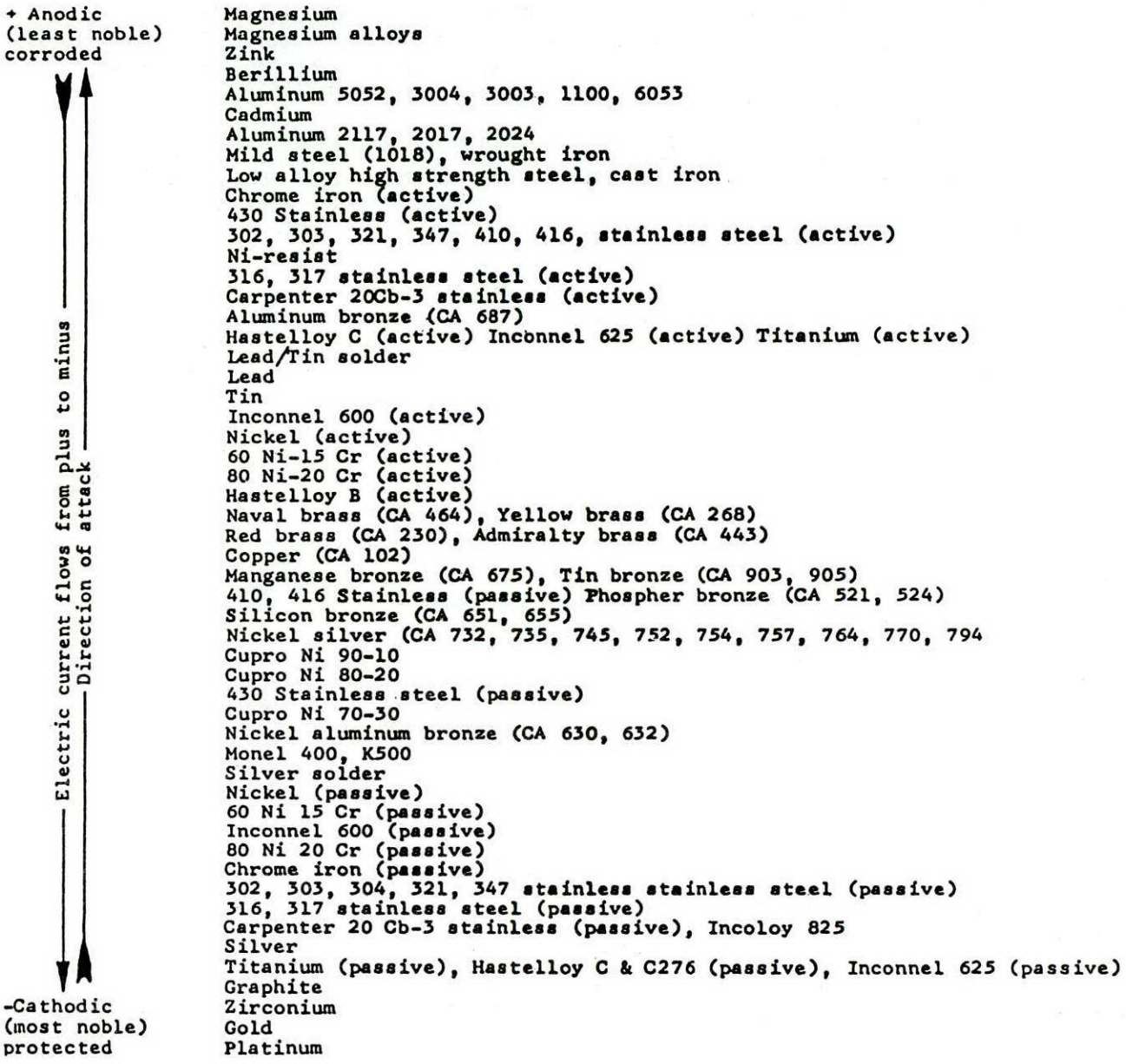

Figure 1 - Galvanic Series Table
Table shows relative degrees of activeness of various metals. The higher on the list, the more active (susceptible to corrosion) the metal. Note the relative positions of aluminum (5th from top, 7th from top) and titanium (5th from bottom).

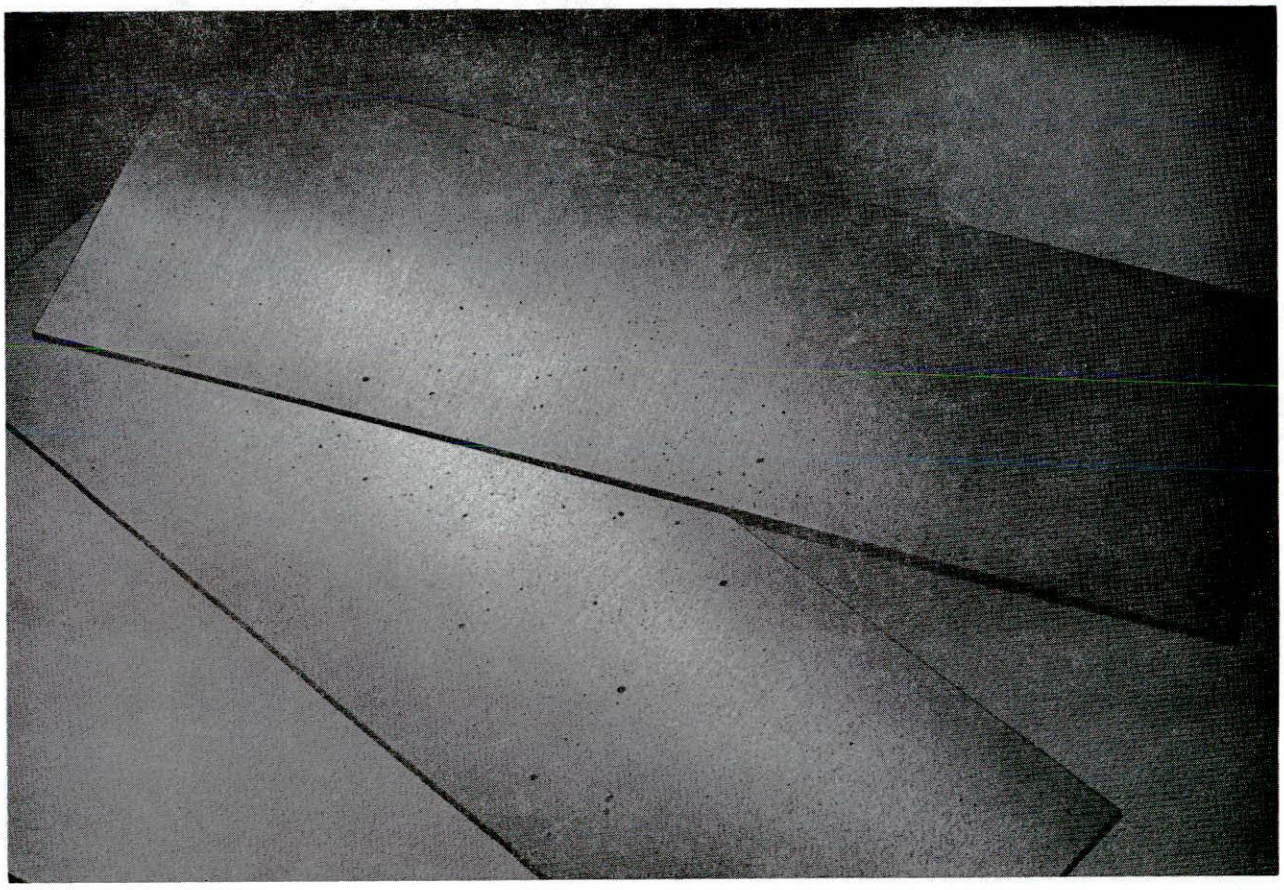

Figure 2 - Black anodized test coupons show the effects of galvanic corrosion. Pitting appears across surface.

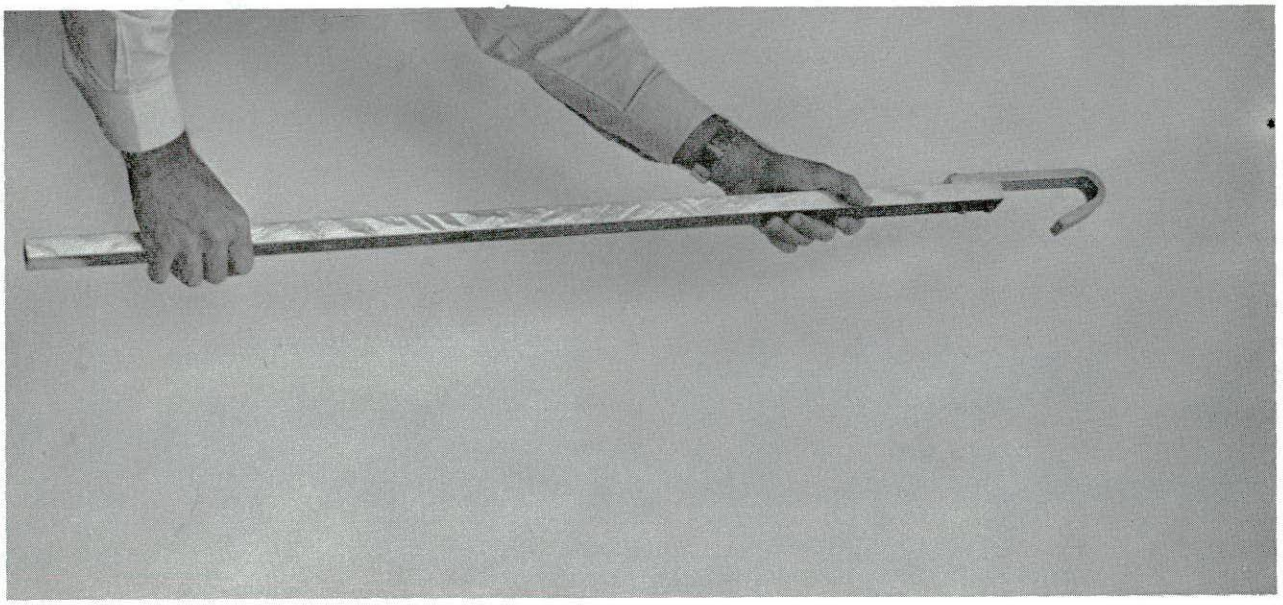

Figure 3 - Sacrificial magnesium anode is used to divert galvanic corrosion attack away from aluminum parts.

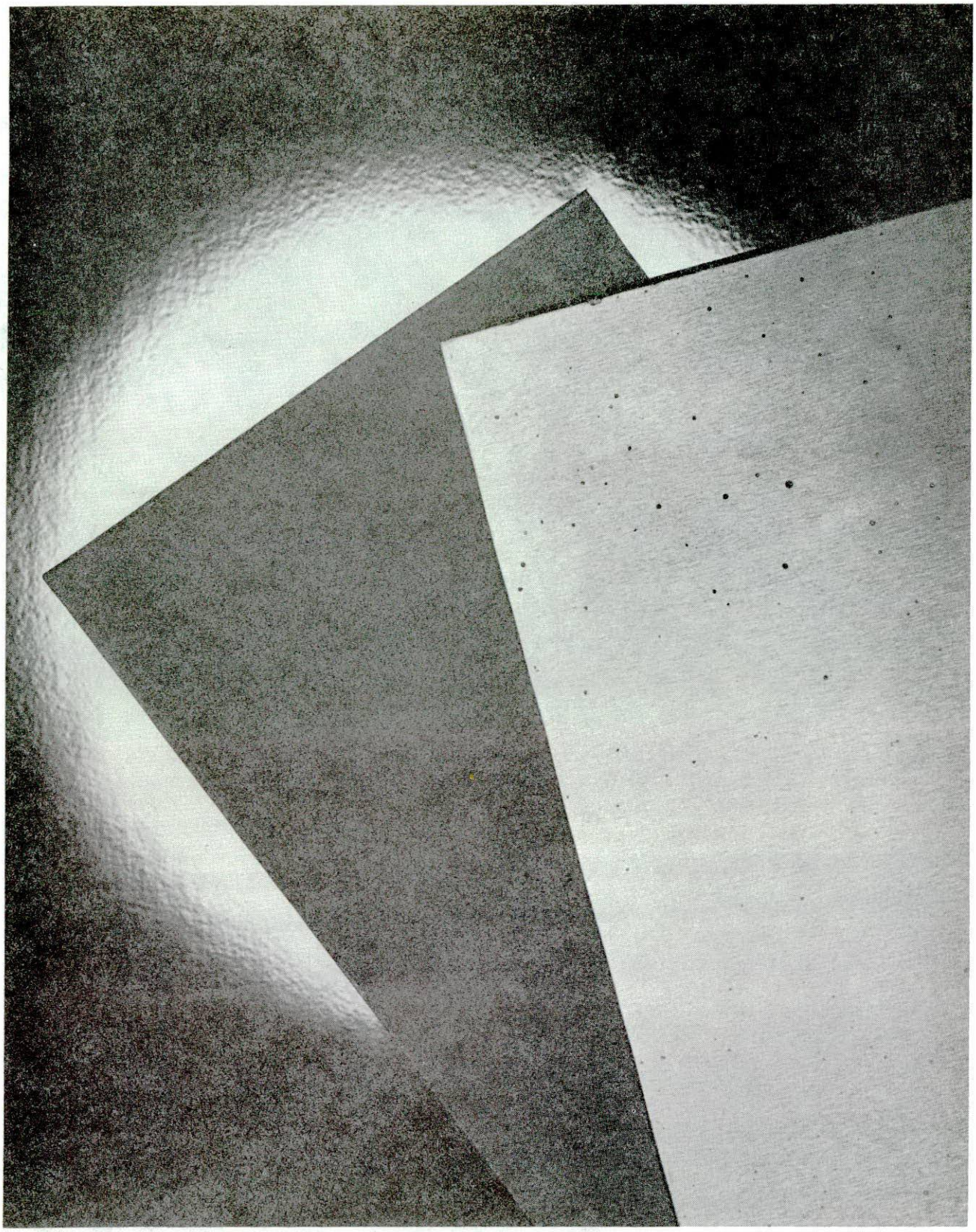

Figure 4 - Test coupon comparison shows pitted part (right) versus part anodized in the same system (left) with a sacrificial nagnesium anode used. Note: different "color" of coupons is due to photographic lighting technique needed to show pitting. Both coupons are black anodized.

L-3

Light Metal Finishing II
Session L

Chromate Conversion Coating Processes of the Conventional and Nonconventional Types for Nonferrous Metals

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CHROMATE CONVERSION COATING PROCESSES OF THE CONVENTIONAL AND NONCONVENTIONAL TYPES FOR NONFERROUS METALS

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Because aluminum is an extremely versatile metal, its domestic and industrial use continues to grow at a steady rate. An additional reason for aluminum's expanding popularity is that aluminum can be pretreated through the same processes that steel and galvanized steel undergo. Thus, aluminum and its alloys can be pretreated for organic finishing through a multi-metal amorphous phosphate or zinc phosphate system. However, the thrust of this talk will be conventional and nonconventional chromate conversion coatings which not only serve to protect nonferrous metals, primarily aluminum and galvanized steel, abainst corrosion but also serve as an excellent bond for the adhesion of paints and adhesives.

The two most common specifications that chromate conversion coatings must meet are: ASTM-B-449 and MIL-C-5541C. The basic cycle needed to achieve standard conversion coatings that conform to these two specifications is given in Figure 1.

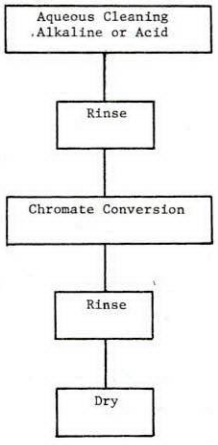

Figure 1

Although it is said that the normal soils found on fabricated aluminum are fairly easy to remove, you must always remember that aluminum and, for the most part, galvanized steel are very reactive and both metals are amphoteric. They react with many soils to form organo-metallic insolubles and their surfaces are easily etched by both soils and cleaners. The quality of an organic finish on aluminum will always be proven by the service it provides. Essentially most finishes are intended for protection, as well as beauty, and in most cases aluminum is used in exterior applications. When properly prepared, aluminum and zinc will accept almost any kind of superimposed finish.

A clean, essentially inert surface is desired or often required to provide optimum adhesion and stability. Production metals are never clean and most finishing techniques possess poor wetting out abilities. This is true of plating and also of powder coatings, high solid paints and, in many cases, waterborne systems. Thus, for proper bonding, cleaning is essential. Any interference, chemical or physical, will weaken the bond between the finish and the nonferrous substrate. Even though such a defect may be initially concealed, the soiled area will cause a deterioration of the finish and eventually attack the substrate itself.

Among the commonly employed cleaning techniques are vapor degreasing and mechanical finishing. Vapor degreasing only removes oils and other petroleum soils. But many soils found on nonferrous metals are fatty, soapy or solid. If vapor degreasing is used for parts with soils other than the petroleum type, degreasing often leaves "baked-on" residues. Abrasive blasting with glass or silica usually 40-80 mesh, can also be used to clean aluminum. Light soils can be removed and this method of surface preparation leaves an anchor profile of about 1 mil in depth.

However, here again, heavily soiled areas must be cleaned prior to blasting if the quality finish is to be expected. In addition, abrasive blasting is not only time consuming and labor intensive, but blasting is also very wasteful of sound metal.

The three parts of every cleaning puzzle are: 1. The metal surface which includes oxide formations. 2. The variety of shop soils. 3. The cleaning method along with the application procedure. A total system approach, cleaner vs. soil, application method vs. surface area to be finished, and mechanical vs. chemical must be considered in order to determine the best production procedure. The largest problem that we encounter is the unlimited combinations of soil in a production shop. Liquid and solid soils are quite different mechanisms. Because of this wide range in the type and the extent of the soils on nonferrous metals, aqueous cleaners are generally the most effective and the most economical.

Keeping in mind the sensitivity of nonferrous metals and the variety of soils encountered, non-etch cleaners are preferred. Non-etch cleaners are of the non-silicated type and possess a mild pH, usually below a pH of 10.0. They are highly buffered and are available for either spray or tank systems. These non-silicated alkaline cleaners generally possess excellent wetting out abilities and can therefore by used at fairly low temperatures. Since these alkaline cleaners are not inhibited, the common operating temperature does not normally exceed 150°F. Aluminum is never found in a nonoxidized state and an added benefit from some of these non-silicated cleaners is their ability to offer light deoxidation which helps to develope a more uniform chromate conversion coating.

Silicated alkaline cleaners are inhibited and therefore can be higher in alkalinity, up to and including a pH of 12.0, and can also be operated at higher temperatures, up to and including 200°F. For soils which require saponification, the higher degree of alkalinity and temperature often makes silicated cleaners more heavy duty. Thus, alkaline cleaners for nonferrous

metals provide a wide choice in the degree of alkalinity and temperature ranges to accomodate the various soils and oxide states of metals.

Under certain conditions, such as ground-in soils which include roll formed nonferrous metals, sanded nonferrous metals and buffed nonferrous metals, cleaning can be improved by providing a controlled attack rate on the substrate. Light etching helps to dislodge ground-in particulate matter and the hydrogen gas formed during etching provides a slight degree of scrubbing action. However, in the case of a quality standard chromate conversion coating, etching of aluminum surfaces is considered poor production practice since it tends to reduce the overall protective qualities of chromate conversion coatings, e.g., salt spray resistance. Since we wish to avoid fairly heavy etching in order to obtain a high degree of corrosion resistance, acidic cleaners should be discussed. Acid cleaners are not commonly used when the primary requirement is soil removal, because they are less effective than most alkaline systems. Acidic cleaners are employed most often to level out or remove surface oxides from nonferrous metals as well as surface smut deposits. Cleaners containing phosphoric acid and fluorides are able to dissolve not only oxide films, but also oxidation products which develope in humid storage conditions or during heat treatment. Their cleaning abilities can be greatly improved through the use of synergistic blends of wetting agents and solvents. The actual etch can be very closely controlled through the use of proper concentrations, temperatures and time cycles. Acidic cleaners designed for additional etching can be based on sulfuric acid and occasionally nitric acid with or without the fluoride assist. These acid cleaners, as a group, develope a micro-etch and like alkaline etch cleaners, they are capable of producing a light satin finish with no-to-very-little alloying smut. Often, this light etch can be used from a quality control standpoint because if the surface is very uniform, all traces of organic soils must have been removed. Under precisely controlled conditions, acidic cleaners can be used with a high degree of success prior to chromate conversion coatings and also adhesive bonding.

Cleaning and surface conditioning or controlled etching develope good-to-excellent adhesion but do little for severe corrosion resistance. The selection of a final finish will depend upon the end-use requirements for the nonferrous metals. Organic finishes derive their physical and chemical properties from the nature of the polymer as well as the molecular weight of the polymer. Likewise, the total finish obtains its long term surface life from the proper conversion coating. Quality finishing demands a conversion coating which provides an inert bridge between the metal and the organic finish. A conversion coating describes the surface film formed by the reaction in which a portion of the base metal is converted to one of the components of the film. As a result, the film becomes an integral part of the metal surface, exhibiting excellent adhesion properties. The most widely employed amorphous chromate conversion coatings are generally applied from acid solutions and they are nonporous, gel-like structures containing hexavalent chrome, trivalent chrome and oxides of the base metal being coated. The fact that these coatings contain high quantities of hexavalent chrome highlights their highly corrosion resistant nature and the leachable hexavalent chrome gives them a self-healing characteristic preventing corrosion when the coating itself is damaged.

Present day conversion coatings for aluminum of the acid chromate type have three major constituents:

1. Acid chromates
2. Acidic etchant
3. Accelerator or complexing agent

The acid chromates are usually chromic acid and sodium or potassium dichromates. These provide the bulk of the coating. The etchants are acidic silicofluorides, fluorides or fluoroborates and provide the biting action into the aluminum surface without vigorous heating of the coating solution. Their extreme activity also overcomes the natural inhibition of the acid chromates on aluminum or other nonferrous surfaces. The last and the smallest constituent, but equal in importance, is the accelerator. These are proprietary and are widely varied in nature, usually metallic inorganic compounds and complexed with trivalent chromium iron. The basic reaction then is the pickling of the nonferrous metal, a resulting pH increase or reduction in acidity at the solution-metal interface with the subsequent coating being developed. Where zinc is being chromated, ferricyanide accelerators are not normally used since they form insoluble zinc salts. The other additional bath modification is the absence of the fluoride ion with other proprietary activators being used. The controls for chromate conversion coatings are listed in Figure 2.

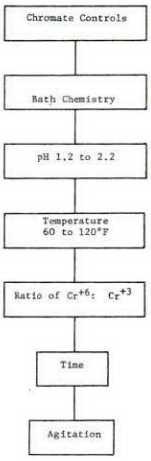

Figure 2

As stated above, the base metal, including various aluminum alloys, must be considered with respect to conditioning of the metal itself and the bath chemistry. Different chromate baths may require a specific pH range for maximum coating deposition and performance. Lighter coatings, such as colorless coatings, offer less enveloping or physical barriers and have less corrosion resistance than the gold, gold iridescent or brownish heavy coatings. For zinc plated work, galvanized steel and cadium plated parts, the pH of the chromate bath is generally low, approximately 1.2. As the pH is lowered, the bath becomes more aggressive on the base metal and the reaction products stay soluble, tending to reduce the coating weight or thickness. Excessively high pHs, beyond suggested operating parameters, reduce the rate of metal attack to a point where the reaction ceases and a powdery coating

of poor quality or no coating forms. Chromating baths can be made more active to accommodate varying metal activities by increasing the temperature. The ratio of hexavalent chrome to trivalent chrome is important and is usually maintained by supplier recommendations which include specialized upkeep compounds along with a bleedoff to eliminate the trivalent chrome contamination buildup which is a natural byproduct of the solution's reaction with the base metals. Time is fairly self explanatory in that longer times generally product heavier coatings. Agitation of the solution, spray washer applications in general, result in fresh solution contacting the work surface.

This speeds up the reaction and provides heavier coatings in a shorter time and perhaps a somewhat more uniform film formation.

Standard conversion coatings can be used with and without paints for a high degree of corrosion protection. Where aluminum always receives a paint film, amorphous chrome phosphate coatings can be substituted. Amorphous chrome phosphate coatings are also produced in acid solutions but these solutions contain phosphoric acid, hexavalent and trivalent chrome, and fluorides. They are the most widely used conversion coatings for aluminum extrusions and are used almost exclusively for architectural exterior products. The resulting film is primarily chrome phosphate and aluminum phosphate and the color is a characteristic green from its reduced chrome content. The conditioning cycle for the aluminum is slightly different and set forth in Figure 3.

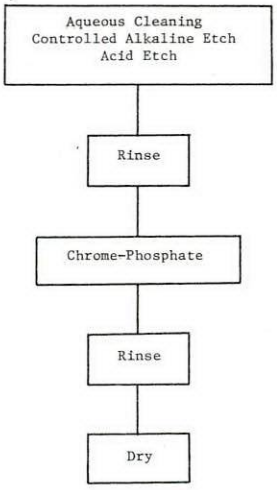

Figure 3

Since aluminum extrusions generally contain a heavy non-uniform oxide skin, some metal removal by controlled alkaline etch cleaning or acid cleaning is necessary, if not highly desirable. The chrome phosphate controls are also slightly different and they are listed in Figure 4.

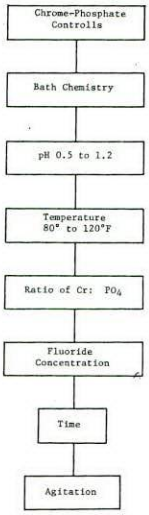

Figure 4

The bath composition may change slightly from one supplier to another. As you can see, the pH of a chrome phosphate solution is generally lower than standard chromates and this allows additional attack or oxide removal in the conversion coating solution itself. Temperature is not critical and the average is 100°F. The ratio of chrome to phosphate is fairly wide providing the pH is correct for the coating weight desired. The fluoride concentration is replenished along with the chrome and phosphate levels. For short treatment times, several seconds, fluoride concentration is increased. If exposure times can be lengthened, the fluoride level can be less. Supplier recommendations should again be closely followed. The fluoride level in the operating solution enables the user to effectively dissolve surface oxides from difficult to coat aluminum extrusions and castings due to the bath's considerable activity which makes initial conditioning treatments somewhat less critical.

Pretreatments, such as the two just discussed, are essentially five sided:

1. They remove soils and surface imperfections
2. They create bonding sites
3. They establish a corrosion barrier
4. They neutralize surface pH changes
5. They do all four functions economically

To help industry combat pollution and keep the high performance benefits of chromates, no-rinse reactive chromates are being used in production. These new active prepaint treatments do not form the troublesome soluble solution byproducts. Therefore, rinsing is not required--no rinsing, no pollution. Exposure time of nonferrous metals to these solutions is not a factor. The solutions are used at ambient temperatures, although they can be heated to facilitate the reaction which takes place during curing. The treatment requires no on-the-job chemical balancing such as adjustment of hexavalent to trivalent chrome and fluoride levels. These reactive no-rinse pretreatments must be applied to clean, waterbreak-free surfaces and again aqueous cleaning is required. Cleaners must be tailored to the soils and also offer

compatability with the particular no-rinse treatment being applied. Similar to chromates and chrome phosphate, the application is generally by spray or flow on, but immersion is also possible. These no-rinse prepaint treatments have multimetal capabilities and when combined with the proper organic finish, they can meet very stringent corrosion requirements such as the AEMA Specifications.

The quality of aluminum finished with an organic coating is a direct reflection of the prepaint system, the paint's characteristics, the operator's experience, and his conscientious observance of the proper processing procedures. In the next several years, industrial finishers will be faced with the need to improve quality, reduce pollution and conserve materials. Chromates are still required in many application because of their high performance properties.

M-1

Electroforming
Session M

Flexible Circuits Manufactured by an Electroforming Process

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FLEXIBLE CIRCUITS MANUFACTURED BY AN ELECTROFORMING PROCESS

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ABSTRACT

Flexible copper circuits called wiring harnesses are becoming more common in consumer products such as automobiles, business machines, and cameras. Flexible circuit manufacture by conventional substractive processes is a well established process. A new production process for making flexible circuits by an additive process is described. Copper circuits are electrodeposited on a metal strip, masked appropriately, and transferred to an adhesive-coated, plastic film in a continuous operation. Equipment and process steps are described.

INTRODUCTION

Processes for manufacturing one- and two-sided flexible circuitry are well known in the industry including a method for electroforming circuits continuously (1-4). This paper describes details for the flexible circuitry manufacturing method not yet disclosed. Process steps for manufacturing one-sided flexible circuitry by this additive process include (1) conditioning a stainless steel belt, (2) applying an ultra-violet light cured resist, (3) electroforming the copper, (4) transferring the circuits to the flexible base and (5) separating the circuits from the stainless steel belt. A solution maintenance system is used in combination with insoluble anodes to replenish the copper in the electroforming solution.

PROCESS DETAILS

Mandrel Preparation

In this process a thin, 0.20 to 0.25 mm (0.008 to 0.010 inch) stainless steel belt is reused many times. After each use it is cleaned to remove the resist remaining from the last operation then polished with a fine abrasive such as 320 grit silicone carbide. The choice of grits depends on the pressure and speed of the mechanical polishing system. High speed and low pressure conditions might require the use of 240 grit or coarser abrasive to develop enough microroughness on the strip to provide the required mechanical bonding of both the resist and electroformed copper. In the printing industry, this is called graining. Figure 1 shows the equipment for cleaning and polishing. The copper must adhere during electroforming, rinsing and drying. It must release after the adhesive is applied and the strip bent during the bonding and separating steps which are shown in Figures 2 and 3, respectively.

Resist Materials

There are many resist materials which can be used for electroforming copper circuits. However, the ultra-violet cured resists were chosen for use because of a short cure time, freedom from pin holes, and adequate adhesion to the grained stainless steel. Figure 4 shows the equipment for applying the UV cure resist. Because the line speed is typically about 2 meters per minute, a relatively inexpensive step and repeat process using mechanical silk screen equipment was used. Continuous printing process could be used but might be much more expensive for the initial equipment costs.

Electroforming Cell

The electroforming cell described previously (3) contained two insoluble anodes with the electrolyte flow introduced between these anodes. Figure 5 is a drawing illustrating the flow paths. The stainless steel strip is held against a contact block of graphite by a partial vacuum. The solution flow entering the two plating zones between the moving strip and the two anodes had some nonuniform turbulence, and low current density zones. These conditions were eliminated by the improved cell design.

Improvements (5) have been made and are illustrated in the drawing shown in Figure 6. A single anode is used with an inlet at one end which directs the flow parallel to the strip movement. This inlet also acts as an electrical shield to prevent deposition of copper at low current density on the stainless steel strip until the full turbulent solution flow impinges on the strip. Thus electroforming is initiated at ideal conditions of high flow and high current density. Solution flows out the end opposite the inlet and returns to the reservoir. A vacuum on the carbon block electrical contact insures a low resistant contact between the stainless steel strip and the carbon block. More details of the cell design are contained in Reference 5.

Solution Maintenance

The electroforming cell uses an insoluble lead-tin (93 Pb-7 Sn) alloy anode to insure that the gap between the surface of the anode and the stainless steel strip (mandrel) remain the same. The use of soluble anodes would cause non-uniform dissolution across the anode because the circuit pattern is seldom if ever uniform in density. Those areas, such as lines parallel to the travel direction, require more current and cause a corresponding larger local current on the anode causing non-uniform electrochemical attack (corrosion).

A solution maintenance problem was introduced with the use of an insoluble anode. However, a system (6) was developed for replenishing the copper using the reaction products of the electrolysis to chemically dissolve scrap copper metal. The reactions are:

Electrolysis

$$CuSO_4 + H_2O + 2e \rightarrow Cu + H_2SO_4 + 1/2\ O_2\ (gas)$$

Chemical Replenishment

$$1/2\ O_2\ (gas) + Cu\ (scrap) + H_2SO_4 \rightarrow CuSO_4 + heat.$$

The reactions are basically simple. The required rate was obtained by contacting scrap copper with both the electrolyte containing the excess acid and the atmosphere in the enclosed cell containing the liberated oxygen. As shown in Figure 7, the electrolyte is sprayed over scrap copper while the oxygen enriched gas is blown through the make-up tank. The driving force for the reaction is the oxygen and the copper metal. The reaction is exothermic and proceeds spontaneously. It is important to maximize the contact between the atmosphere and the scrap copper and a fine spray is used.

If complete immersion of the copper in the electrolyte were used, the reaction rate would be reduced because of the low solubility of oxygen in the electrolyte. Experimental results confirmed these low reaction rates when air saturated electrolyte was pumped over copper. Based on solubilities of oxygen in water at 40 C, (0.00308 g/100 ml water) 8171 liters (2160 gallons) of water are required to contain enough oxygen to dissolve 1 Kg of copper metal.

The system as shown in Figure 7 lends itself to automatic controls. The oxygen enriched gas is passed through the make-up tank continuously while the acid spray is adjusted as needed to maintain the specific gravity or free acid content, whichever is measured.

Rinse Water Effluents

Because the electrolyte system is enclosed in the electroforming cell, the make-up tank and the settling tank, as shown in Figure 7, considerable heat can build up because of the IR drop in the electrolytic zone, even though the gap between the electrodes is small, about 0.318 cm (0.125 inch). This excess heat is removed by evaporative cooling of the electrolyte. The equipment used was a scrubber normally used to remove entrained mist and fumes from exhaust gasses. The air blown through the scrubber removed the heat and evaporated water. The water removal rate was high enough to make room for all the rinse water used to rinse the electroformed circuits. Multiple rinses, as shown in Figure 8, reduce the water volume. This early pilot plant rinse system has been replaced with an improved one. This enclosed system does require that deionized water be used for rinsing to avoid build up of unwanted salts. The electrolyte system and atmosphere is maintained at a slight negative pressure to avoid leakage of mist containing air.

Laminating

Commercially available electrolytic copper foil is made by electroforming and it has excellent mechanical properties. In addition one side typically has a microscopically nodular surface texture to promote adhesion during lamination. The electroformed flexible circuitry made by the process

described in this paper uses a polyester type adhesive with a coupling agent to promote bonding between the copper and the flexible backing. Because the coupling agent was so effective, it was not necessary to electrodeposit a micro-modular surface to promote adhesion. The adhesive is applied to the polyester backing using commercially available coating equipment. A view of this equipment is shown in Figure 9.

When soldered contacts are required to the flexible circuits then a Kapton base and a different adhesive system is required to resist the elevated temperatures. Details of this adhesive system are not available at this time.

Circuit Separation

After the circuits are made and a coating applied to the second side to seal the copper circuits, the individual flexible circuits are separated by a punching operation. Figure 10 shows a punch and die set for separating the circuits.

SUMMARY

The process for electroforming flexible circuitry has been shown to be commercially competitive. Much of the cost advantage for the process is because scrap copper can be dissolved in a completely enclosed system to maintain the electroforming solution composition. The maintenance system depends on oxidizing the scrap copper with excess oxygen generated in the process.

An improved cell design provides a more uniform flow and current density in the electroforming zone.

Effluents needing expensive waste treatments are eliminated by using a completely enclosed copper plating system. The only effluents from the copper plating system are warm air and water vapors. There is an effluent generated when the resist is removed from the stainless steel when the steel strip is cleaned for reuse.

ACKNOWLEDGMENT

The authors wish to thank Koito Seisakasho Company, Ltd., Tokyo for permission to publish this information and for supplying the pictures of the equipment.

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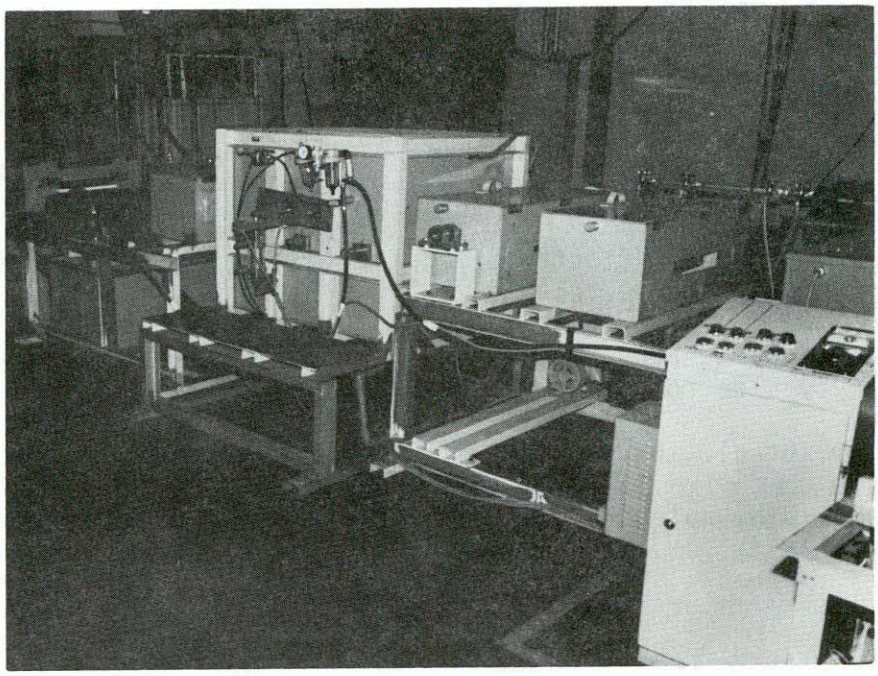

FIGURE 1. CLEANING AND POLISHING EQUIPMENT FOR CONDITIONING THE STAINLESS STEEL BELT

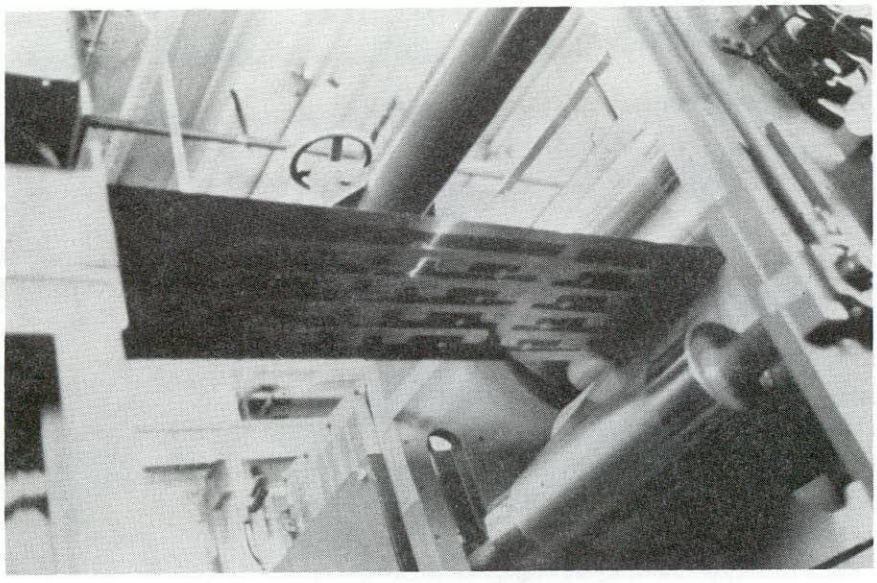

FIGURE 2. BONDING THE PLASTIC FILM TO THE ELECTROFORMED CIRCUITS

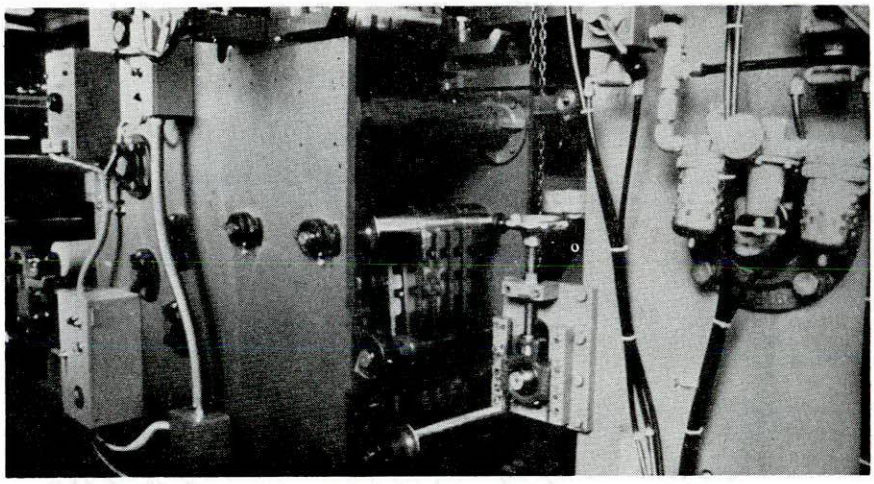

FIGURE 3. SEPARATION OF COPPER CIRCUITS AND PLASTIC FILM FROM STAINLESS STEEL STRIP

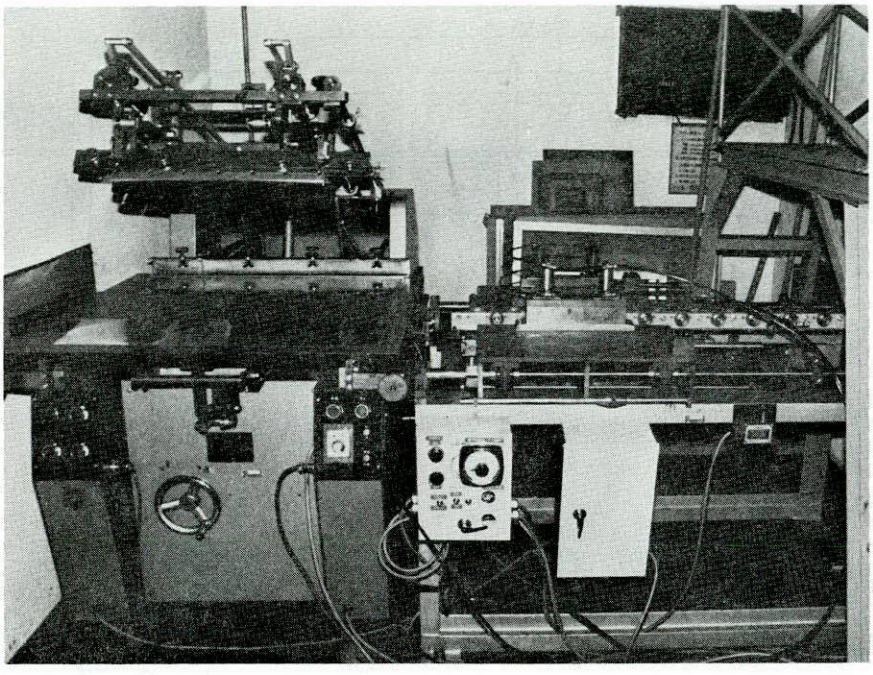

FIGURE 4. SILK SCREEN PRINTER FOR APPLYING UV CURED RESIST

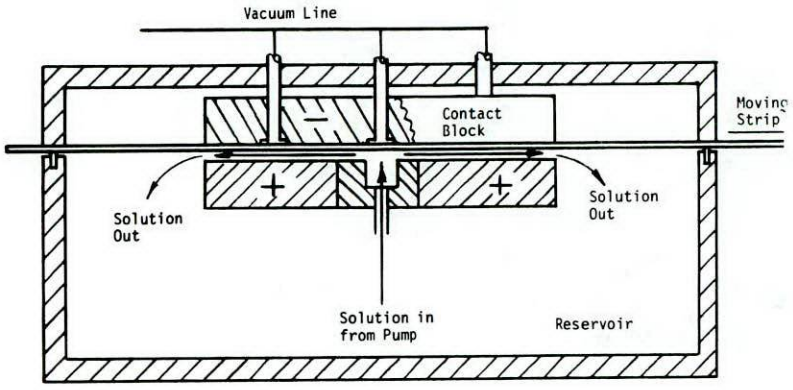

FIGURE 5. DOUBLE ANODE CELL FOR ELECTROFORMING COPPER FLEXIBLE CIRCUITS WITH SOLUTION INTRODUCED BETWEEN THE TWO ANODES

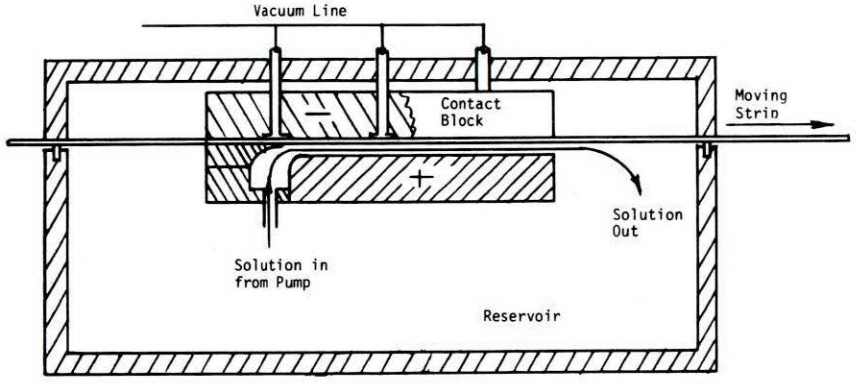

FIGURE 6. SINGLE ANODE CELL WITH SOLUTION INTRODUCED AT UP-STREAM END OF ANODE SYSTEM

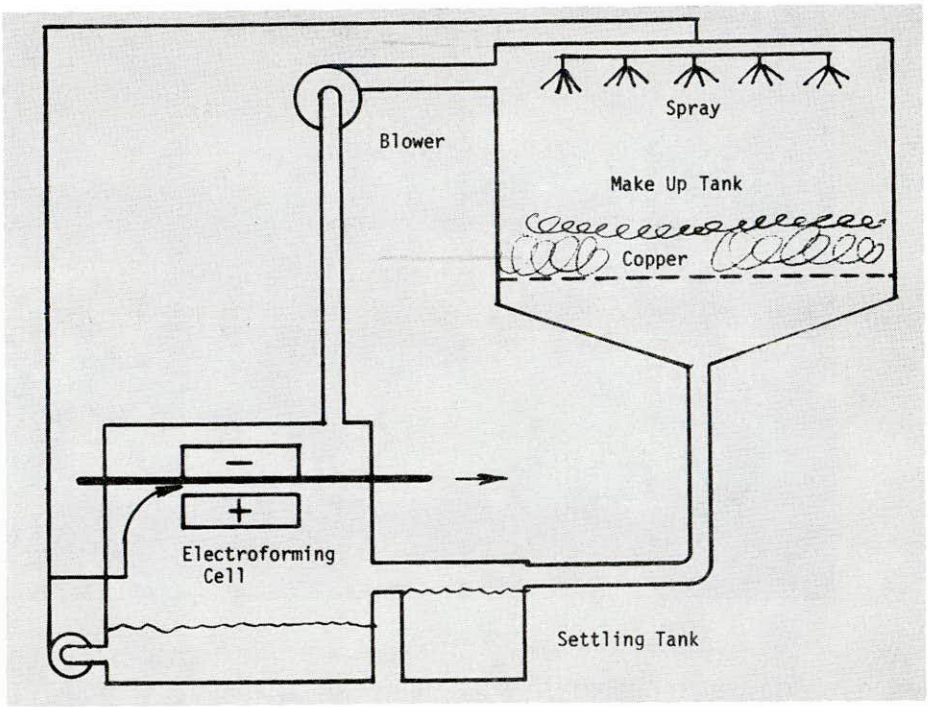

FIGURE 7. SOLUTION MAINTENANCE SYSTEM FOR REPLENISHING COPPER

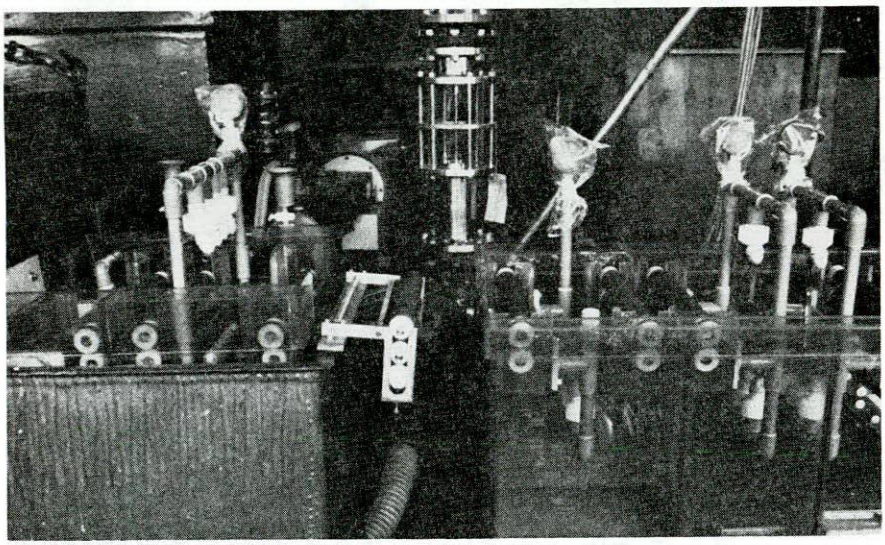

FIGURE 8. MULTIPLE RINSE SYSTEM TO MINIMIZE WATER USAGE

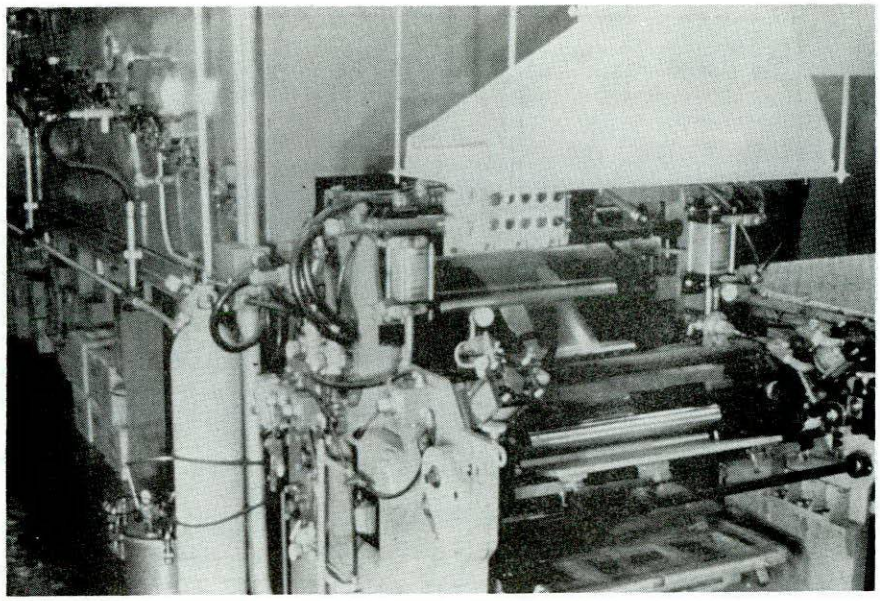

FIGURE 9. COATING EQUIPMENT FOR APPLYING ADHESIVE TO PLASTIC FILM

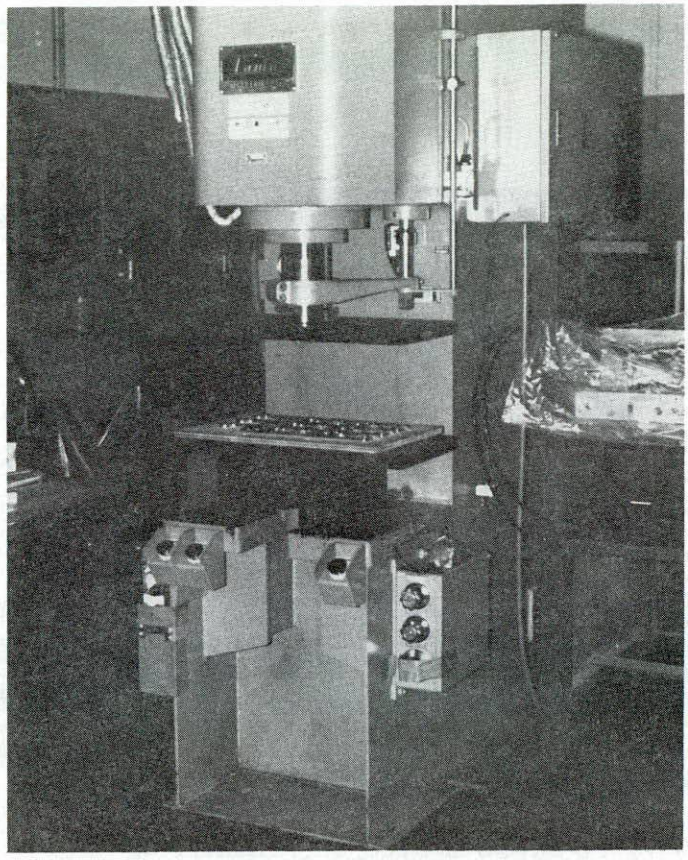

FIGURE 10. PRESS WITH PUNCH AND DIE SET FOR SEPARATING INDIVIDUAL CIRCUITS

M-2

Electroforming Session M

Precious Metal Electroformed Reflectors

David Epner
Cohan-Epner Co.
Brooklyn, NY

PRECIOUS METAL ELECTROFORMED REFLECTORS

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This paper will discuss Cohan-Epner Company's development of techniques and processes required to electroform pure silver optical reflectors.

Cohan-Epner is a small job plating Company in New York (30 employees). It was incorporated in 1913.

The company specializes in unusual and often difficult plating projects, primarily in the precious metals, with many programs first undertaken through an R&D contract.

Such was the case when our company was approached by an overseas manufacturer to develop a pure silver electroformed elliptical reflector.

The manufacturing process was to be designed with techniques that would be appropriate for a high production commercial product.

The reflector design was a rather simple elliptical shape approximately 1/2" wide and 1/2" deep x 3-1/2" long. There were dimensional tolerances on the width, the height and length. These were held to within .001 after machining. The thickness of the silver was .025 to .030.

Because the functional surface of the part was not an imaging optical surface but rather a reflector, the mandrel quality also need not have been that of imaging optics.

Cohan-Epner had had experience some years back with a disposable aluminum mandrel. Combining this knowledge with some recent experience in the fabrication and plating of aluminum extrusions particularly with the surprisingly low cost of tooling the extrusion dies, it was decided to go in that direction with the mandrel, that is, an aluminum extruded mandrel. The extrusion die would have a polished surface in the area of the ellipse to increase the quality of the mandrel. This surface of the mandrel would be polished and buffed prior to plating as well.

The proposed manufacturing approach would build up .025" to .030" of silver on the elliptical surface of a two foot length of extrusion. These two foot lengths would then be sliced into 4" long lengths and machined to final dimensions. Indeed this was the key idea of this fabrication process, that is, to combine electroforming with machining to create the finished product.

To do this the mandrel was designed, of course, to replicate the desired elliptical shape. But more "body" was added to the mandrel than just this elliptical form. These additional surfaces would be kept free of plating.

After the silver ellipse was roughly formed on that functional part of the mandrel, the machinist would use the unplated surfaces of the mandrel for chucking and a datem plane for final dimensioning.

Because of the high purity requirements of the reflector the choice of the silver plating bath was somewhat limited. The bath finally decided upon was made up as follows:

$KAg(CN)_2$	9.45 oz/gal	(2.5 oz/liter)
Free CN	5.00 oz/gal	(1.3 oz/liter)
K_2CO_3	7.5 oz/gal	(2.0 oz/liter)
Current Density:	8 amps/sq. ft.	

The plating rack held 5 bars vertically and was rotated during a 24 hour plating cycle. Periodic reverse was used.

After inspecting for proper silver thickness, a sample of the deposit and of the plating solution was analyzed in our lab for purity. Atomic absorption spectroscopy was used to determine the presence and quantity of metallic impurities.

The plated electroform was then machined to size while still on the mandrel. A hole was bored down the length of the mandrel to speed the dissolving. A 50% hydrochloric acid solution at room temperature was used for dissolving the mandrel. When the silver reflector was freed from the mandrel, it was placed in a conforming buffing fixture and the reflective surface color buffed to a high finish.

The final process step was electro cleaned an enhancement of the silver surface to reflectance of 98% at 700 nm. The measurement of this reflectance value was made on an in-house Beckman DK-2A Spectrophotometer with an Integrating Sphere.

Final cleaning requires that all surfaces in the reflector show no water break when sprayed with an atomized solution of 5 megohm deionized water.

The part is packed in dry nitrogen to maintain reflectance and freedom from impurities during its overseas shipment.

M-3

Electroforming Session M

Electroformed Nickel, "The Modern Tool"

Rich Edwards
Electroformed Nickel Products
Brea, CA

ELECTROFORMED NICKEL, "THE MODERN TOOL"

By Rich Edwards
Electroformed Nickel Products
Brea, California

Introduction

Electroforming provides a precise means of economically replicating a surface or shape of complex geometry. The ability of nickel electroforming to faithfully reproduce large composite forming tools or aircraft/aerospace component parts has been demonstrated with excellent results. This paper will deal with the processes required to produce composite tooling, component parts and the reproduction of holographic, video and fine line images from laser exposed photo resist.

Reinforced Plastic and Advanced Composite Tooling

The aircraft industry today is faced with major changes in manufacturing techniques. In an effort to reduce weight, surfaces that were formerly made of aluminum are now being manufactured of graphite/epoxy or kevlar composites. Composites have replaced up to 40% of aircraft exteriors resulting in a weight reduction of 10%

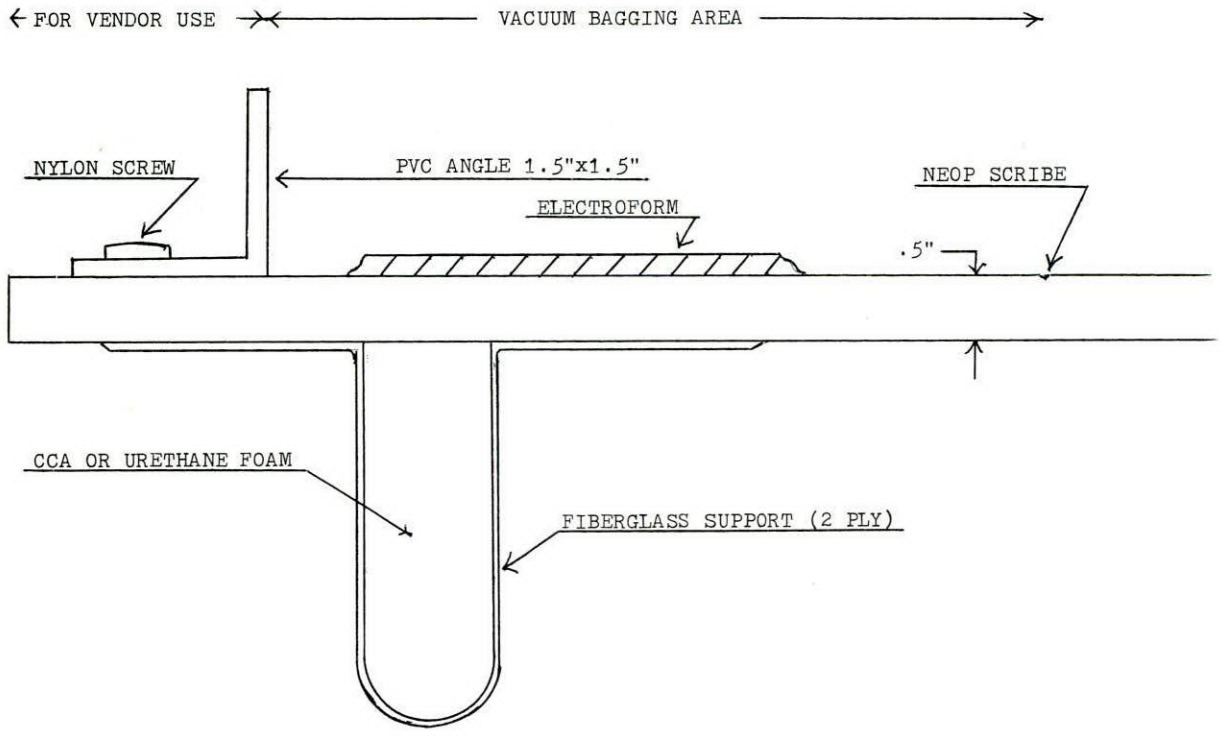
Tool design engineers encouraged to reduce cost, increase production and design hard tooling that will last the full production run of a program have been turning to electroformed nickel tooling. After cycling in an autoclave hundreds of times, electroformed nickel form tools manufactured in the mid 1960's are still maintaining vacuum integrity while producing composite parts.

An electroformed tool begins with the building of a wood model. The model is built to the exact contour of the part including net end of part (NEOP) scribe lines, locating holes and vacuum bagging area. The wood model is painted with a seal coat, sanded and treated with a release wax. (Silicone bearing release agents are not to be used under any circumstances). Next a reinforced plaster reverse is made directly off the wood model. The plaster model, referred to as a splash, is used as an intermediate for development of the plating mandrel.

Most often the mandrel is supplied by the buyer; however, the electroformer must insist that the mandrel is constructed of materials that will remain stable during the electroforming process. The strength designed into the mandrel is dictated by the size and configuration of the electroformed tool. Laminates of epoxy surface coat, epoxy laminating resin and fiberglass up to 1/2" thick are recommended. An egg crate stiffener made of closed cell foam

covered with fiberglass is strategically placed on the back of the laminate to insure that the mandrel will maintain integrity. After the mandrel is separated from the splash, it is inspected for flaws, repaired if necessary, sanded and shipped to the vendor electroformer.

FIBERGLASS REINFORCED PLASTIC (EPOXY) MANDREL



At the electroforming facility the vendor will inspect the mandrel and process for electrodeposition in the following manner.

1. Gently sand entire surface of the mandrel with 400 grit wet or dry silicon carbide paper. This will tend to remove entrapped dust and residual release agent.

2. Attach hangers, electrical connections, weights (if required), PVC angle and shielding.

The PVC angle used at the edge of the tool will serve several purposes. First and most important it will reduce the nodules that grow at an accelerated rate robbing metal and consuming current. It also serves to attach shielding. The PVC angle may be so placed as to define the edge of the tool eliminating the need for subsequent machining.

3. Remove all shielding and PVC angle.

4. Solvent clean mandrel using IPA or acetone.

5. Wash front and back with commercial detergent, rinse well, allow to dry.

6. Mask all surfaces that do not receive electrodeposited metal.

7. Spray surface to be electroformed with colliodal silver paint to form a uniform continuous electrically conductive film. Allow paint to air dry for two hours before testing for conductivity.

8. Conductivity test - attach the common lead of a volt/ohm meter to one electrical connection. With the other lead, touch the silvered surface at various spots. The resistance should be no more than 50 ohms. If resistance is more than 50 ohms, repeat step 7.

9. Remove masking and reattach PVC angle and shielding.

10. Rinse silvered mandrel with D. I. water.

11. Set rectifier at two volts.

12. Submerge mandrel in electroforming tank, increase rectifier amperage to 20 ASF.

13. After one hour lift part from bath to inspect for complete nickel coverage. During this operation a jumper cable should be attached to the cathode to maintain a current flow.

14. When the electroform reaches approximately 50% of its desired thickness, remove it from the tank.

15. Remove nodule growth, grind as required, attach boss blocks and adjust shielding.

16. Activate the exposed surface of the electroform to insure a bond when the mold is returned to the tank.

17. Electroform at 20 ASF until tool reaches its specified thickness.

This completes the electroforming phase of manufacturing a composite form tool.

The last manufacturing operation is to mount the electroform on a stress relieved steel weldment. This is accomplished by attaching the weldment to the electroform before the electroform is released from the mandrel. This is the recommended procedure because it will hold the electroform rigid until the mandrel is removed. Remove the mandrel by forcing wood wedges between the plastic face of the mandrel and the electroform.

With the mandrel removed, the completed tool is inspected for vacuum integrity. Electroforms rarely have vacuum leaks; however, if there is a vacuum leak, it may be corrected with one of several low melting alloys. Before shipping the tool to the buyer, the surface of the tool is sanded with 400 grit wet or dry silicon carbide paper. This operation serves to remove the colliodal silver paint and to give the electroform an improved appearance.

Aircraft/Aerospace Component Parts

When conventional manufacturing methods prove costly or impractical, the electroformer is often called upon to build component parts such as aircraft fuel lines, complex ducting, precision I.D. ball bearing tubes, and abrasion resistant helicopter rotor blade strips.

The routine for making component parts is basically the same as the procedure followed for manufacturing aircraft tooling. A wood or plaster model is made to engineering drawing specifications. This part is called the pattern. From the pattern a two part mold is made. This mold, most often made of fiberglass reinforced plastic, has flanges for clamping and locating pins to register both sides of the mold. This part is referred to as the master.

The master is used to generate the plating mandrel which may be fabricated of epoxy, wax or plaster. The most common material used today is a special wash out plaster. Plaster mandrels must be sanded to remove mold flash lines and the surface must be sealed. Several coats of sealer are used but not so much as to influence the dimensions.

Electroforming Procedure

1. Wash mandrel thoroughly with a commercial detergent
2. Rinse well with D. I. water
3. Air Dry
4. Spray paint with colliodal silver paint.
5. Allow to dry 24 hours. Test for conductivity.
6. Attach shielding if required.
7. Rinse well, D. I. water.
8. Electroform at 20 A.S.F. for predetermined length of time.
9. Remove from bath, check thickness, grind, mask, or adjust shielding as required.

NOTE: Step 9 may have to be repeated several times.

10. Activate nickel to insure bond.

11. Electroform to final thickness.

12. Attach mounting flanges or supports using silver solder.

13. Trim and sand to final dimensions.

14. Inspect to specifications, package and ship.

Replication of Laser Exposed Photoresist Images

Successful replicating of holographic images from photoresist surfaces requires a specialized technology. The photoresist must be applied in a clean room to avoid particulate contamination.

To manufacture a master for the electroforming process, an optical quality glass substrate is coated with an adhesion promoter followed by positive photoresist. The coated glass is mounted in a complex computer controlled laser cutting machine. By exposing the photoresist with ultraviolet light from the laser, an image is encoded on the photoresist. The encoded glass/photoresist master is developed to remove the exposed portions of photoresist, and then forwarded to the electroformer for permanent metal replication. The laser generated image has a depth of 1/4 to 1/2 micron. Holographic images are a series of lines containing variations in depth and width, video discs are a series of billions of tiny pitts. At the electroforming facility, which must be a reasonably clean facility, the glass is mounted in a fixture that has been fabricated to include edge guards and electrical connections.

Electroforming Process

1. Clean photoresist using proprietary cleaners, conditioners and procedures. Do not use solvents, solvents disolve photoresist.

2. Render entire surface conductive using reduced silver technique. Proprietary silvering solutions that will not damage photoresist surface should be used.

3. Preplate in a closely controlled low stess, low temperature electrolyte to avoid images distortion.

4. Plate at 20 A.S.F. to desired thickness (0.040")

5. Remove from bath, carefully seperate electroform from fixture. The photoresist will come off the glass sticking to the electroform.

6. Strip photoresist with proprietary stripper, acetone, M.E.K., or 4-6 oz/gal caustic soda. Extra caution, do not touch, the fine surface of the electroform can be scratched by a cottonball.

7. Mount master electroform in electroforming fixture.

8. Clean and passivate silver faced electroform.

9. Electroform at 20 A.S.F. to desired thickness (0.040").

10. Remove from bath, carefully seperate electroform (matrix) from the master. At this time, temporarily submerge the matrix in a tray of D.I. water. This will protect the matrix while the master is being prepared for storage. Rinse master with D.I. water, blow dry (do not touch), cover with protective coating.

11. Mount matrix in electroforming fixture.

12. Clean and passivate.

13. Electroform at 20 A.S.F. to desired thickness (0.004" - 0.015").

14. Carefully seperate electroform (stamper) from the matrix.

15. Rinse all parts with D.I. Water.

16. Blow dry and protective coat all image surfaces.

Considerable research and development in this process has yielded consistant results with excellent quality. This is not a simple process and minor variations in process, chemistry, environment, water quality and photoresist will yield inconsistant quality.

Conclusions

The advantages of electroforming with nickel has proven that it is a valuable method of producing high quality permanent tooling. When properly designed, electroforming is an economical method for manufacturing hard tooling and/or complex component parts.

Acknowledgements

The author would like to take this opportunity to thank the following individuals for their contributions to this paper. Rick Schneck, Consulting Engineer; Tom Henderson, Electroforms, Inc.; Carol Fite, Executive Secretary.

M-4

Electroforming
Session M

Electroformed Boiling Surfaces

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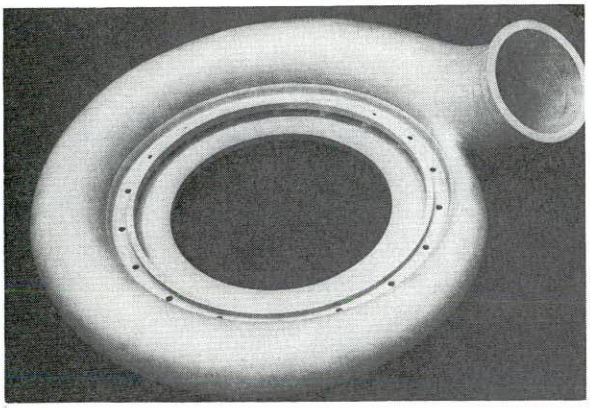
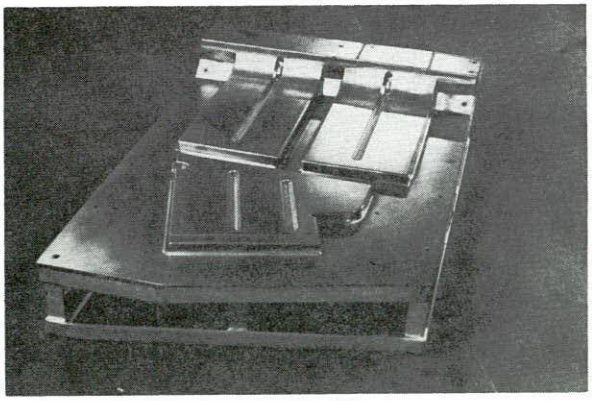


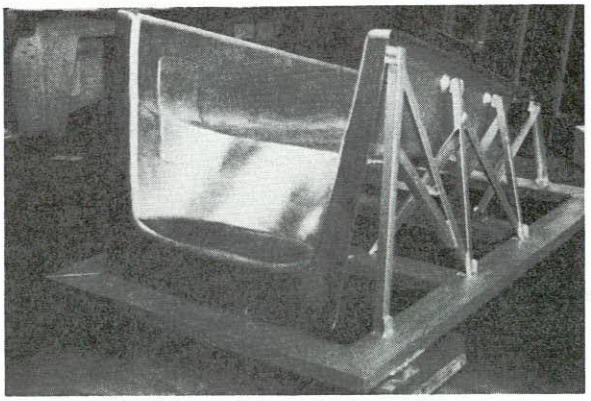
Electroformed nickel duct with mounting ring and stiffeners brazed in place.



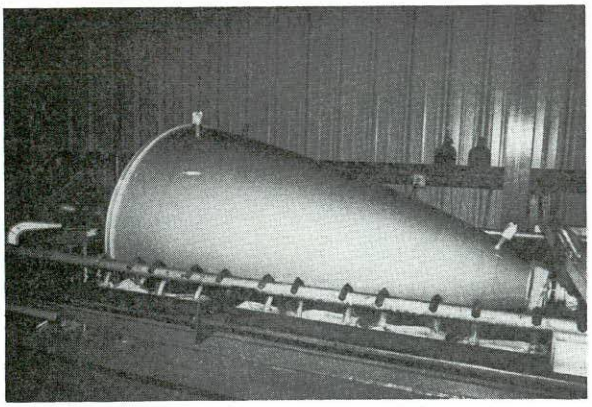
Tri-vent duct includes grown on flanges.
Photos by Electroforms, Inc.



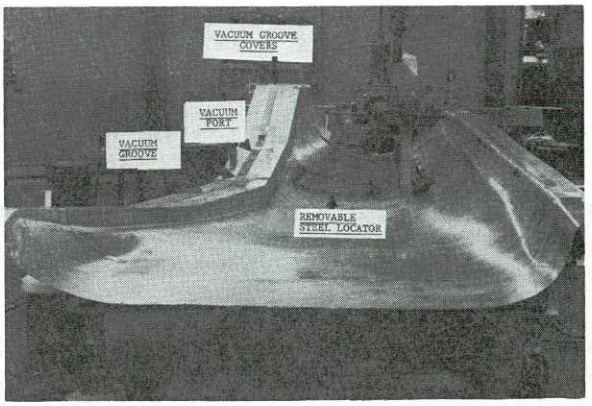
Electroformed nickel tool will form composite parts to inside mold line.



Completed nickel form tool with welded support structure.
Photos by Mafix, Inc.



In process nose cone form tool includes encapsulated vacuum ports.



Electroformed nickel facing sheet with removable locator.

ELECTROFORMED BOILING SURFACES

Clarence Albertson, George Nichols and John Rasmussen

Roy C. Ingersoll Research Center, Borg-Warner Corporation

Des Plaines, Illinois

Introduction

I would like to describe the development of electroformed high heat flux boiling surfaces, using an aqueous copper sulfate-sulfuric acid plating bath. We will describe what a high heat flux boiling surface is, show the various types of boiling surfaces, and review process work on electroformed copper surfaces conducted in our laboratory.

Boiling Surfaces

Vapor-filled, interconnected, re-entrant cavities on a heated surface promote bubble nucleation and boiling, with a smaller temperature drop, compared to plain and finned surfaces. Fig. 1 illustrates re-entrant cavities of this type. The boiling performance of a surface is related to the number, size and shape of these cavities, thermal conductivity of the coating material, surface tension, heat of vaporization, viscosity and vapor pressure of the boiling fluid[1]. A high flux boiling surface is defined as a surface which will transfer more than 1000 Btu/hr/ft^2/^{o}F. One of the first high flux boiling surfaces was a 0.007" thick, 60% porous, matrix of copper particles brazed on the OD of a tube[2] (see Fig. 1). More efficient heat exchangers for petroleum refineries were made of this tubing, starting about 1967. Another paper[3] reported that flooded evaporators for centrifugal refrigeration equipment can be made with about half the length of high flux surfaced tubes compared to finned tubes, due to the higher boiling efficiency of the porous surface.

Types of High Flux Boiling Surfaces

Porous, high flux boiling surfaces can be classified as metallurgically-bonded metal powders[4,5], mechanically formed surfaces[6,7] and electroformed surfaces[8,9,10,11,12,13,14]. An example of each type is shown in Fig. 1. Fig. 2 shows a variety of boiling surfaces made by electroplating, composite plating, electroforming around an open cell sponge, and electroless coating of magnetically-aligned iron particles.

Rolled Copper Nodule High Flux Boiling Surface

Exploratory tests were run to see if adherent, copper-nodule surfaces could be plated which would enhance boiling heat transfer. A commercial plating bath[15] was used containing 225 g/L hydrated copper sulfate, 56 g/L sulfuric acid and additives. Copper tubes 3/4" OD x 7-1/2" long were alkali cleaned, uniformly etched in 50% nitric acid, air dried, sanded with 60 grit emery cloth and plated at room temperature in a verticle position, in a 2" ID copper tube anode plating cell. Dendrites were grown at high current density and then reinforced and bridged by continuing to plate at normal current density. Plating conditions, which yielded a dense, adherent, porous, nodular coating were:

Tube No. Buildup		Dendrite Growth
1	15 sec at 100 A	3/4 hr at 5 A
2	12 sec at 100 A	1/2 hr at 3 A

Hydrogen gas evolved strongly from the cathode during the dendrite growth step. Nodule heights were not uniform, producing a rough surface. Tube 1 was resistant to light abrasion, but Tube 2 lost some copper particles when abraided. The plated tubes were rolled between the three rolls of a sheet metal bender to partially compact the nodules, give the tubes a more uniform OD, and improve abrasion resistance by work hardening. The rolled coating was about 0.005" thick on Tube 2, shown in Fig. 3.

Tube 2, containing a tubular heating element, was tested for heat transfer in a pool of R-12 refrigerant. It caused vigorous boiling of R-12 with only a $2^{o}F$ temperature difference between R-12 liquid and the copper tube, at a heat input of 10,000 Btu/hr/ft^2 of surface. For comparison, a commercial 3/4 in. OD tube with 26 fins/in. required a $7^{o}F$ temperature rise to dissipate the same heat flux (Fig. 4). Looking at Fig. 4 another way, for a $2^{o}F$ temperature rise, the finned tube transferred 700 Btu compared to 10,000 Btu for Tube 2. About 14 times more heat was transferred by electroformed Tube 2. In a life test, Tube 2 maintained its high heat transfer for 15,000 hrs of boiling in R-12 containing 1/2% lubricating oil, and remained in good mechanical condition. This exploratory work demonstrated that a dendritic copper nodule surface can promote boiling heat transfer at high heat flux.

Factors in Process Optimization

It was decided to optimize this electroforming process to economically produce refrigeration tubing for flooded evaporators. The tube surface must be abrasion-resistant for insertion through header holes, stiff enough not to sag between supports, and fatigue resistant to the bumping vibration of boiling liquid. Work hardened, 3/4-in. OD copper tubes up to 20-ft long are used commercially. An inexpensive plating process is needed to plate the tube with

a porous, abrasion-resistant boiling surface. Effective pore cavity diameter is over 2 mils for R-11, and 1/2 mil for R-12 and R-22[3]. Quality control is needed to achieve consistent pore size and structure for high heat transfer, and to meet abrasion and fatigue requirements.

Plating Setup

A plating fixture (Fig. 5) was built to rotate the tube in a horizontal position to allow scale-up of tube length, more even evolution of hydrogen, uniform plating around the tube and bath agitation. Heavy wall 3/4-in. OD tubes about 8" long of Type 122 copper alloy, specified by our heat transfer group, were used for better boiling heat transfer tests. Solid commercial phos-copper anode sheets 5 in. x 8 in. were positioned on each side of the tube in a rectangular plastic tank. Frictional electric contact was made between the end of the tube and a copper plate. The tube was rotated at 11 rpm unless otherwise specified, with an "O" ring belt and pulley. A 15 V, 100 A, DC power supply was used.

Experimental Work

Runs were made to evaluate the performance of the rotating tube fixture and to learn how electrolyte ingredients influence the structure of the plated coating. Eight-inch tubes were cleaned, acid etched, sanded with emery cloth and plated at room temperature, with one-inch anode to tube spacings. Dendrites were grown at high current density and then built up for 1-hr at 5 A in the same electrolyte used for growing the dendrites. Test data are given in Table I.

Uniform, densely-packed nodule or hole coatings plated on the tubes. The fixture performed satisifactorily and was used for continuing work. Dendrites were grown for about 1 minute at 100 A; however, anode polarization caused current to drop in several of the runs in Table I. Anodes were immersed about 3-1/2 in. deep in these runs. Anode area was insufficient to prevent polarization. Anode polarization was avoided, after these runs, by using a tank deep enough to fully submerge the 5-in. deep anodes.

Dendrite Growth Conditions

Exploratory tests indicated that dense, adherent nodular coatings would be built up on 8-in. tubes when dendrites were grown at 30 A to 100 A for at least 4000 A-sec in a (210-75)* plating bath. Poorly developed nodular coatings formed on smaller dendrites grown with less than 4000 A-sec of current. A couple of dendrite growth and buildup cycles yielded a dense, nodular coating structure, for example, 60 sec at 40-A growth, 3/4-hr at 5-A buildup, 45 sec at 40-A growth, 3/4-hr at 5-A buildup.

*(210-75) 210 g/L copper sulfate and 75 g/L sulfuric acid.

Tube Rotation Rate

The effect of tube rpm on coating structure was observed in a (210-75) bath. Dendrite structure was unaffected from 7 to 11 rpm. At increasing speeds, from 16 to 56 rpm, dendrite tips were progressively broken off, producing a more dense, less porous coating after the buildup step. Subsequent work was done at 11 rpm which is about the highest speed the fragile dendrites can withstand.

Bath Composition Effects

In the first set of runs, copper sulfate concentration was held constant at 210 g/L and acid concentration varied from 25 to 100 g/L. In the second set, acid concentration was constant at 75 g/L and copper sulfate varied from 120 to 240 g/L. One extreme electrolyte contained 92.5 g/L copper sulfate and 341 g/L sulfuric acid. The results are summarized in Table 1.

In the first four runs at 210 g/L, copper sulfate, dendritic nodular surfaces formed in all cases. Coating adhesion was good in all but the highest acid concentration run. Although anode polarization occurred in the four runs, good, dense, nodular deposits were formed.

In the next four runs at 75 g/L sulfuric acid, good nodular deposits formed at copper sulfate concentrations of 200 and 240 g/L. At concentrations of 160 g/L copper sulfate and lower, the character of the plated coating changed significantly. A smoother, abrasion-resistant, porous coating formed instead of the more fragile rougher nodular dendrite coatings. This new structure was called a honeycomb coating (see Fig. 6). It was decided to optimize this honeycomb structure for boiling heat transfer because it does not require a rolling step to improve abrasion resistance.

Coating density was estimated by dividing the g/cm^2 columns in Table 1 by the corresponding thickness. Coating density ranged from 1.7 g/cc for Tube 17 to 5.2 g/cc for Tube 13. The density of copper metal is 8.9 g/cc. Highly porous surfaces were produced.

Holes and spaces between nodules varied from 0.5 to 8 mils in diameter. Electrolyte composition, dendrite growth current and the amount of buildup all influence the size of surface holes or pores.

Surface Conditioning

An automatible, reproducible surface conditioning method is desired for a production process. Sand blasting with a controlled abrasive and knurling were evaluated for making a reproducible starting surface. Tubes were cleaned in an alkaline cleaner and then either sand blasted with silicon carbide particles or knurled. The tubes were etched in a dilute-nitric-sulfuric acid

bath, rinsed and plated in a (160-60) plating bath. Dendrites were grown for 1 min. at 500 A/ft^2 and built up for 1 hr at 40 A/ft^2 into a honeycomb coating[12]. Boiling heat transfer data are tabulated:

Tube Treatment	Btu/ft^2/^{o}F in R-12
100 mesh SiC	1192
60 mesh SiC	1150
30 mesh SiC	1100
240 Tpi Knurl	1122

The honeycomb structure forms on the knurled ridges, with a beautifully uniform pore structure, approximately 57,600 pores/in^2. On sand blasted surfaces, the number of pores increased as grit size decreased.

Effect of Bath Temperature

Eight-inch tubes, sand blasted with 60-mesh silicon carbide and acid etched were plated from 10° to 40°C at dendrite growth currents of 50 to 80 A in a (170-60) plating bath with 1-hr buildup at 5 A to learn which plating conditions give better honeycomb coatings. Test data are given in Table 2. More adherent coatings were produced by growing the dendrites at 80 A for 1 min. dendrite growth, compared to 50 A for 2 min. The coating formed at 10° had smaller visible pores than 25° and 40° coatings. Coating structure changed from predominately honeycomb to predominately nodular as temperature increased to 40°C. Coating adhesion decreased as temperature increased. Based on these results, bath temperature was held between 20° and 25°C and higher dendrite growing current densities were used in subsequent work.

Effect of Process Conditions on Structure & Heat Transfer

Boiling heat transfer tests and coating inspection were used to evaluate the electrolyte composition and plating conditions which gave good performance in the honeycomb coating range, i.e. copper sulfate content, less than 180 g/L in the plating bath. Eight-inch tubes were cleaned, sand blasted with 100-mesh silicon carbide, etched for about 15 seconds in a solution containing 12% nitric acid and 25% sulfuric acid, rinsed and plated at 11 rpm at 23°C. Data are given in Table 3.

Baths containing from 160 to 120 g/L copper sulfate and 25 to 75 g/L sulfuric acid all yielded fair to good honeycomb coatings. Adhesion was generally good, excepting Tubes 131 and 144, which appeared to have insufficient buildup, only 1/2 hr at 5 A. Tube 133 also had poor adhesion. Visual hole diameter in the honeycomb surfaces was about 0.002 in. Tubes with well-formed, adherent coatings were generally made at higher dendrite forming A-sec. conditions followed by 1-hr buildup at 5 A. The best looking tubes, Nos. 118 and 156, were made in a (140-50) plating bath.

Dendrites were grown on Tube 156 by slowly cycling the current manually from 30 to 100 A for a 1-min. period. For Tube 118, the dendrite growth current was gradually reduced from 95 to 70 A at 50 to 60 sec. A scanning electron microscope photo of Tube 156 (Fig. 7) shows the fine structure in the coating.

Tubes 118 and 156 were evaluated for heat transfer in R-12 and R-11 in the pool boiling rig; see data in Table 4. These tubes have very good boiling heat transfer. Temperature differences of less than $1^{o}F$ were required to transfer 1000 Btu/hr[1]/ft[2] in R-12 and less thant $2^{o}F$ difference to transfer 10,000 Btu/hr/ft[2]. Refrigerant 11 does not transfer heat as well as R-12. Temperature differences of 5° to $7^{o}F$ were required to obtain 10,000 Btu/hr/ft[2] in R-11 with these boiling surfaces. Also, Table 4 shows that the heat transfer of these surfaces compares favorably with that of commercial, brazed granule boiling surfaces[4].

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Table 1

Effect of Bath Composition on Coating Properties

Tube No.	Electrolyte Composition (g/l) $CuSO_4.5H_2O$	H_2SO_4	Dendrite Formation	Tube Length (cm)	Weight Gain(g)	Coating Thickness (cm)	Coating Weight (g/cm^2)	Coating Properties
13	210	25	40 sec @ 95-100 A 20 sec. @ 95-55 A	20.9	5.64	.0085	.044	Dendrites vary in height from short to very tall. Uniform plating all over. Fairly well developed - looks good.
9	210	52.5	1 min. @ 100A	20.95	5.55	.024	.043	Good nodule development at each end, but light in the middle.
16	210	75	40 sec @ 95-100A 20 sec @ 95-30A	20.7	5.60	.010	.0445	Good combination of holes and dendrites.
17	210	100	40 sec @ 95-100A 20 sec @ 95-30A	20.6	4.50	.021	.036	Rather heavy deposit of well developed dendrites (nodules) but adhesion is zero.
21	240	75	25 sec @ 95-100A 35 sec @ 95-30A	20.6	3.92	.011	.0315	Fairly uniform dendrite formation and development. Slightly heavier plating at one end with poor adhesion at that end.
23	200	75	30 sec @ 95-100A 30 sec @ 95-25A	20.6	4.51	.008	.036	Small diameter holes in dendrite coating. Light plating uniformly distributed over entire surface.
25	160	75	1 min @ 95-100A	20.6	5.20	.016	.041	Uniform plating all over. Holes are prominent.
27	120	75	1 min. @ 95-100A	20.5	4.19	.0075	.034	Holes predominate over dendrites. Plating is uniform.
11	92.5	343	20 sec @ 95A 20 sec @ 90-60A	20.85	4.66	.032	.037	Fairly uniform hole development. Not nodular. Holes are small in diametermeter (ca. 2.2 mil diameter) and uniform in size.

Table 2

Effect of Bath Temperature on Coating Structure

Tube No.	Temp. °C	Dendrite Growth Current-Time	Coating Properties			
			Adhesion	Microstructure	Uniformity	Pore Size, in.
15	10	80A-1 min.	Good	Some dendrites Honeycomb, fine porosity	Good	0.0002-0.001
16	10	50A-2 min.	Fair	Honeycomb with some columnar on the top of the honeycomb	Good	
4	25	80A-1 min.	Good	Honeycomb	Good	0.001-0.003
12	25	50A-2 min.	Poor	Honeycomb and columnar	Poor	
6	40	80A-1 min.	Fair	Mostly columnar, some honeycomb	Good	
14	40	50A-2 min.	Poor	Mostly columnar	Poor	

Table 3

Effect of Process Conditions on Honeycomb Coatings

Tube No.	Electrolyte Composition (g/L) $CuSO_4.5H_2O$	H_2SO_4	Dendrite Formation Conditions in Seconds @ Amperes	Buildup in Hrs @ 5A	Coating Wgt. (g)	Coating Thick. (in.)	Structure Development	Adhesion	Average Hole Dia(in)	No. of Holes per in^2
108	160	75	50 @ 95-100+ 10 @ 95-35	1	6.08	.0069	Fair	Good	.0020	-
109	160	75	50 @ 95-100+ 10 @ 95-30	1	6.18	.0077	Fair	Good	.0020	-
118	140	50	50 @ 95-100+ 10 @ 95-70	1	5.18	.0085	Good	Good	.00276	55,000
131	140	25	60 @ 80	1/2	-	-	Good	Bad	.0026	
132	140	25	30 @ 85	1	5.03	.0054	Poor	Good	.0014	52,000
133	120	75	40 @ 100	1	5.76	.0079	Good	Bad	.0020	
144	120	75	40 @ 70	1/2	-	-	Poor	Bad		
150	120	75	40 @ 70	1	4.28	.0049	Fair	Good		
156	140	50	60 @ 20-100 Fluctuating	1	5.64	.0061	Good	Good		
157	140	50	60 @ 20-100 Fluctuating	1	6.31	.0061	Good	Good		

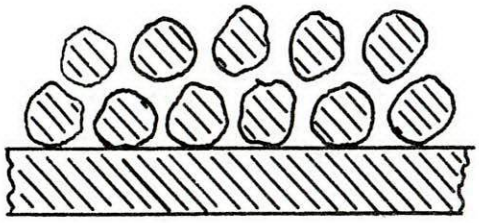
Table 4

Pool Boiling Heat Transfer Data

Heat Flux Density Btu/hr/ft^2	T(^{o}F) for Various Tubes					
	Tube 118		Tube 156		Brazed Granule Tube	
	R-12	R-11	R-12	R-11	R-12	R-11
1,490	0.65	--	0.68	--		
1,785	0.72	--	0.70	--		
2,980	0.95	--	0.81	4.58	0.53	3.08
4,470	1.15	--	0.90	--	0.82	3.42
5,960	1.30	4.66	0.98	4.86	1.06	3.86
8,940	1.50	5.54	1.08	4.74	1.43	4.44
11,900	1.70	6.36	1.25	4.91	1.91	5.01
14,900	1.90	7.29	1.50	5.39	2.44	5.69

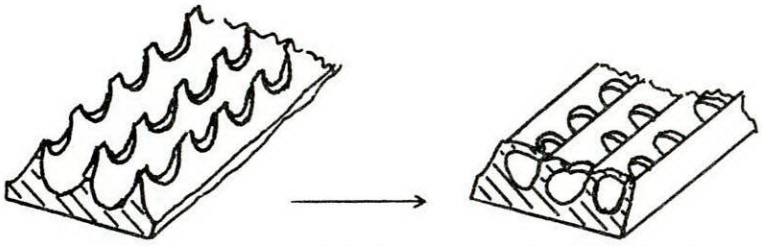
FIGURE 1

TYPES OF BOILING SURFACES



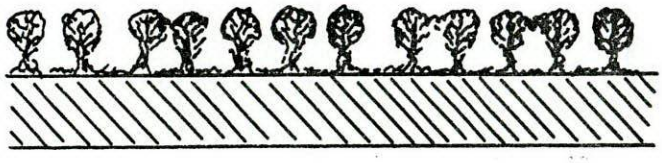
METALLURGICALLY BONDED

Brazed Powder 4



MECHANICALLY FORMED

Bent Fins 6

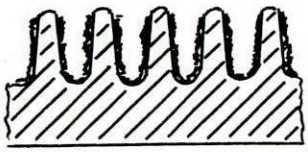


ELECTROFORMED

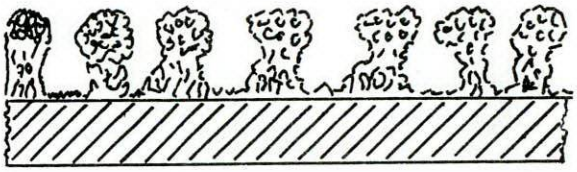
Rolled Dendrites 11

FIGURE 2

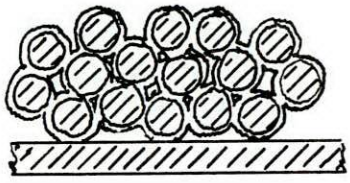
ELECTROFORMED BOILING SURFACES



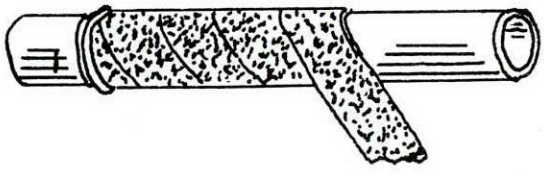
Porous Copper 13



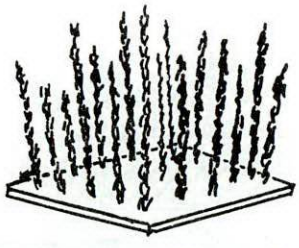
Honeycomb 12



Metal Particles
Plated Together 8

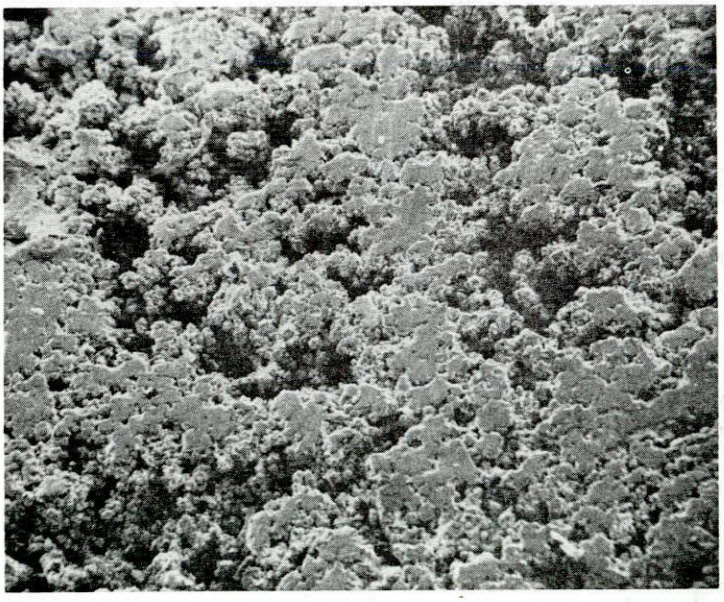


Plated Open-Pore
Sponge 10



Electroless Bonded
Magnet Aligned
Iron Powder 14

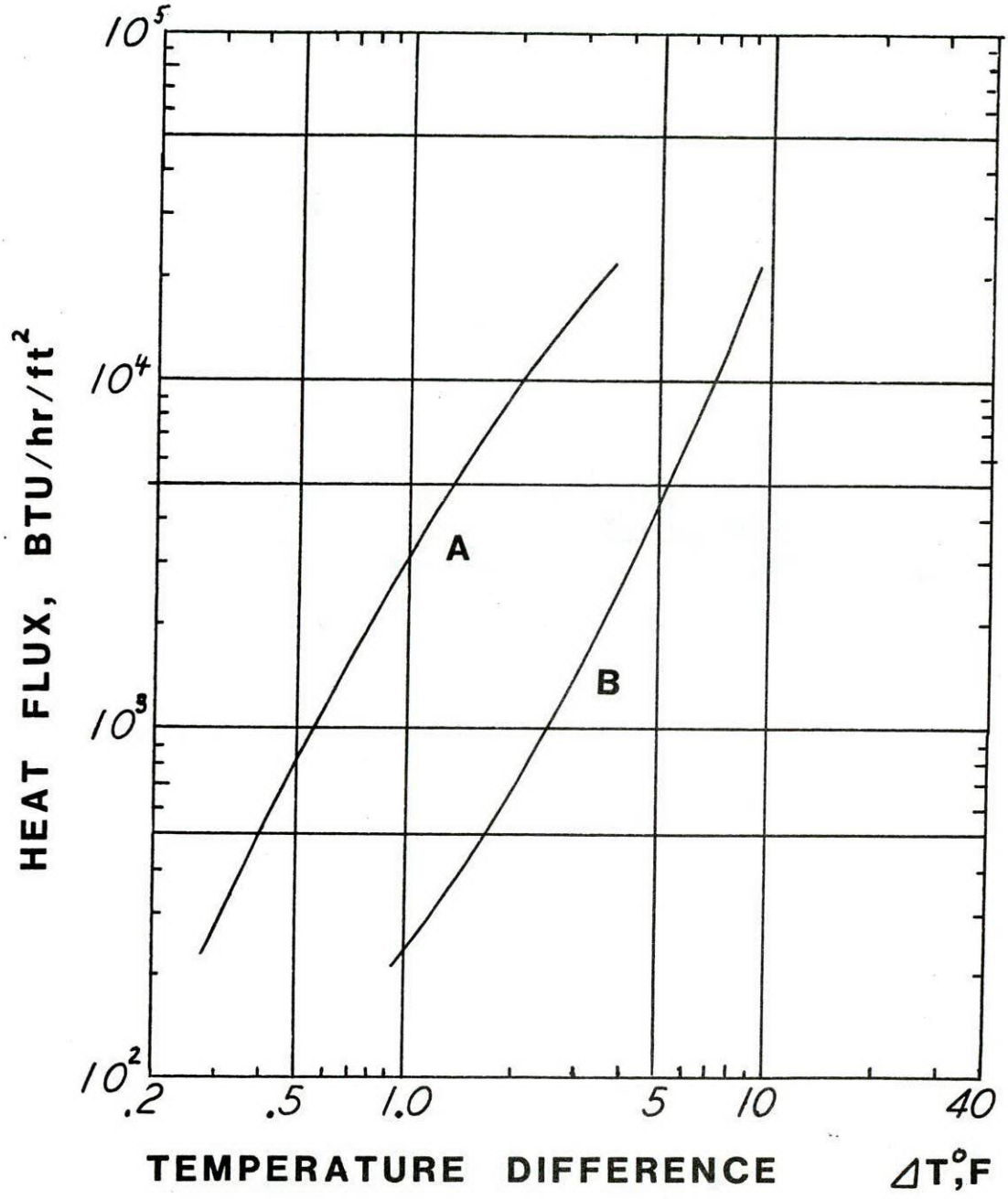
FIGURE 3



ROLLED COPPER NODULE COATING

FIGURE 4

HEAT TRANSFER DATA



A- Rolled, Nodule Coated Tube

B- 26 Fin per inch Tube

FIGURE 5

PLATING APPARATUS

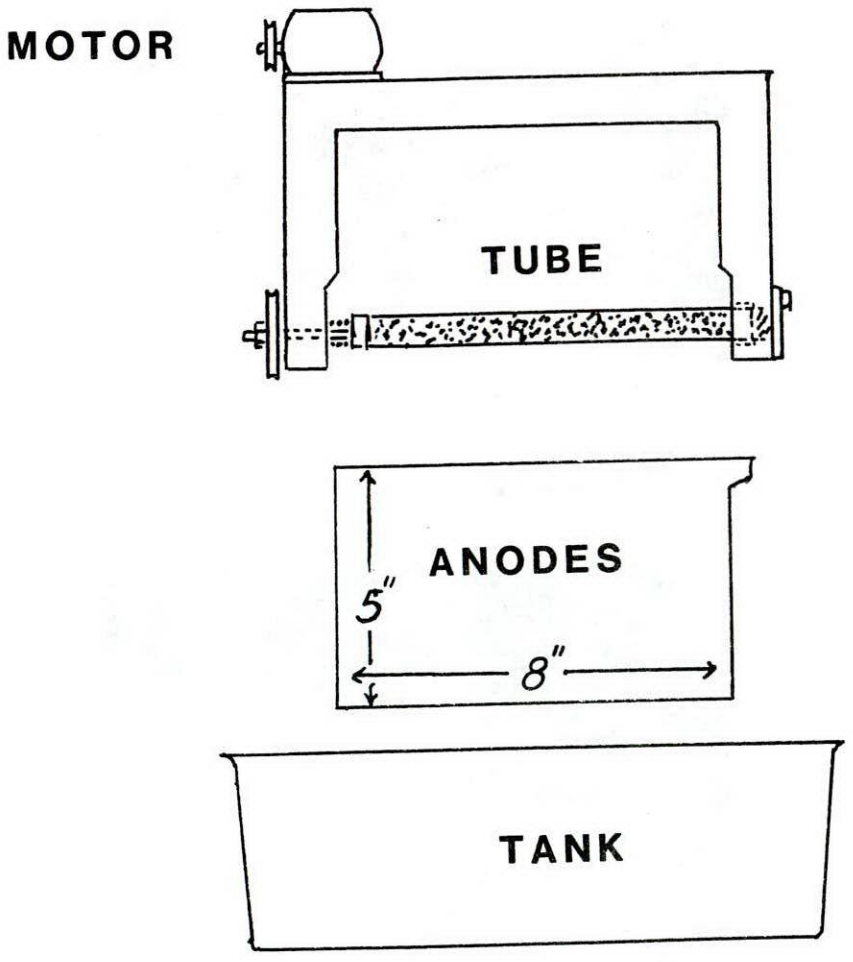


FIGURE 6

HONEYCOMB SURFACE

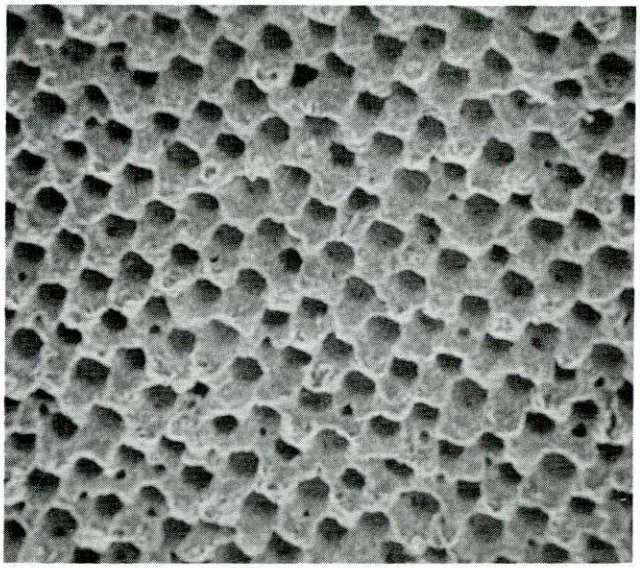
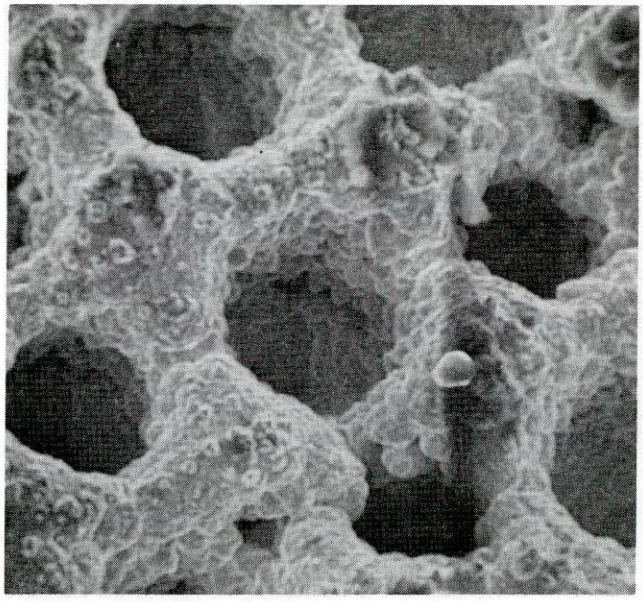


FIGURE 7



HONEYCOMB STRUCTURE

M-5

Electroforming Session M

Electroforming in Japan

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ELECTROFORMING IN JAPAN

- A Look Back and a Look Forward -

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In Japan, as in other countries, the electroforming industry enjoyed a good start with the production of molds for printing plates, lithography rolls, toys, and matrix tooling for phonograph records. Chrome decorative plating of small parts supplemented the income derived from electroforming.

During the sixties and early seventies, electroforming benefited from the accelerated development of the automobile and electrical appliance industries.

The oil shock of 1983, due to its effect upon major industries, put a halt to the rapid advance of electroforming. Demand for electroformed parts declined; thus the electroformers were unable to expand with new equipment and additional personnel.

During this crisis the mass-production manufacturers were concerned that, in the wake of the oil-shock slow-down, small companies - such as electroformers - would be put out of business and thus deprive them, the large manufacturers, of the requisite electroforms for their tooling.

To solve this imminent problem, some leading manufacturers chose to absorb their supplier - the electroforming company - for relatively small capital outlay.

This absorption was beneficial in several ways. It provided the operating and expansion capital which smaller companies lacked; and, in turn, the electroformers provided the manufacturer with a bonus of high technology in their own specialized field; a combination that helped the larger manufacturers to broaden their capabilities and to look forward with assurance to a renewal of their normal production pace.

During the acceleration years, there had been a resurgence of research and development in high-technology fields - including metal fabrication - with resulting improvements in methods and processes awaiting financial backing and adoption by industry.

However, the economic sag that afflicted America was also severe throughout Japanese industry, deepened significantly by national restrictive policies.

In spite of this full-scale setback, a positive note should be added here to this effect: for major electroformers 1982 electroforming sales were approximately 80% of the 1981 peak. Although total sales decreased, orders for more varieties of molds increased - thus opening up new markets.

It may be of interest to know that, in Japan, electroplaters are now entering the electroforming field. As they do so, they learn anew that the two systems are not identical - neither in chemical structure nor in shop practise; nor do they serve the same markets.

Electroplating can be used as a major mass-production system; whereas electroforming is an electro-chemical system providing precise configuration tooling to serve the mass-production market.

In addition, electroforming is unequalled in its capacity to produce high-precision molds that duplicate complex configurations with unerring fidelity. Examples include medical instruments, optical lenses, rocket engine components and other critical parts required for space and aircraft vehicles.

A current example of the high precision assured by the electroforming method is the development of the artificial heart system. Molds for a recently introduced ventricular assist system were made wholly by electroforming. Minutely calculating the inherent swelling and contraction is a major step in production of a successful mold.

Another development of interest to electroformers is the monolithic molding method now being adopted in Japan. It has been customary to mold parts individually for the vehicular industry, for assembly by others.

The single monolithic mold may obsolete many types of multiple molds. It also presents new problems of its own. The molding dies equipped with heating and cooling pipes are becoming larger and more intricate, often presenting such problems as expansion of the scale of the equipment. The successful reproduction of a monolithic mold requires the technical expertise of veteran electroformers who have consistently kept abreast of every new development of the art and who themselves have enriched their knowledge with their own investigative experiments.

An example of such venture thinking is the cobalt-nickel alloy bath. This sytem of electroforming was originated and developed in the States. It has been reduced to shop practise and has been in successful operation now for almost a decade.

The cobalt-nickel system provides hard-wear surfaces that are almost immune to degradation of any measurement. Its hardness range is from 285 Brinell (machineable) to 550 Brinell (not machineable).

It is our hope that other alloy combinations now being investigated may provide deversified electroforming systems with varying degrees of resistance; perhaps such combinations as Nickel-Manganese; Nickel-Tungsten; Nickel-Cobalt-Manganese; Nickel-Iron.

Another expectation is that the inclusion of fluorine compound will provide necessary lubricity for easier release of a molded product.

We also look forward to development of composites in an original layer containing insoluble particles of aluminum oxide, boron nitride, and other elements providing wear resistance: a prime requisite for space product.

The conclusion to be reached is that, as in any business, problems may beset the electroforming industry; but creative work and venture thinking will help us all meet our shared objective: to solve technological problems and continuously improve the end product.