AMERICAN ELECTROPLATERS' SOCIETY, INC.
66TH ANNUAL TECHNICAL CONFERENCE — ATLANTA, GA

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Light Metals Finishing I
Session A

Automatic Anodizing Processes

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Light Metals Finishing I
Session A

Pitting Problems in Hardcoat Anodizing

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PITTING -- A PROBLEM WITH HARD ANODIZING

By

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INTRODUCTION

Hard anodizing is a variation of the conventional aluminum anodizing process that produces wear-resistant oxide coatings 10 to 60 times the thickness of the sulfuric acid coatings normally used for corrosion protection (fig. 1). The coatings formed are generally dark gray (varying with the anodizing process and the alloy), can be polished to achieve a very fine surface finish, and are considered file-hard. Hard anodizing is used on Boeing airplanes as a .001- to .003-inch-thick wear-resistant coating for nonlubricated wear surfaces, for spherical bearings, and for the I.D. bores of hydraulic actuators. Hard anodizing is also used for rework where a surface buildup less than .002 inch is required.

Boeing's principal use of hard anodizing is on the wear and seal surfaces of aluminum hydraulic actuators. Hard anodizing permits the lightest weight actuator design and, accordingly, is the most widely used wear surface for aluminum actuator bores. Hard anodizing can produce surfaces that have outstanding service performance, showing no detectable wear during the life of a hydraulic actuator.

The typical sequence of operations for fabricating hydraulic actuators (fig. 2) has been as follows:

1. Machine to pre-shot peen dimension and an RHR 32 finish.

2. Shot peen to prevent a fatigue life reduction due to hard anodize.

3. Finish machine to an RHR 16 finish, with the final bore honed oversize to allow a surface growth of half of the hard anodize coating thickness (fig. 3).

4. Hard anodize to a specified thickness or dimension.

5. Hone to an RHR 8 finish and to the final bore diameter.

PROBLEM AREAS

Several problems can arise during hard anodizing: pitted coatings, soft coatings, insufficient coating thickness or surface growth, and burning. Problems with soft coatings, burning, or coating thickness are normally detected during the post-anodize inspection and are resolved by correcting processing deficiencies, and will not be discussed further. Pitted coatings are not detected by the conventional inspection techniques, and these defects can degrade the service life of an actuator. The sharp edges of pits (figs. 4, 5, and 6) can cause excessive wear of actuator seals and permit fluid leakage to the point where the performance of the hydraulic actuator is degraded.

Pitting of honed hard anodizing has been a chronic problem for years. Minor modifications in the anodizing process and in the pre- and post-anodizing operations have been beneficial; however, the pitting problem has never really been eliminated. Microexamination (fig. 7) shows that the pits are actually voids in the hard anodize coating that have been exposed during honing. Control of pitting is therefore obtainable only by controlling those factors that cause void formation in the coating during hard anodizing.

THE ANODIZING MECHANISM

The basic reaction in all anodizing processes is the electrolytic conversion of the aluminum surface to aluminum oxide. The aluminum is immersed in a moderately active acid solution and an external anodic potential is applied. Oxide nucleation initiates at those microscopic sites with the lowest electrical resistance until a nonconductive oxide film is formed. Adjacent areas then become of lower resistance value, and oxide growth progresses laterally in all directions from the nucleation site, as shown in figure 8. Lateral oxide growth continues and impacts with growth from neighboring nucleation sites until the entire aluminum surface is covered with a cellular oxide film or barrier layer, having the close-packed hexagonal cell form shown in figure 9. A further increase in the anodizing potential (voltage) causes pores to form in the oxide film, and the oxide growth progresses into the aluminum with the barrier layer constantly reforming between the bottom of the pore and the oxide/aluminum interface (fig. 10).

The thickness (angstroms) of the barrier layer formed during anodizing in sulfuric acid solutions is approximately 8 times the applied voltage. The cell diameter is twice the barrier layer thickness plus the initial pore thickness of about 120 A. The pores develop a somewhat conical shape due to attack by the solution during prolonged anodizing and, to an even greater extent, during the period between the time the current is interrupted and the acid is completely removed by rinsing. The pore structure and cell size are relatively stable during anodizing, but can be altered (with the pores either branching or condensing) by an abrupt change in the voltage or by inhomogeneities at the oxide/aluminum interface that permit localized variations in current distribution.

The oxide film is influenced by the composition of the aluminum alloy. During anodizing, most of the nonaluminum alloying constituents, including copper and zinc, are dissolved. Copper contents much above 2% result in the formation of lower density, soft coatings with large pores and in electrochemical dissolution of high current density areas of the part during anodizing in dilute solutions. Silicon particles have low conductivity and are unaffected by the anodizing process and are entrapped by the oxide film. Iron-containing particles are conductive and dissolve slowly, leaving aluminum protrusions in the oxide.

PROCESS EVALUATION

Virtually all hard coating is accomplished by anodizing in a refrigerated sulfuric acid solution. Principal processing modifications used are the addition of oxalic acid (Alumilite Process) or glycerine and glycolic acid (MAE Process), saturation with carbon dioxide (Martin Process), superimposed AC (Hardas Process, Scionics Process), superimposed DC pulses (Permaloy Process), etc. The purpose of each of these processes is to build up a thick, microporous aluminum oxide at a rate sufficient to prevent excessive acid attack on the pores (soft coating), without causing localized electrical overheating (burned areas). All of these processes are capable of producing hard, wear-resistant coatings .002 inch thick that are satisfactory for many applications. Metallographic evaluation of hard anodize films produced by a number of suppliers utilizing the above processes showed that all of these processes also tend to produce coatings that contain objectionable voids that become post-honing pits.

Parametric studies at Boeing have established that hard anodize pitting is due to gas-rupture voids (fig. 7) in the coating caused by boiling of the anodizing solution in the pores at local areas of high current density.

The primary nucleation site for gas-rupture voids was found to be iron-containing particles in the aluminum, such as intermetallic impurities (fig. 11) or honing residues. The iron-containing particles were conductive and dissolved slowly during hard anodizing, producing protrusions in the oxide coating with such high current densities that voids occurred. The number of voids formed decreased markedly when higher purity, low-iron alloys were used (fig. 12). An improvement in process reliability was also attained by not using pre-anodizing honing stones that had previously been used on steel parts, since they tended to imbed iron particles in the aluminum.

A large amount of heat is generated at the oxide/aluminum interface during hard anodizing, and is referred to in this paper as "electrical" heating. Conventional hard anodizing processes are accomplished at a current density of 36 ASF at up to 48 volts, and can generate an average of 1.7 kilowatts of heat within each square foot of aluminum surface being anodized. Variations in current density cause localized areas to generate heat at rates very much higher than the average. It was found that the heat input must be minimized, and that the heat generated during anodizing must be removed by high-velocity forced-circulation cooling. Such cooling is required to prevent the solution in the pores from overheating and boiling and thus producing large gas-rupture voids or attacking the pores to produce soft coatings.

Void formation was found to be most severe when hard anodizing the 2XXX-series alloys (fig. 13). This was attributed to variations in current density associated with nonuniform copper distribution and the relatively high iron content of the 2XXX alloys.

Void formation was found to increase with coating thickness (fig. 14). This was due to the poor thermal conductivity of the aluminum oxide. As the oxide thickness increased, it was increasingly difficult to remove the electrical heat that developed at the oxide/aluminum interface.

A rough surface prior to hard anodizing resulted in two undesirable effects (fig. 15): asperities that developed high current densities and caused voids during hard anodizing, and a rough oxide that required an increased coating removal to obtain the required finish during final honing.

A major reduction in gas-rupture void formation was obtained by utilizing a slow current buildup and a lower than normal current density. The current was smoothly increased from 0 to 30 ASF over a 20-minute period. (Industry practice is to immerse the parts and immediately increase the current density to 36 ASF.) The ramp current buildup stabilized the oxide pore structure at a smaller cell size and 2-8V lower voltage. The reduced voltage and current density result in substantially reduced electrical heating during anodizing. The effectiveness of this procedure, coupled with forced circulation for improved heat removal, have permitted formation of void-free coatings up to .007 inch thick (fig. 16).

Optimum processing was obtained using a solution containing approximately 13% sulfuric acid and 1% oxalic acid by weight, at 50 $\pm$ 2°F. This solution provided the best void-free combination of coating hardness and thickness for 6XXX and 7XXX alloys. This, and other dilute solutions were not suitable for 2XXX alloys: high current density areas (part corners and areas near the coating rack) were visibly dissolved during anodizing in solutions containing less than 20% sulfuric acid. Attempts to achieve better cooling by anodizing at lower solution temperatures were self-defeating: the solution resistance and anodizing voltage increased, substantially increasing the electrical heating and void formation.

NEW PROCESS REQUIREMENTS

The following process will provide "pit-free" hard anodize coating on 7XXX alloy surfaces. "Pit-free" is defined as:

- No more than 10 pits, .0005 to .001 inch in diameter, in any .5- by .5-inch square.
- No more than four pits, .001 to .008 inch in diameter, in any square inch.
- No pits greater than .008 inch.

1. Surface Roughness. The surface finish prior to anodizing should not exceed half the value required after hard anodizing and final honing. For example, an actuator bore requiring an 8 RHR final finish requires a 4 RHR finish prior to hard anodizing.

2. Surface Condition. The honing stones used prior to anodizing must not have been used on steel parts.

3. Coating Thickness. The as-anodized coating thickness is maintained as thin as possible. This requires pre-anodize honing to very close tolerances coupled with minimal coating removal during post-anodize honing. Optimum is to hard anodize .0025 to .0030 inch thick and hone to the specified final dimension and surface finish by removing a nominal .0005 inch of coating. Typical drawing dimensions are shown in figure 17.

4. Anodizing Solution. The Alumilite solution is used: 16-20 oz/gal sulfuric acid, 1.5-2.5 oz/gal oxalic acid, 48-52°F.

5. Anodizing Procedure. The current density is smoothly brought up to 30 ASF over a 20-minute period, and maintained until the required oxide thickness is obtained, normally about 90 minutes.

6. Solution Agitation. The solution is force-pumped at 130 ft/minute over the surfaces being hard anodized, in order to prevent heat build-up and the double problem of void formation and soft coatings.

7. Final Honing. Post-anodize honing is controlled to remove .0005 inch/surface nominal, using 600-800 grit size silicon carbide or diamond stones. Low speeds and filtration of the honing fluid are used to meet the dimensional and finish requirements, and to avoid honing-induced damage to the hard anodize.

8. Inspection. Finish-honed hard anodized surfaces are inspected for pitting by visual examination under oblique lighting, and by sweeping the surfaces with the sharp point of a lightly held dental explorer (fig. 18). Pits cause an appreciable drag or "catch" when swept with the sharp point of the explorer.

Developmental work is continuing in the following areas:

1. Higher Purity Alloys. The use of alloys with lower iron levels is being evaluated. Figure 12 shows the effect of reduced iron content on the microstructure of hard anodize coatings. The substitution of 7175-T736 aluminum for 7075-T73 can reduce iron levels from an average of .3 to .1%. The substitution of 2214-T6 for 2014-T6 would reduce the average iron level a similar amount; however, this higher purity alloy is not widely available.

2. 2XXX-Series Alloys. Work is continuing to develop an improved process for pit-free hard anodizing 2XXX alloys.

CONCLUSIONS

1. A process has been developed for producing essentially pit-free hard anodize coatings on 7XXX-series aluminum hydraulic actuators.

2. The process uses a dilute sulfuric-oxalic acid solution with a slow current buildup, reduced current density and voltage, and forced solution circulation to minimize localized overheating and void formation in the coating.

3. Process implementation requires only minor equipment modification.

4. Boeing is evaluating process improvements for 2XXX-series alloys and the advantages, if any, in using higher purity aluminum alloys.

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FIGURES

1. Effect of Anodize Time on Oxide Thickness (After R. V. Vanden Berg, Products Finishing, Feb. 1960)

2. Hard Anodize Process Flow Chart

3. Configuration for Hard Anodizing Cylinder Bores

4. Sectioned Actuator Housing Showing Defective Hard Anodized Bore

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16. "Pit-Free" Oxide Layer Developed by the Improved Boeing Hard Anodizing Process

17. Hard Anodize Bore Design Dimensions

18. Dental Explorers for Evaluating Pitting and Soft Coatings

Oxide Buildup During Anodizing

(Adapted from: R. V. Vanden Berg; Products Finishing, 24 (1960) No. 5 p. 24-35)

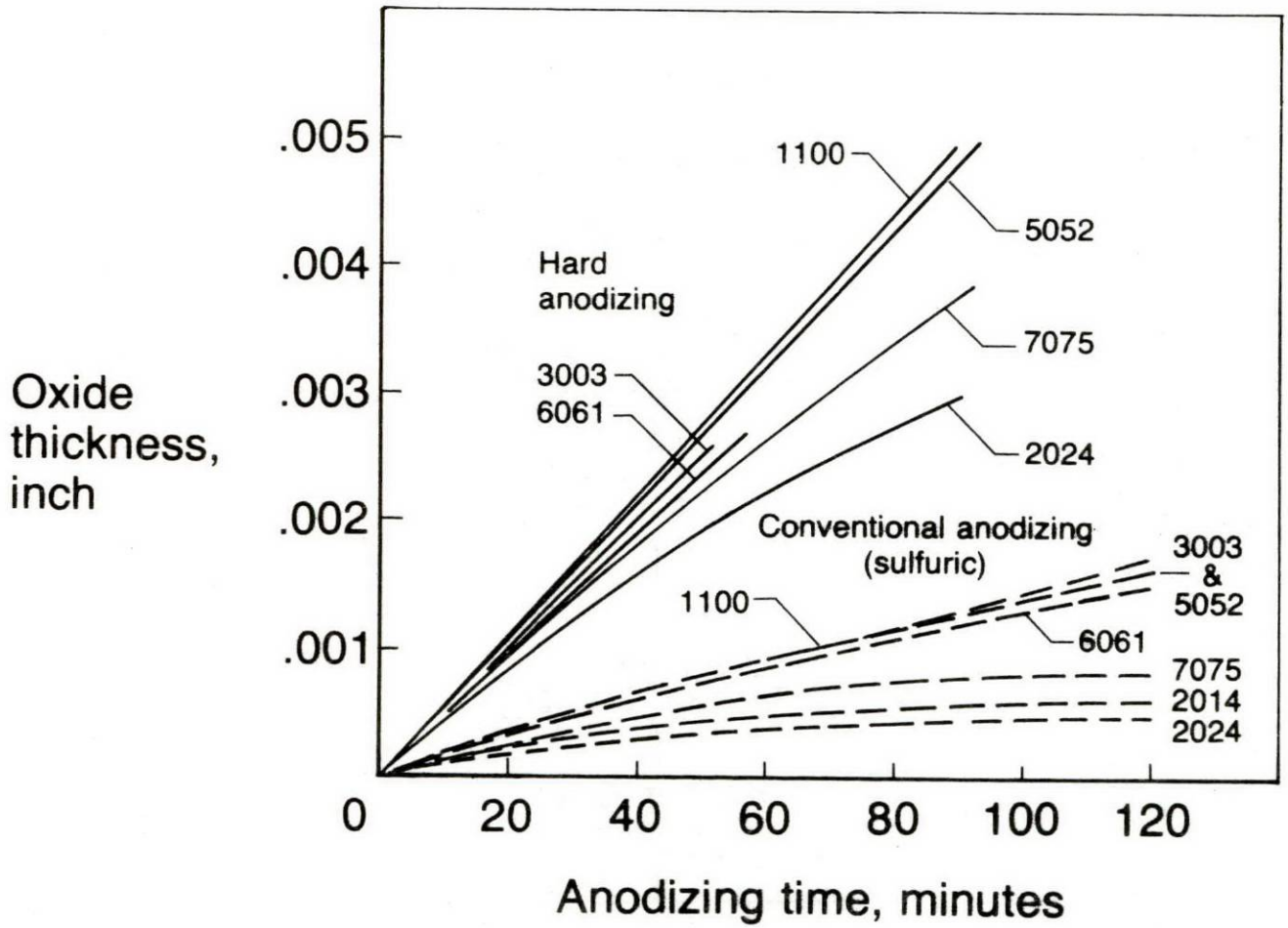


FIGURE 1

Hard Anodize Process Flow Chart

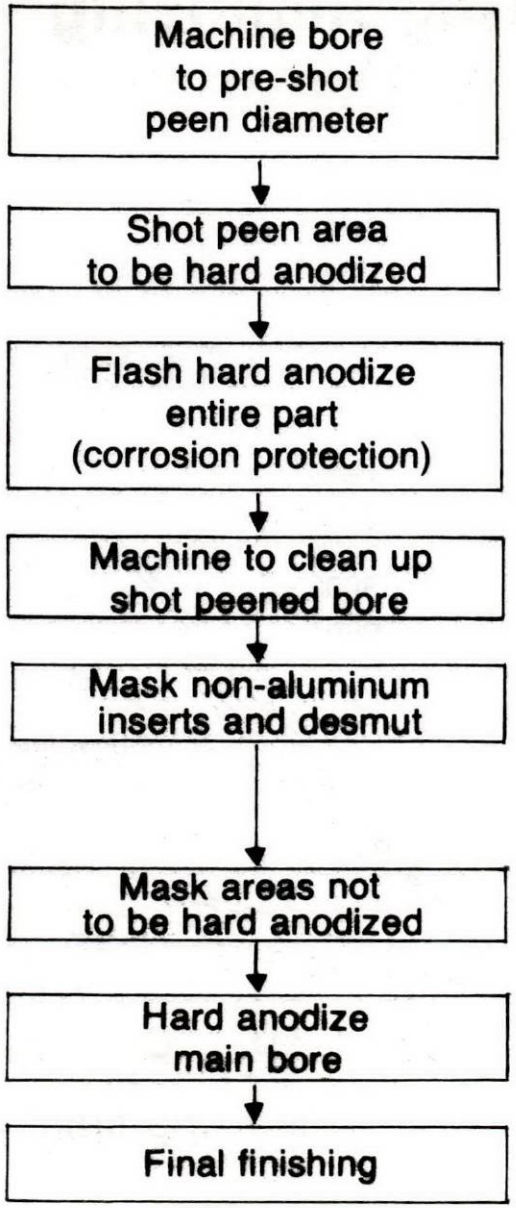


FIGURE 2

Configuration for Hard Anodizing Cylinder Bores

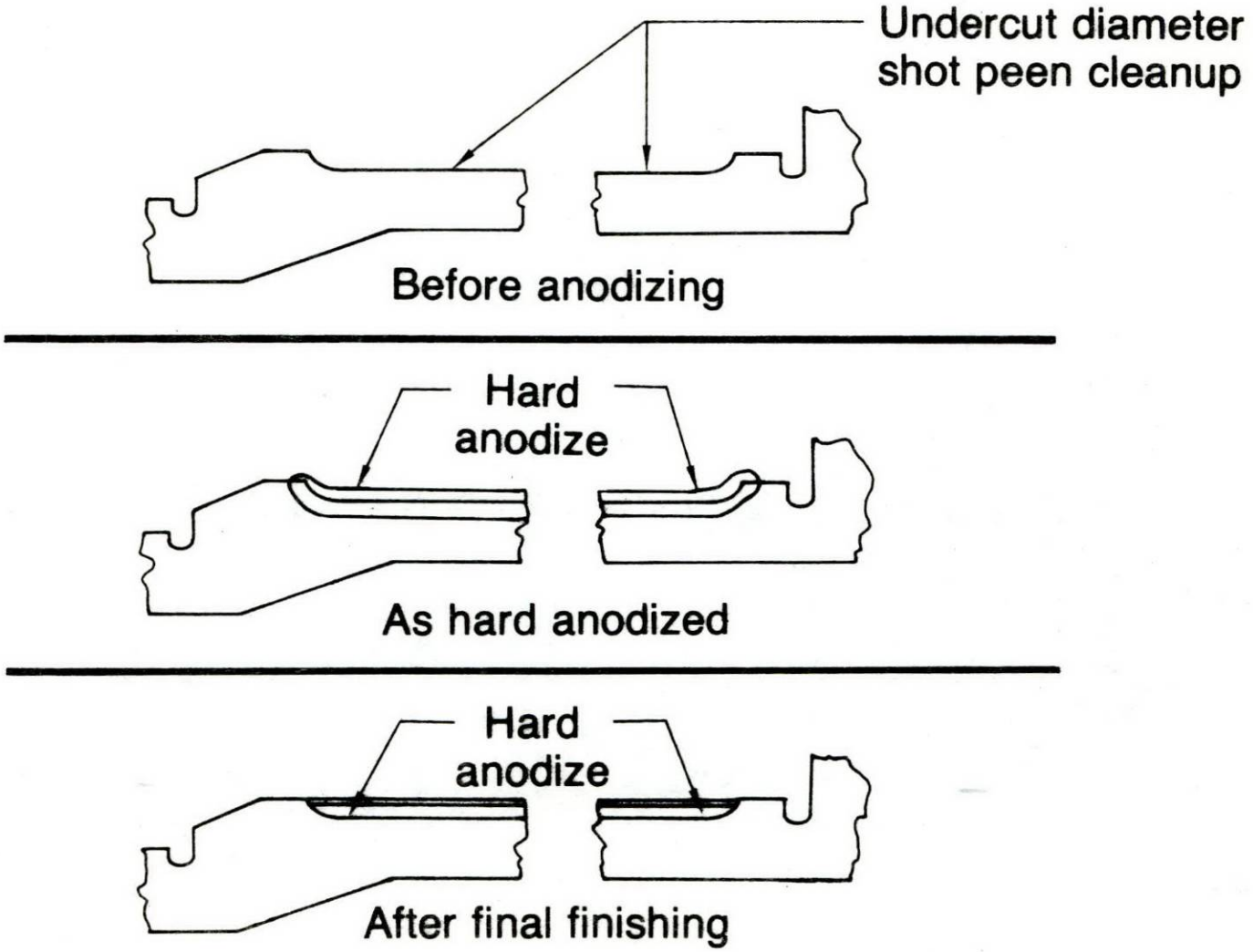


FIGURE 3

Sectioned Actuator Housing

Defective Hard Anodized Bore

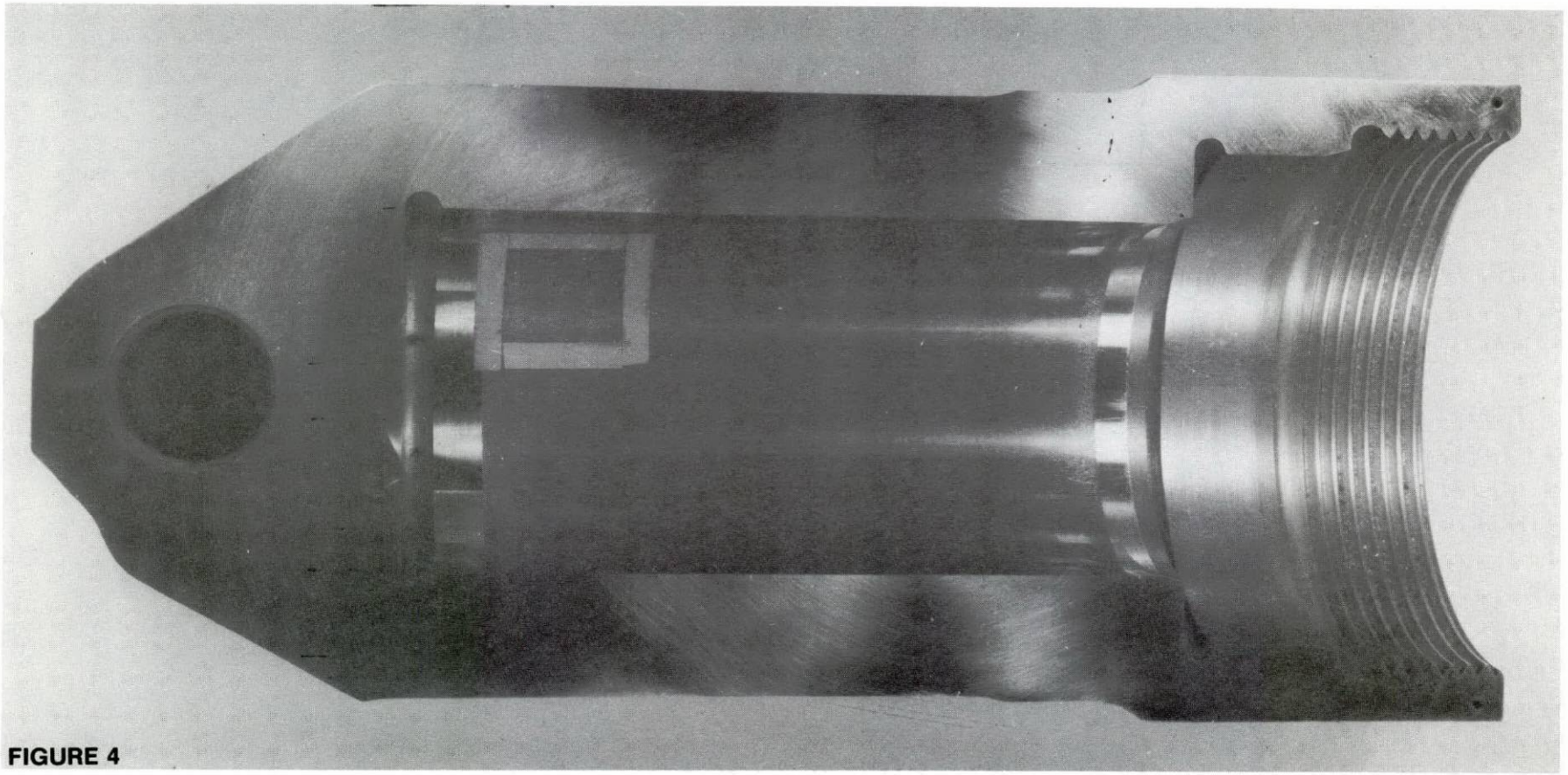


FIGURE 4

Close Up of Defective Bore

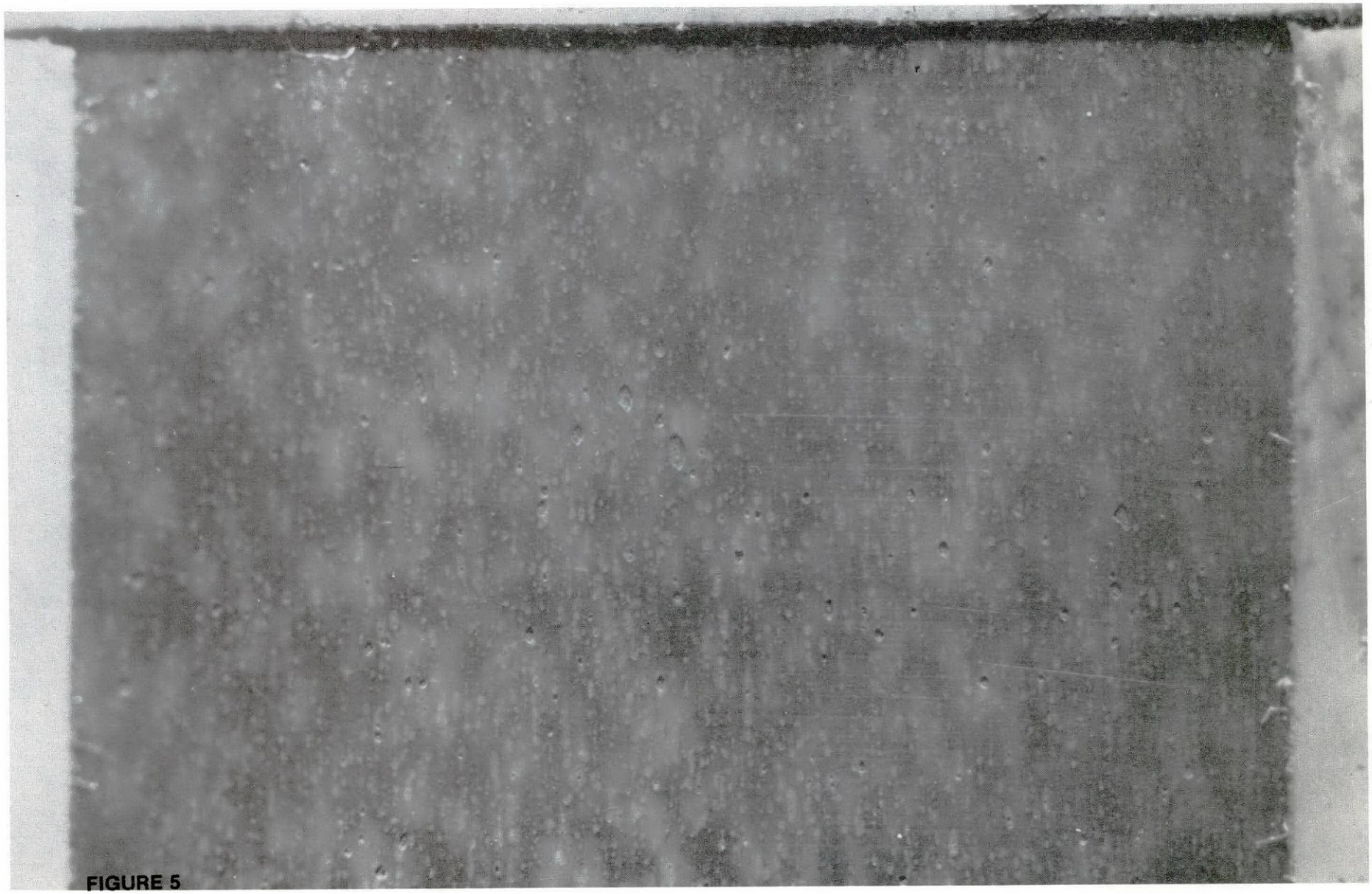


FIGURE 5

Cross-Section of Oxide Layer

7075 Material – Conventional Process

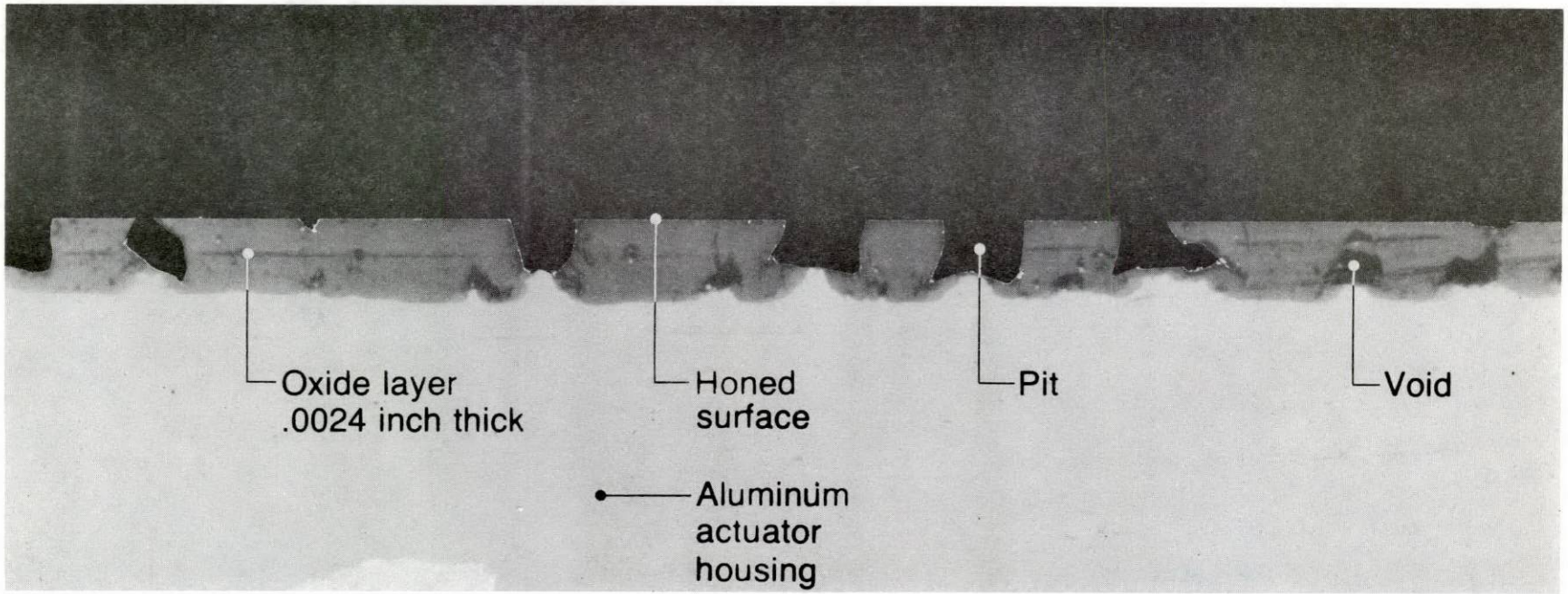


FIGURE 6

Gas-Rupture Voids in Oxide Layer

7075 Material – Conventional Process

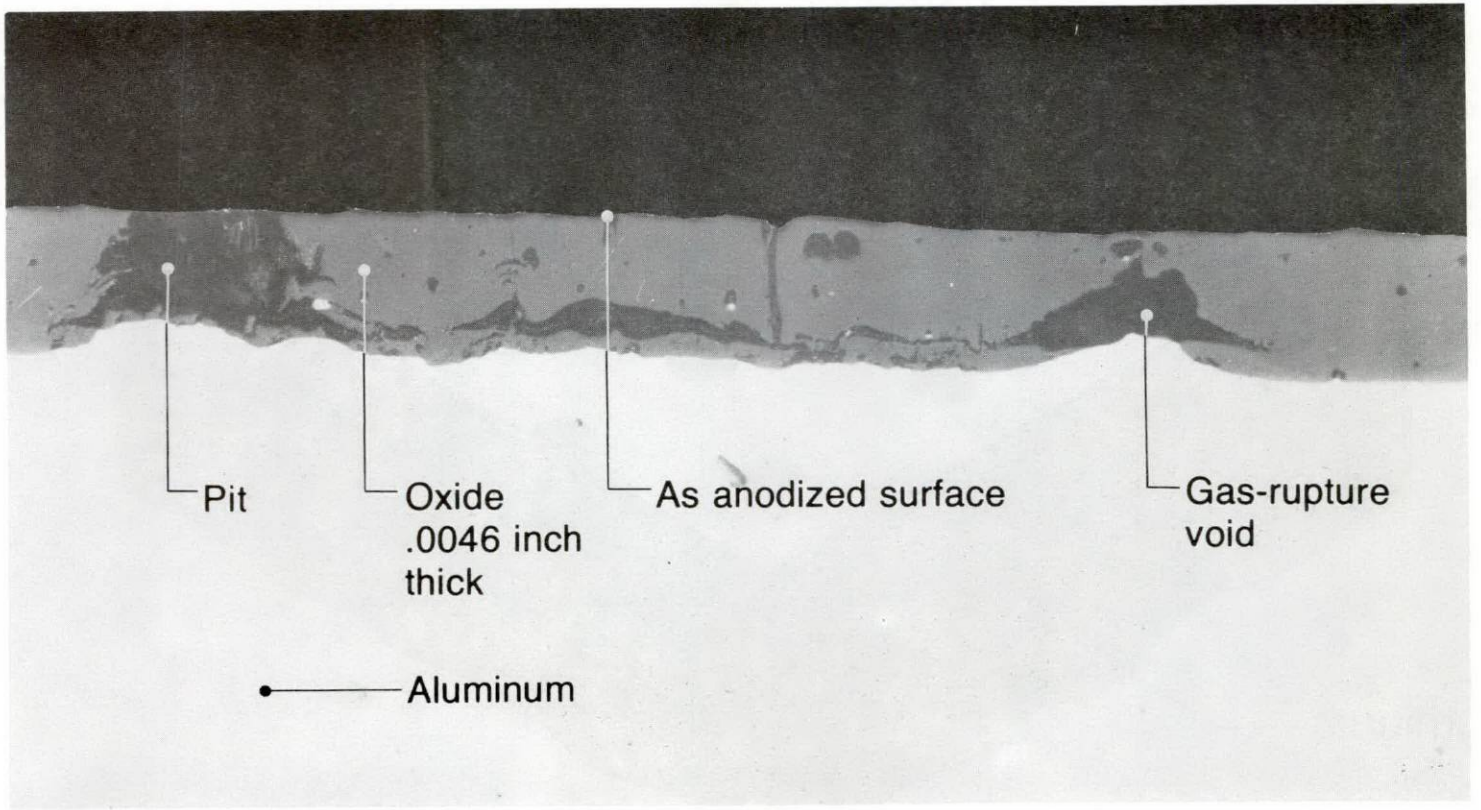


FIGURE 7

Oxide Nucleation Sites

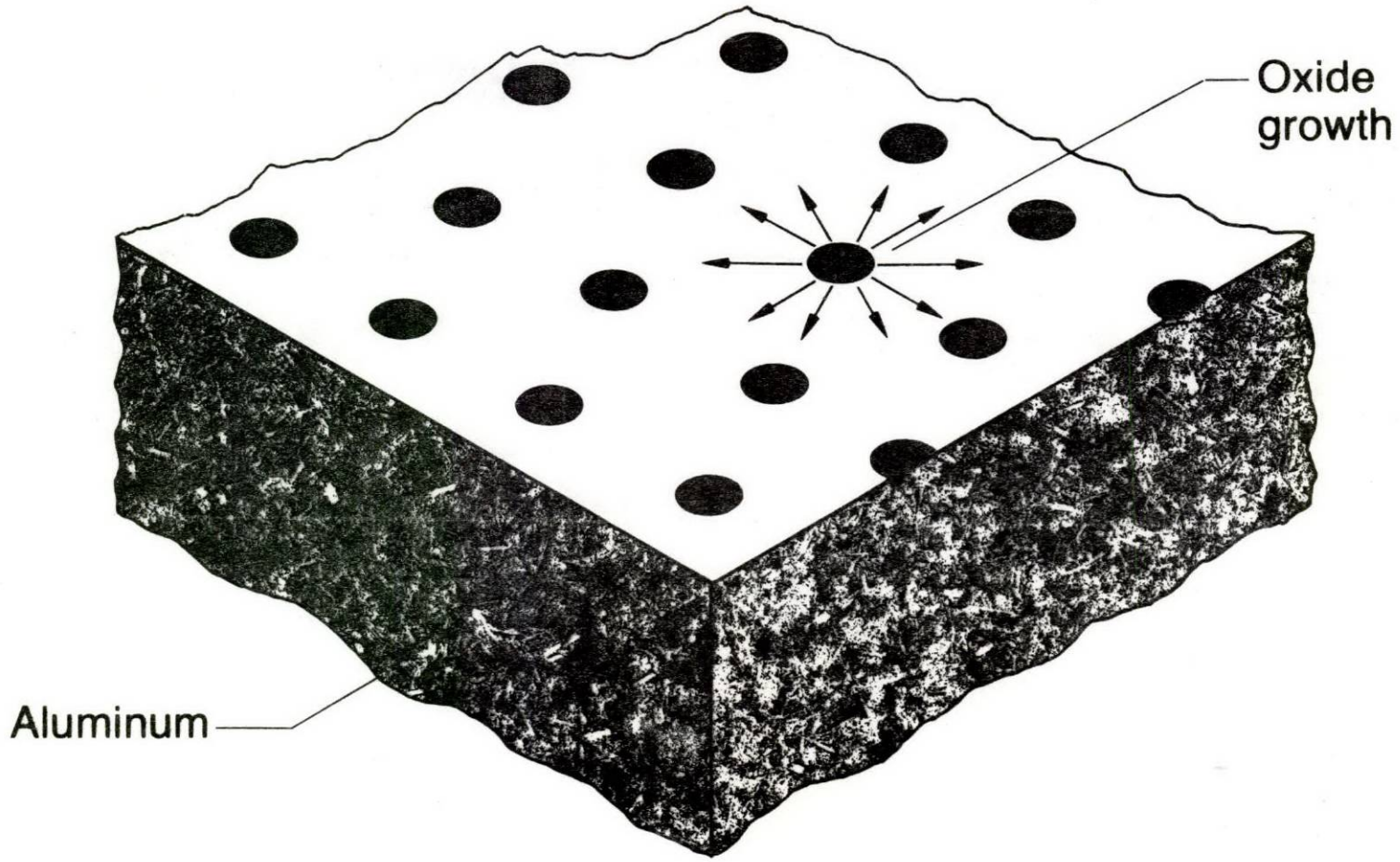


FIGURE 8

Formation of Hexagonal Cell Structure

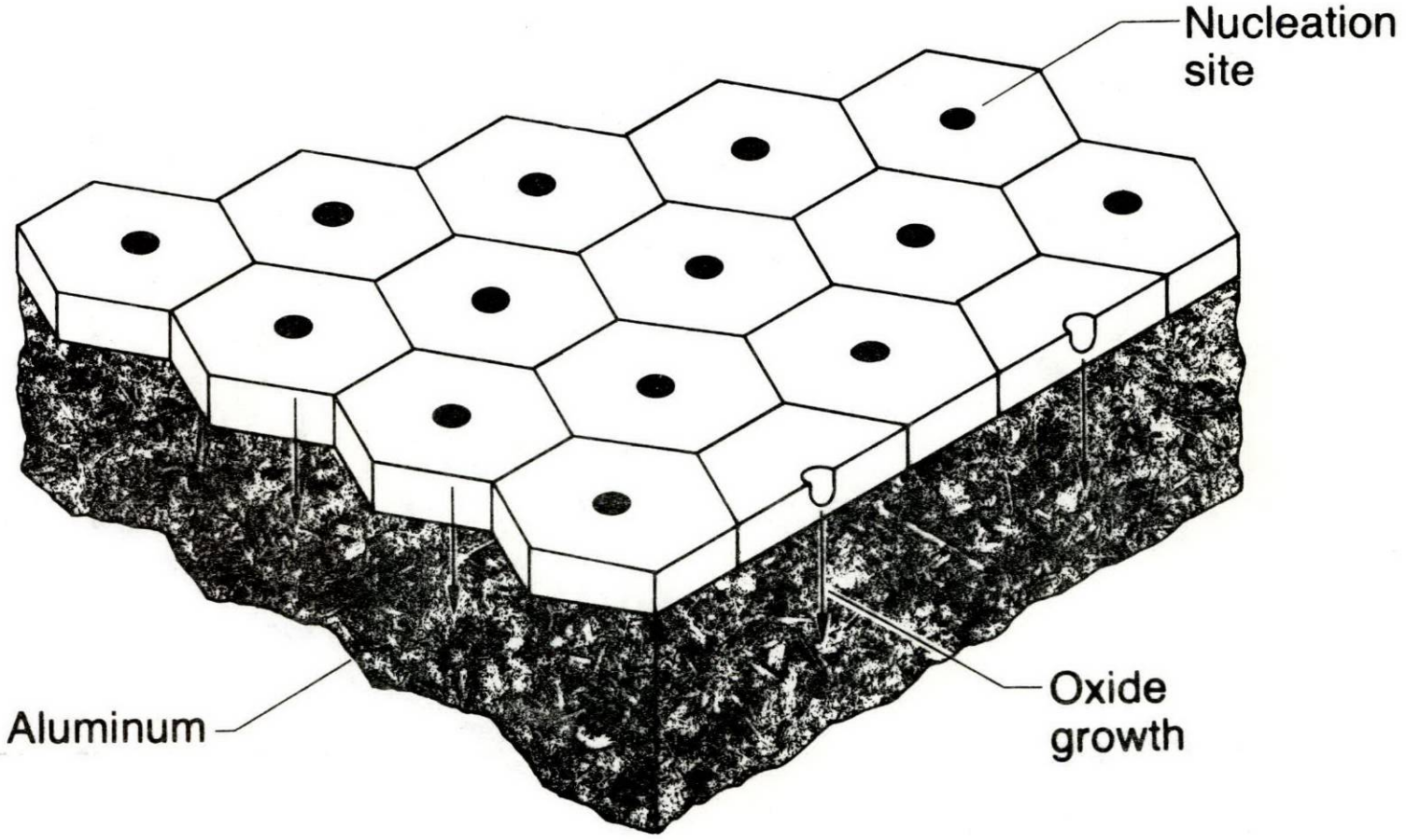


FIGURE 9

Developed Cell and Pore Structure

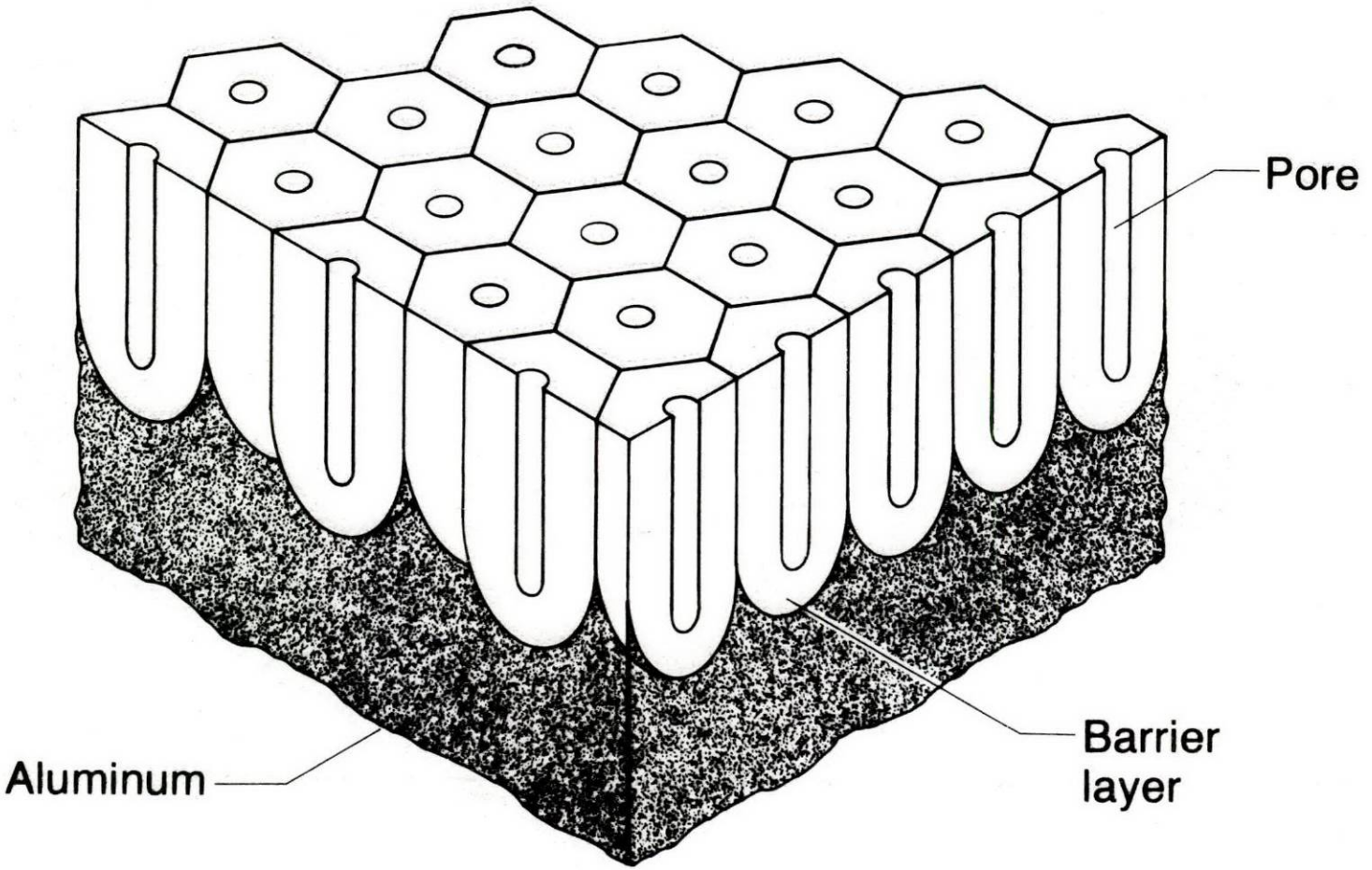


FIGURE 10

Void Formation at Iron Intermetallic

7075 Material – Conventional Process – .0027 Inch Coating

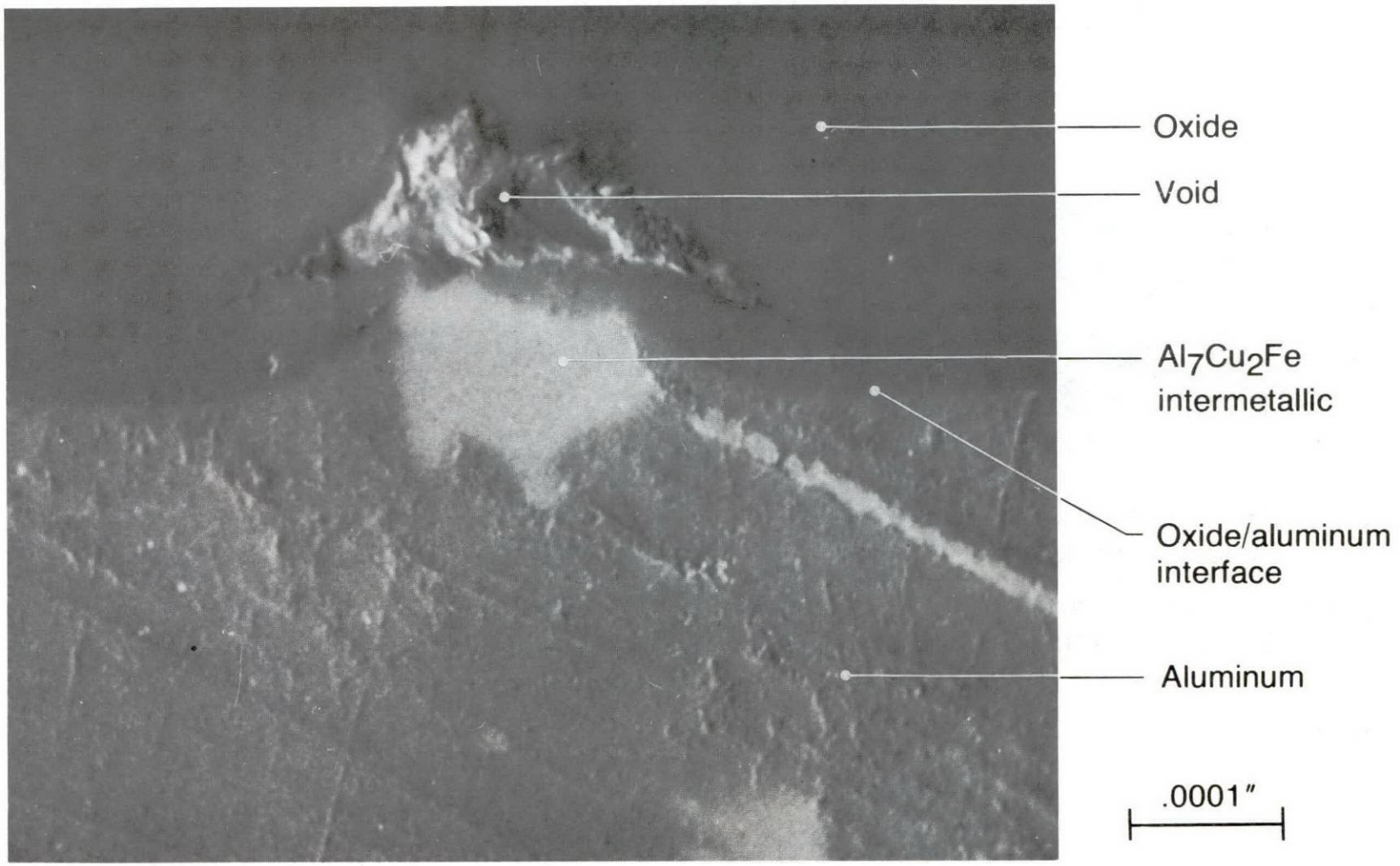


FIGURE 11

Effect of Alloy Purity

7075 and 7050 Materials – Improved Boeing Process

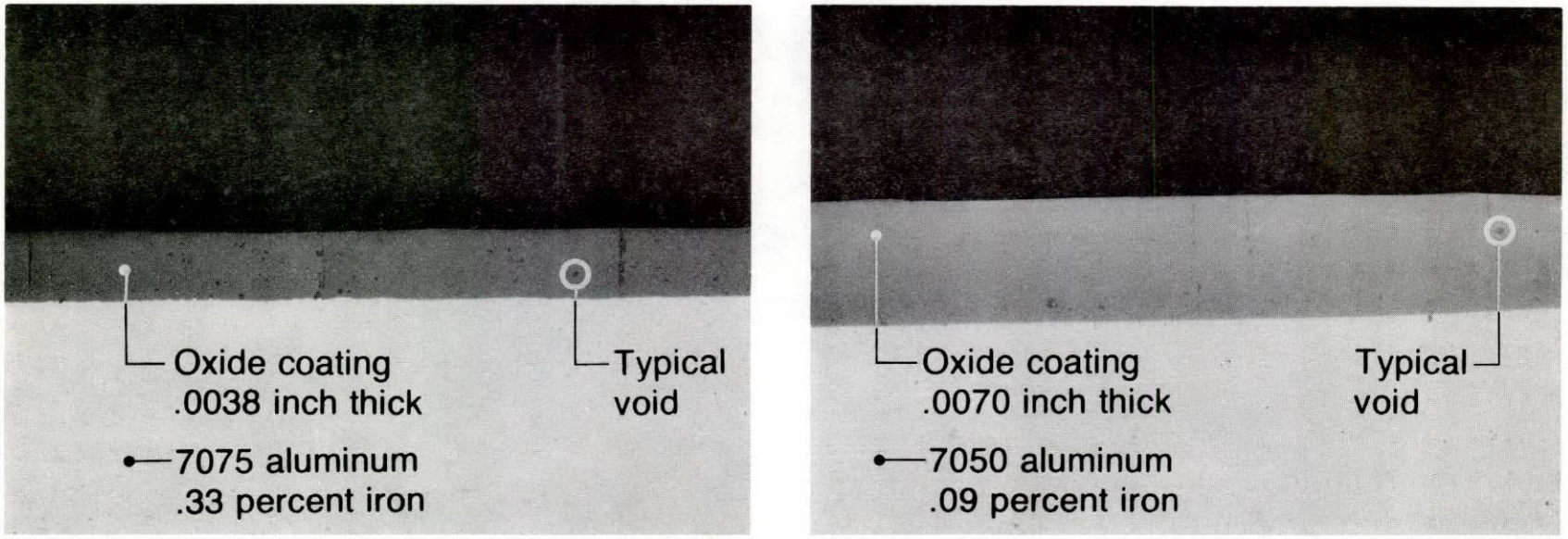
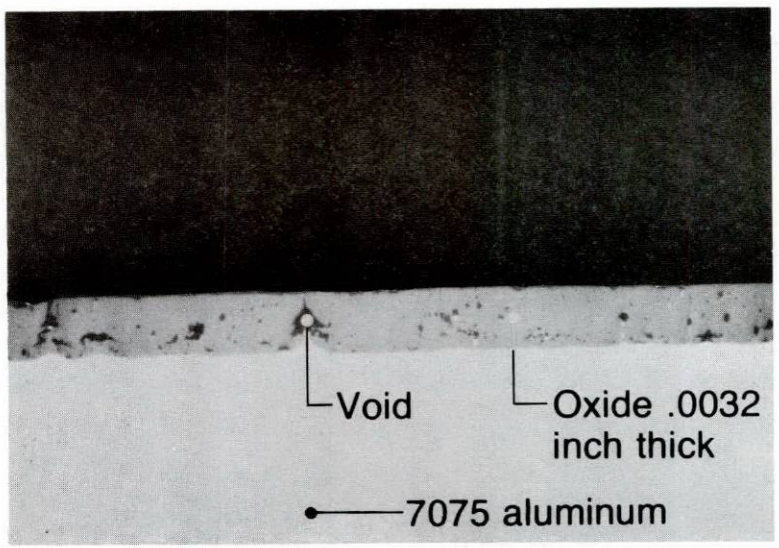


FIGURE 12

Comparison of Oxide Films

7075 and 2024 Materials – Conventional Process



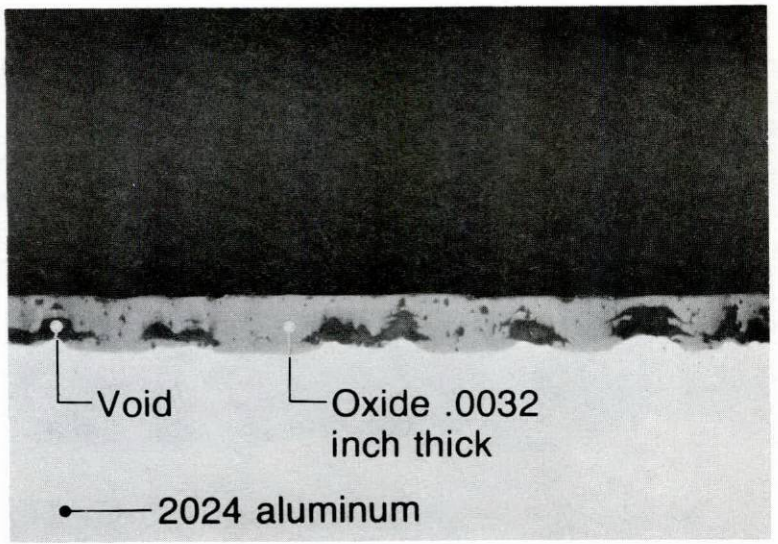
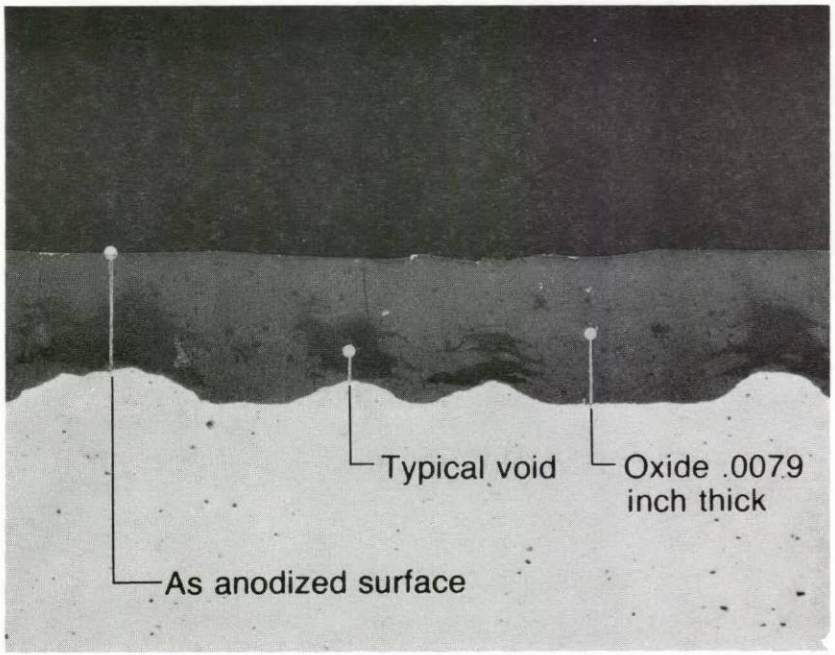


FIGURE 13

Comparison of Oxide Quality

Thick and Thin Layers – 7075 Material – Conventional Process



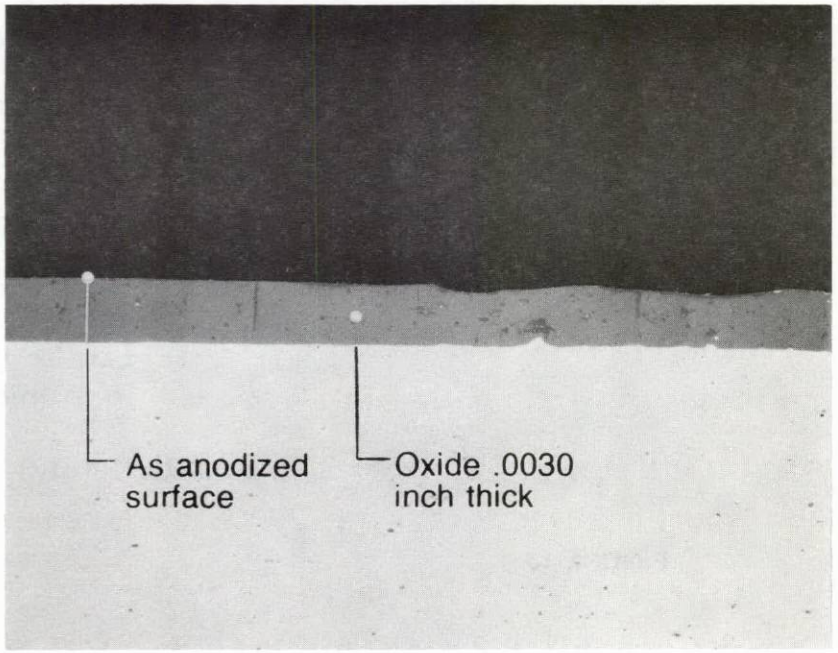
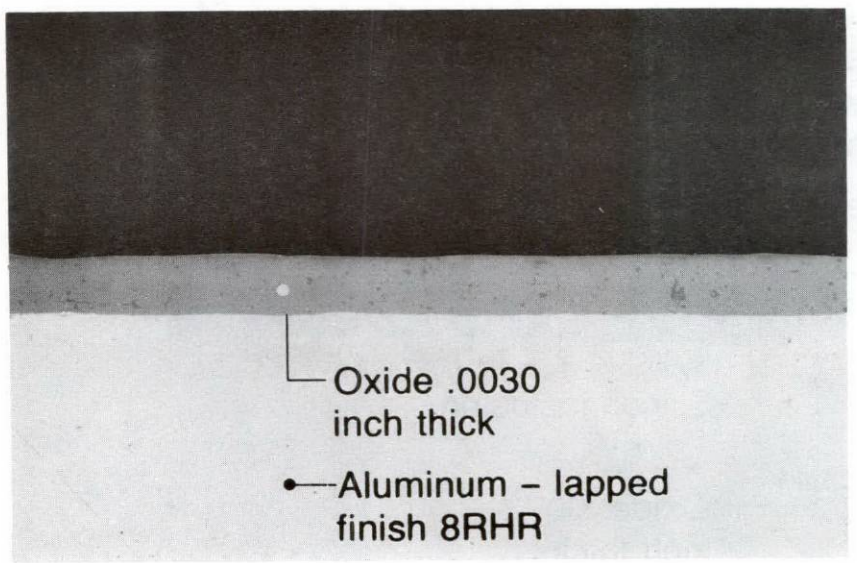


FIGURE 14

Effect of Surface Roughness

7075 Material – Conventional Process



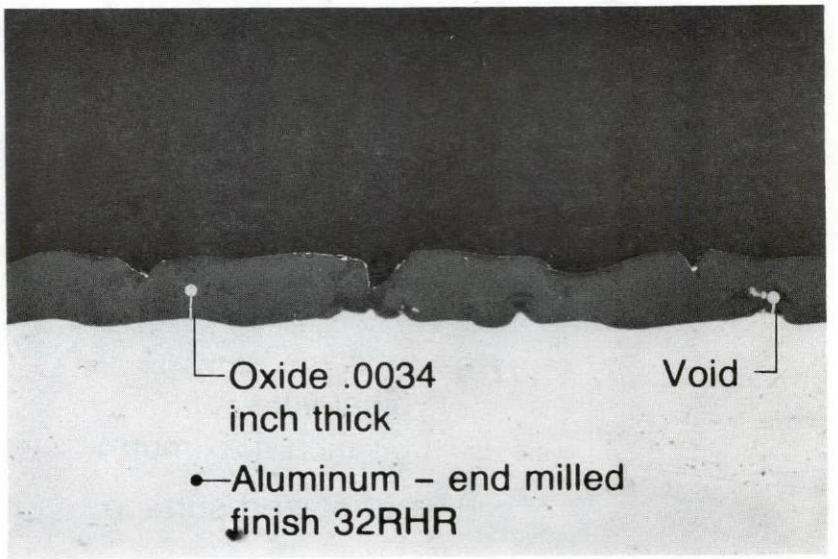


FIGURE 15

"Pit-Free" Oxide Layer

7075 Material – Improved Boeing Process

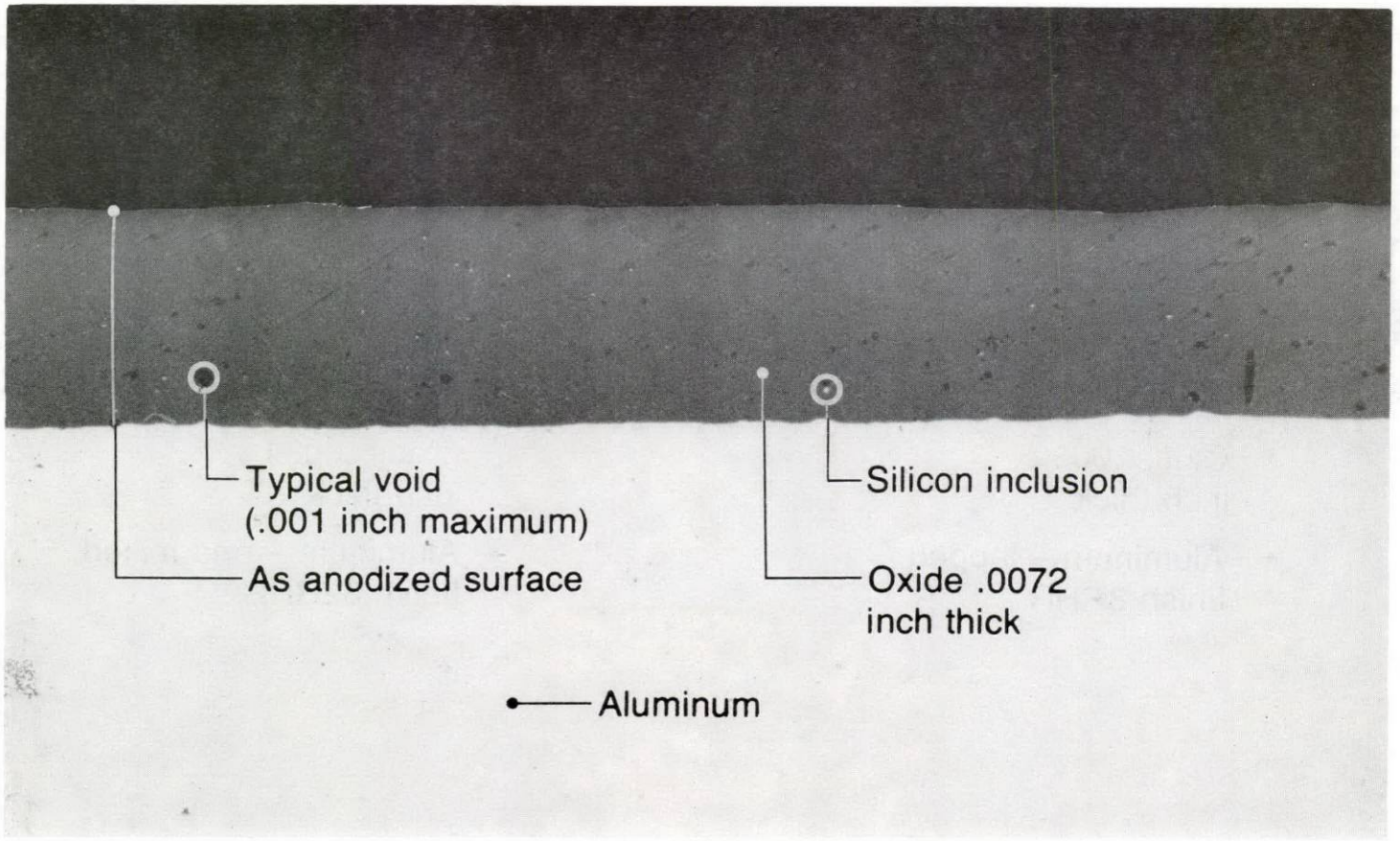


FIGURE 16

Hard Anodize Bore Design Dimensions

(All Dimensions in Inches)

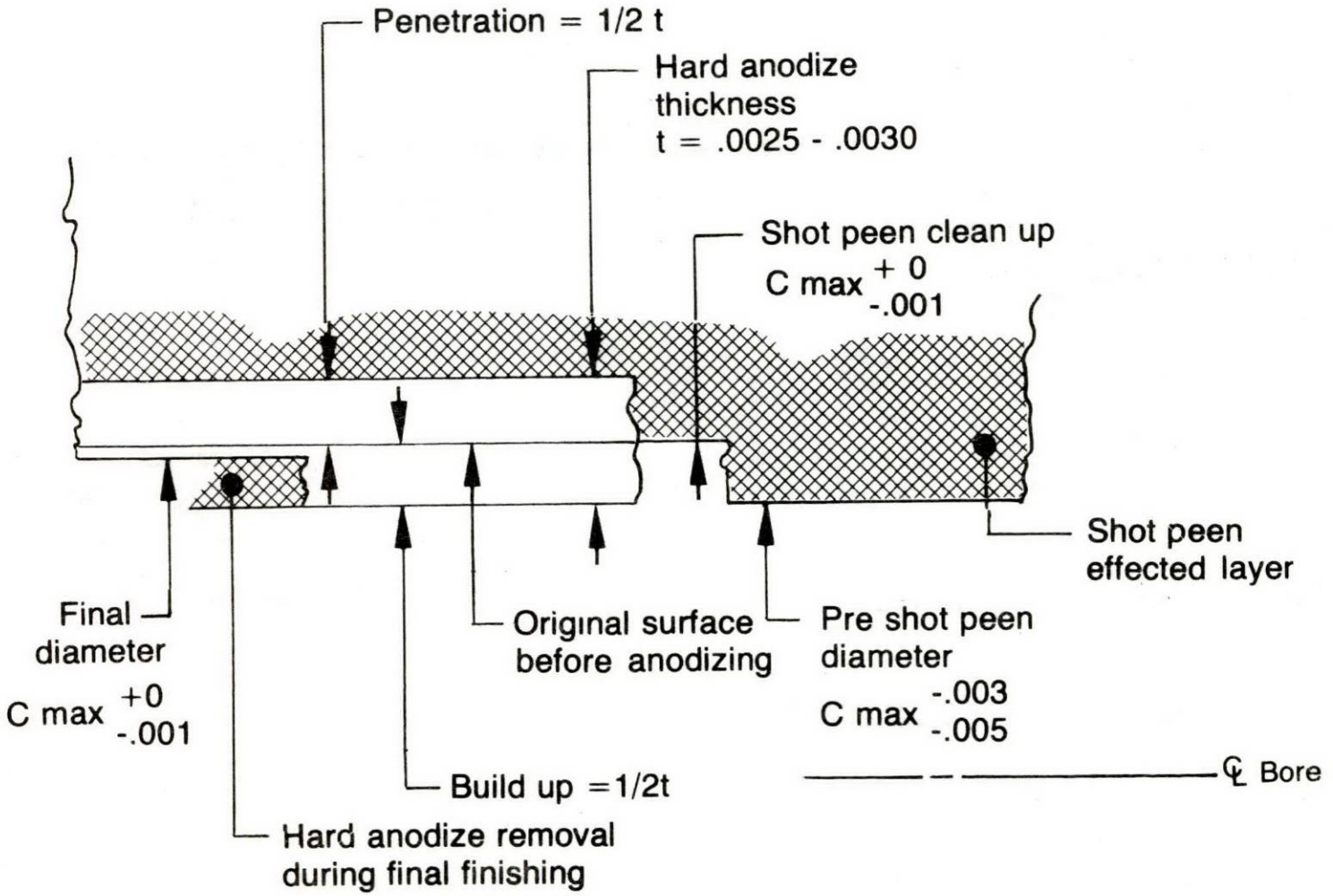


FIGURE 17

Dental Explorers for Evaluating Pitting

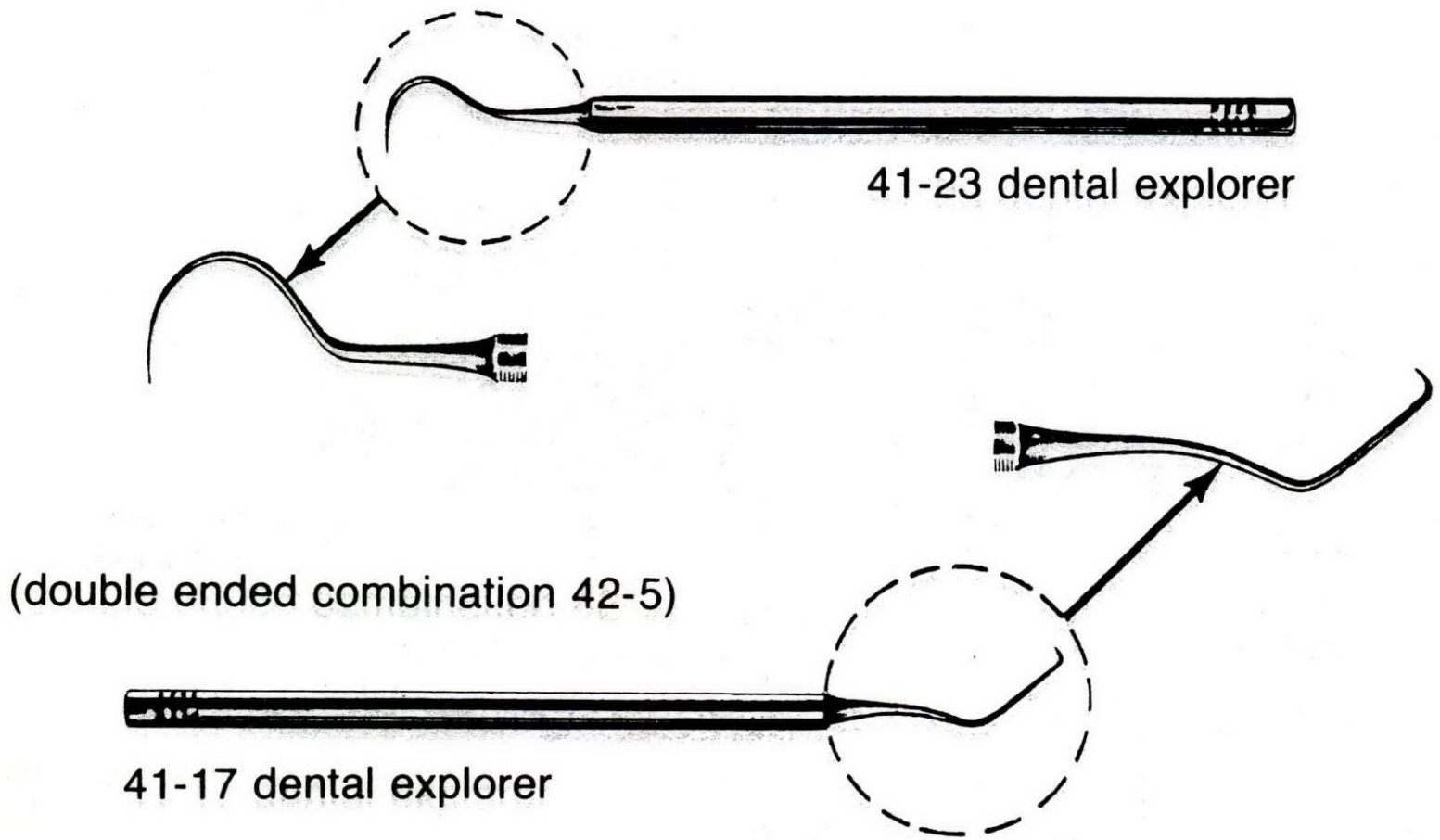


FIGURE 18

A-3

Light Metals Finishing I
Session A

20 Volt Chromic Acid Anodizing Process

E. W. Turns, R. E. Forrester Jr. and A. C. Porter
General Dynamics
Ft. Worth, Texas

THE 20 VOLT CHROMIC ACID ANODIZE PROCESS FOR ALL ALUMINUM ALLOYS

By E. W. Turns, R. E. Forrester and A. C. Porter

ABSTRACT

Prior to this paper it was necessary to apply sulfuric acid anodize to aluminum alloys containing more than 5 percent copper or 7.5 percent total alloying elements. Specifications dictated that those alloys such as overaged 7000's be subjected to sulfuric acid anodize whose inherent disadvantages are heavier coating weights to achieve equivalent salt spray corrosion resistance and reduced fatigue strength.

A detailed, thorough study of the chromic acid anodize process variables revealed that all aluminum alloys can be anodized at 20 volts using several process temperatures. A companion study of a variety of post anodize seal methods disclosed that a 5% sodium dichromate seal provides improved salt spray corrosion resistance and substantially superior paint adhesion, particularly after delays and precleaning prior to painting.

This improved performance process also provides an economic advantage since all of a plants products may be anodized using only one universal process.

INTRODUCTION

The chromic acid anodizing process for corrosion protection of structural aluminum alloys was invented and subsequently patented by Bengough and Stuart in 1923. Their process, called the Bengough-Stuart[1] cycle, utilized a complex voltage control procedure (0 to 40 volts in 15 minutes, 35 minutes at 40 volts, 5 minutes from 40-50 volts and 5 minutes at 50 volts) applied to aluminum alloys in a 3% by wt. chromic acid aqueous solution operated at 100°F. In 1937, Robert W. Buzzard[2] at the National Bureau of

Standards found that by increasing the chromic acid concentration to 10% by wt. the complicated voltage variance cycle could be eliminated and the process time decreased.

At that time the U.S. Navy[3] issued specification SR19c requiring salt spray exposure of 30 days with subsequent tensile elongation losses of the treated aluminum alloys not to exceed 10%. Later, in 1941, a Government specification AN-QQ-A696[4] specified a 250 hour salt spray resistance for aluminum alloys containing less than 5% copper. This specification required a 40 volt D.C., 95°F, 10% by wt. chromic acid anodize at 95°F.

Military Specification MIL-A-8625A for all departments and agencies of the U.S. Department of Defense was first issued in 1954. It specified a 40 volt process. Change B (1969) to that specification dropped the 40 volt process requirement. At this time MIL-A-8625C, Amendment 1 specifies the current chromic acid anodize requirements[5]. It is a performance specification, requiring certain performance in coating weight, salt spray corrosion resistance, etc., whereas the previous "A" version specified a 40 volt process.

A search of the literature 6, 7, 8 revealed that variations in process operating parameters could have distinct effects on coating weights and subsequent salt spray corrosion resistance. A test plan was developed and a program was conducted to determine the effects of single, controlled, variations in voltage and temperature on anodizing of 2024 in the -T3 and -T81 tempers and overaged 7000 series aluminum alloys.

SUMMARY

Aluminum alloy specimens were anodized using constant chromic acid content solution but varying the voltage, time and solution temperature. Voltage variations of 18, 20, 22, 30, and 40 volts were made on individual sets of duplicate coating weight test specimens. Also temperature variances of 95, 105, and 115°F were applied and their effects on coating weights were obtained for the overaged 7000 series aluminum alloys without significant changes in the 2000 series coating weights.

The variables study revealed that a voltage of 20 and a temperature of 105°F for a unit time provided the highest anodize coating weights and small differentials between the two series of aluminum alloys. A process temperature of 95°F provided more uniform coating weights with only slight decreases in coating rate (coating weight/unit time).

Other process variables investigated, and their ultimate effect on salt spray corrosion resistance and paint adhesion, were sealing methods and percent hydration. Sealing methods investigated were hot water, chromic acid, Alodine 1200S* and sodium dichromate seals. These sealing methods investigations included the effects of delay times between anodizing and paint-

* Amchem Products, Inc.
Ambler, Pa.

ing. Ultimately, three promising 20 volt processes were evaluated for salt spray corrosion resistance, initial and delayed application paint adhesion and degree of reduced fatigue strength. With a sodium dichromate seal the 20 volt process met or exceeded the program objectives. The 20 volt, 95°F, 45 minute chromic acid anodize with a dichromate seal was the final selection based on salt spray corrosion resistance and paint adhesion.

OBJECTIVES

1. UNIFORM COATING WEIGHTS ON ALL ALLOYS
2. PASS MIL-A-8625C (1) SALT SPRAY REQUIREMENTS
3. PASS MIL-F-18264D PAINT ADHESION (WET TAPE)
4. REDUCE PROCESS TIME

PROCEDURES

TECHNICAL APPROACH:

1. Apply voltage variations of 18, 20, 22, 30, and 40 volts for one hour.
2. Apply temperatures variances of 95, 105, and 115°F for one hour.
3. Determine and plot their effects on coating weights.
4. Select the voltage, extrapolated time and temperature which provides the most uniform coating weights.
5. Apply these select parameters to test specimens and determine salt spray corrosion resistance and paint adhesion.

6. Select the three most promising processes

   a. Investigate sealing methods

   b. Concurrently determine

      (1) Salt spray corrosion resistance

      (2) Initial paint adhesion

      (3) Delay time paint adhesion

      (4) Metal fatigue strength reduction

TEST SUBSTRATES:

Substrates were aluminum alloys, .040" bare sheet; 2024-T3, 2024-T81, 7075-T73, 7475-T73, and 7475-T7351 plate. Plate specimens 0.125" thick of 7475-T7351, were sawed from .520" thick plate and tested with the "as sawed" surface. Their thickness was approximately 0.125". During the program it was determined that 2024-T3 and 7475-T73 alloys responded to treatment and were representative of the above group; therefore subsequent data was obtained on just those two substrates.

TEST SPECIMENS:

1. Coating weight: .040" x 4" x 4" in duplicate
2. Salt Spray: 5 specimens .040" x 3" x 10"
3. Paint Adhesion: .040" x 3" x 10" in duplicate

TEST FINISH:

Variations of chromic acid anodize, Process Standard[9] 74.02-3 and MIL-A-8625C.

SEALING METHODS:

1. Deionized water at 170°F (3 to 6 minutes)
2. Chromic acid (100 PPM) at 170°F and 200°F (3 to 16 minutes)
3. Sodium dichromate (5%) at 200°F. (4 to 16 minutes)
4. Alodine 1200S at room temperature (1½ minutes)

INTERIM CLEANING:

Post anodize and at specific delay times as reported later.

1. MIL-C-25769[10]

   1:10 water volume ratio, spray flow coating for five minutes, tap water rinse and dry

2. MIL-C-38334[11]

   1÷10 water volume ratio, spray flow coating for 2 minutes, tap water rinse and dry

3. MIL-C-5410[12]

   1:15 water volume ratio, spray flow coating for 2 minutes, tap water rinse and dry

4. MIL-C-5541[13]

   Alodine 1200S
   1 oz/gal, spray flow coat for 2 minutes, tap water rinse and dry

5. MIL-C-38736[14]

General purpose (solvent) cleaner applied by hand wipe with cheesecloth.

PAINT (SECONDARY, FINAL) FINISH:

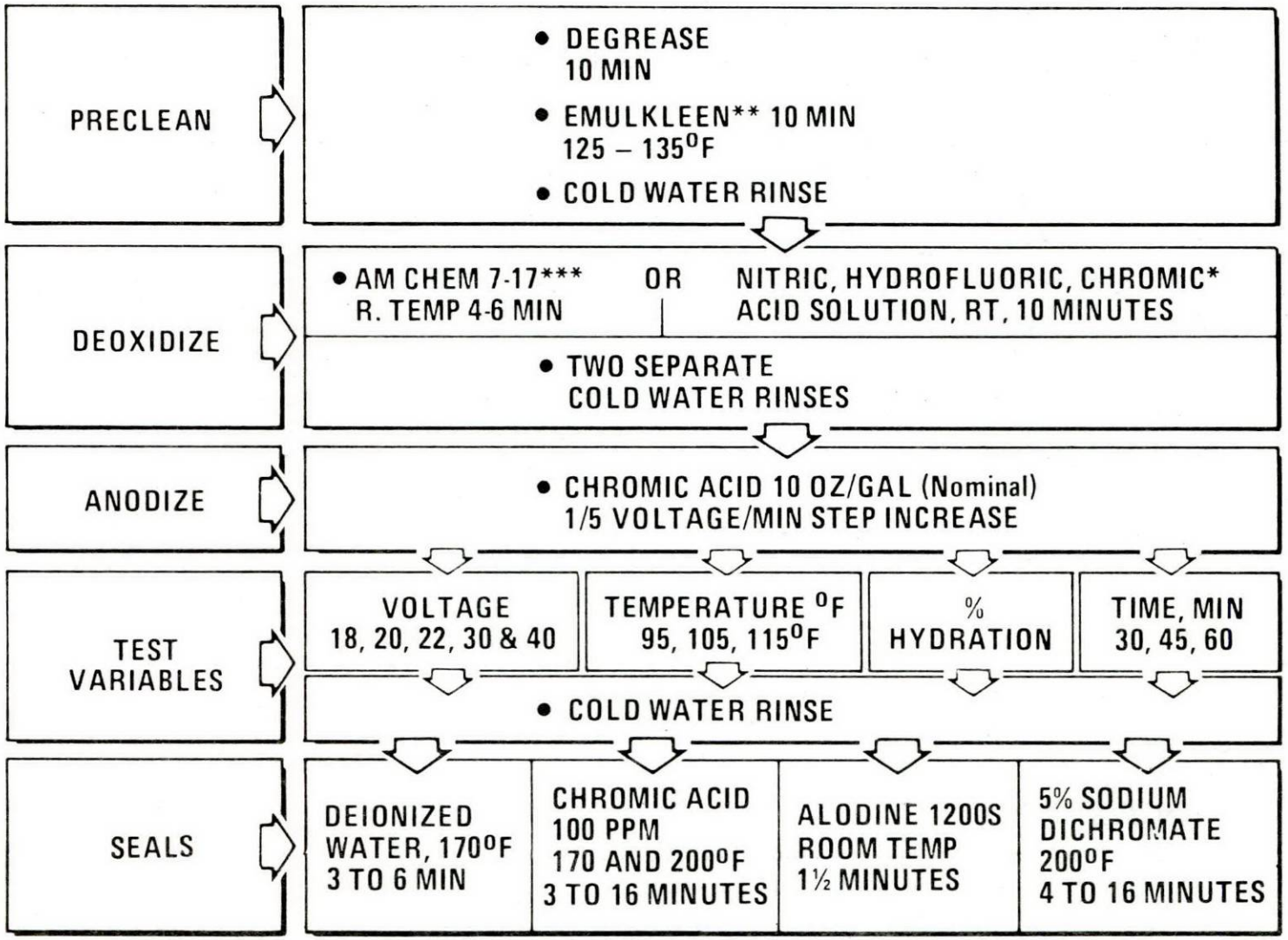
- o One coat of MIL-P-23377[15] primer with a cured finish thickness of 0.0004" to 0.0007". The cure period was seven days at room temperature.
- o Two coats (five minutes between coats) of MIL-C-27725[16] polyurethane fuel tank coating with a finished cure thickness 0.0008 to .0012". Cure period was 14 days at room temperature.

DETAILED EXPERIMENTAL PROCEDURES:

Specimen fabrication, age, temper verification, identification and test distribution was as illustrated in Table I. Cleaning and anodizing was accomplished as shown in Table II. Post anodize delay times, cleaning and subsequent painting and paint adhesion testing was as shown in Table III.

Coating weights were determined by "before" and "after" stripping weight loss differential as detailed in MIL-A-8625C. Salt spray exposure was 336 hours in 5% salt spray at a 6° angle from vertical as specified. The "pass" or "fail" criterion was as specified in paragraph 3.10.1.2, "the specimen panels or finished products shall show no more than a total of

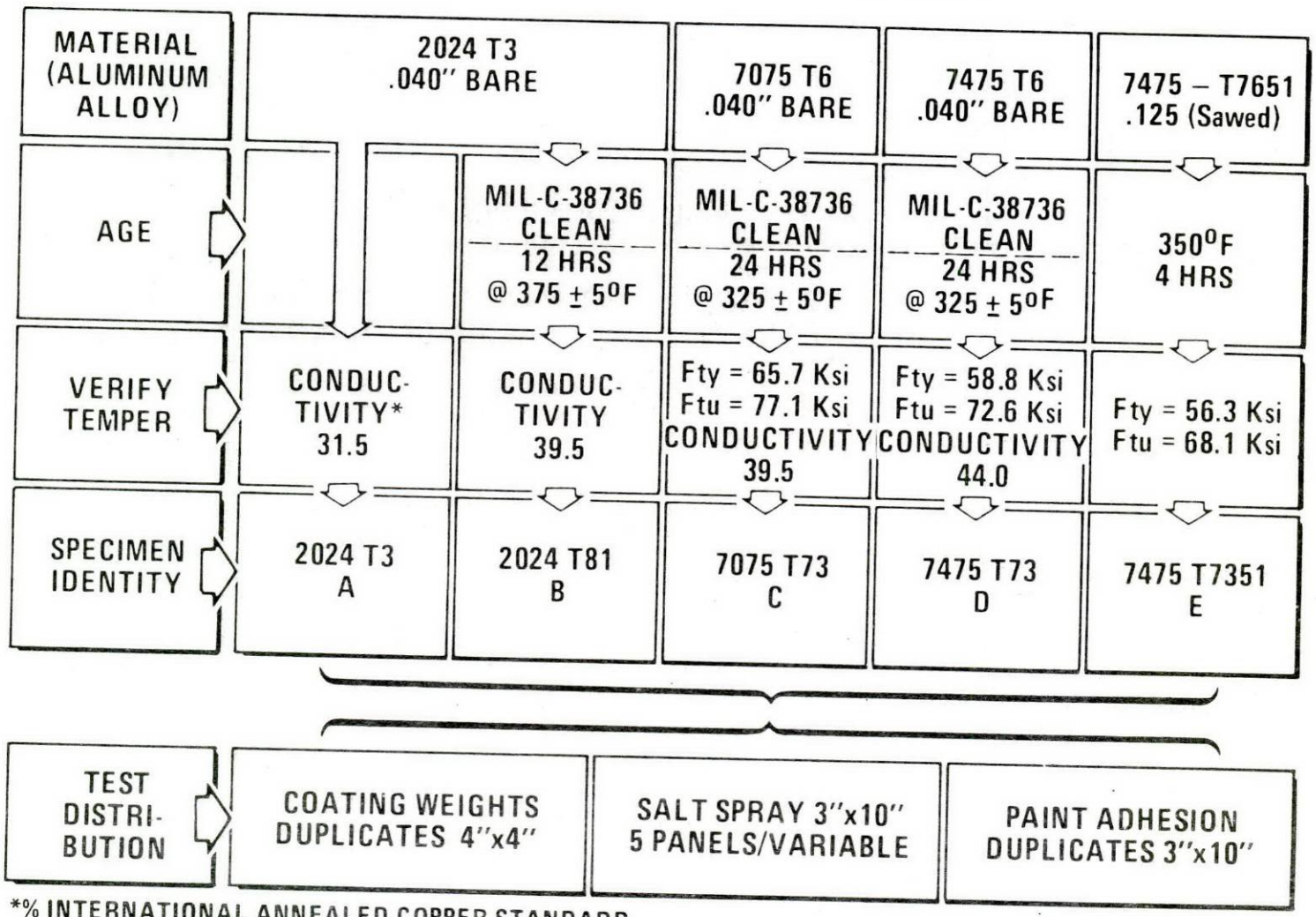
Table I SPECIMEN CLEANING AND ANODIZING*



*PER PROCESS STANDARD 74.02-3 **TURCO PRODUCTS, CARSON, CALIF

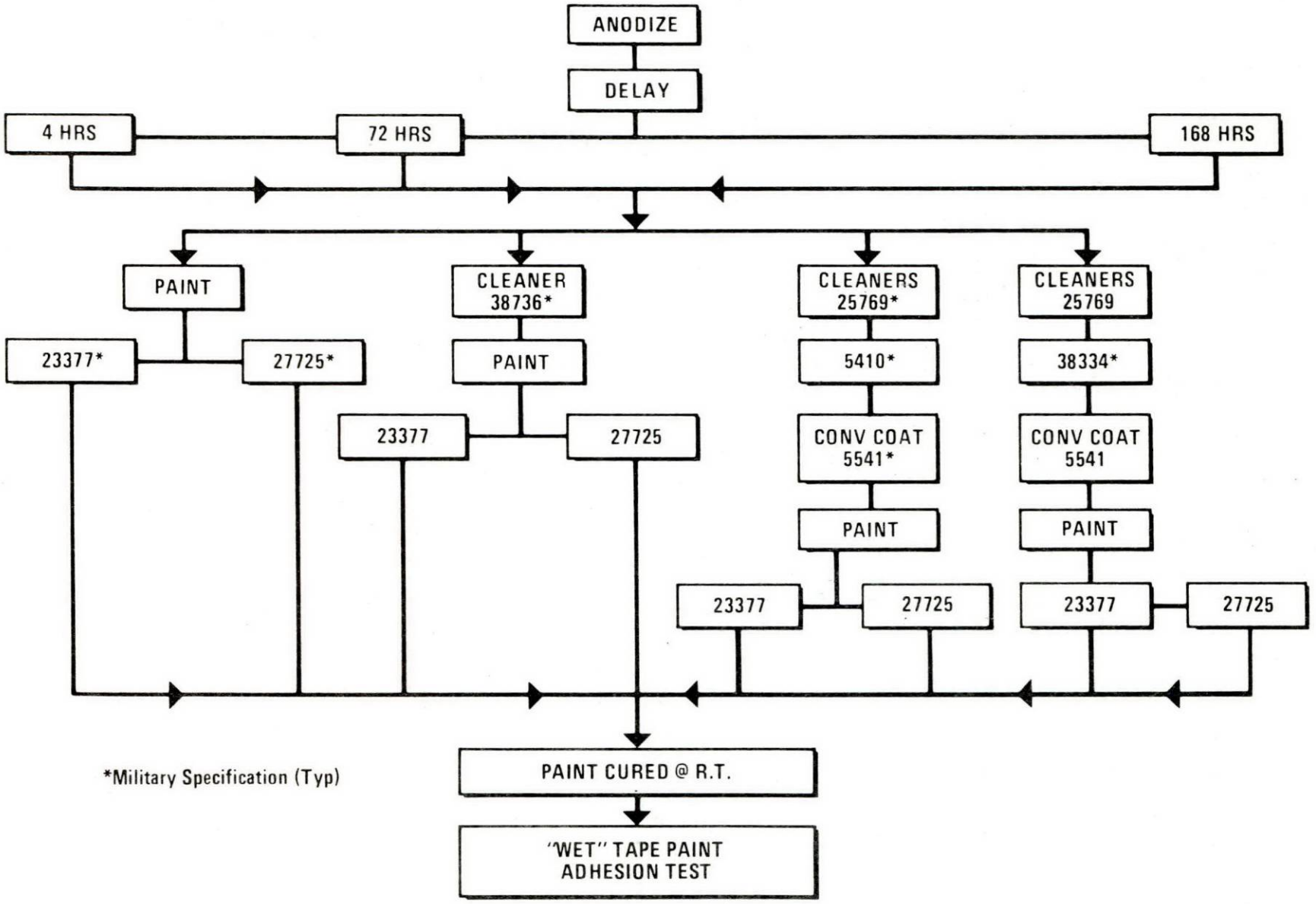
***AM-CHEM PRODUCTS INC, AMBER PENN

Table II SPECIMEN PREPARATION AND TEMPER VERIFICATION



*% INTERNATIONAL ANNEALED COPPER STANDARD

Table III THREE PROCESS EVALUATION (20 Volt CAA) ANODIZE/TIME DELAY/CLEAN/PAINT/TEST
2024-T3 AND 7475-T73 ALLOYS



15 isolated spots or pits, none larger than 1/32 inch in diameter, in a total of 150 square inches of test area grouped from five or more test pieces; nor more than 5 isolated spots or pits, none larger than 1/32 inch in diameter, in a total of 30 square inches from one or more test pieces; except those areas within 1/16 inch from identification markings and electrode marks remaining after processing".

Paint adhesion tests panels with the controlled variations in anodize process parameters received one coat of MIL-P-23377 epoxy primer or two coats of MIL-C-27725 fuel tank polyurethane coating to required thicknesses as specified earlier. After the required paint cure period, paint adhesion specimens were soaked 24 hours in distilled water and scribed as specified in MIL-F-18264 [17]. An X-ACTO knife was used for scribing and 3M* tape number 250 was used to apply adhesive stresses on the paint to anodize bond. Any microscopic (4X) evidence of loss of paint adhesion along the scribe lines was regarded as an adhesive failure of the paint system to the chromic acid anodize.

*3M Company
St. Paul, Minnesota 55101

Metal fatigue (substrate) effects of the various selected anodize processes was determined. Substrates for the various chromic acid anodize coatings were bare aluminum alloy 7475-T7351.

These $K_t = 2.4$ test specimens were fabricated as shown in Figure 1. The stress concentration of $K_t = 2.4$ is the stress at the edge of the center specimen hole provided by that particular hole/specimen dimension. The K_t value is based on Peterson's[18] curves. These test specimens were tested on a BLH* Model SF-10-U test machine. The R value (ratio of min. to max. loads) was 0.1 for the applied tension-tension fatigue loads. Triplicate specimens were run for each test variable. A standard four stress level fatigue curve was run with bare controls and 25 KSI was chosen as the most significant portion of the curve. A number of other specific conditions such as reamed holes, and ream followed by chem film were also determined for reference.

* Baldwin-Lima-Hamilton Co.
Philadelphia, Pa.

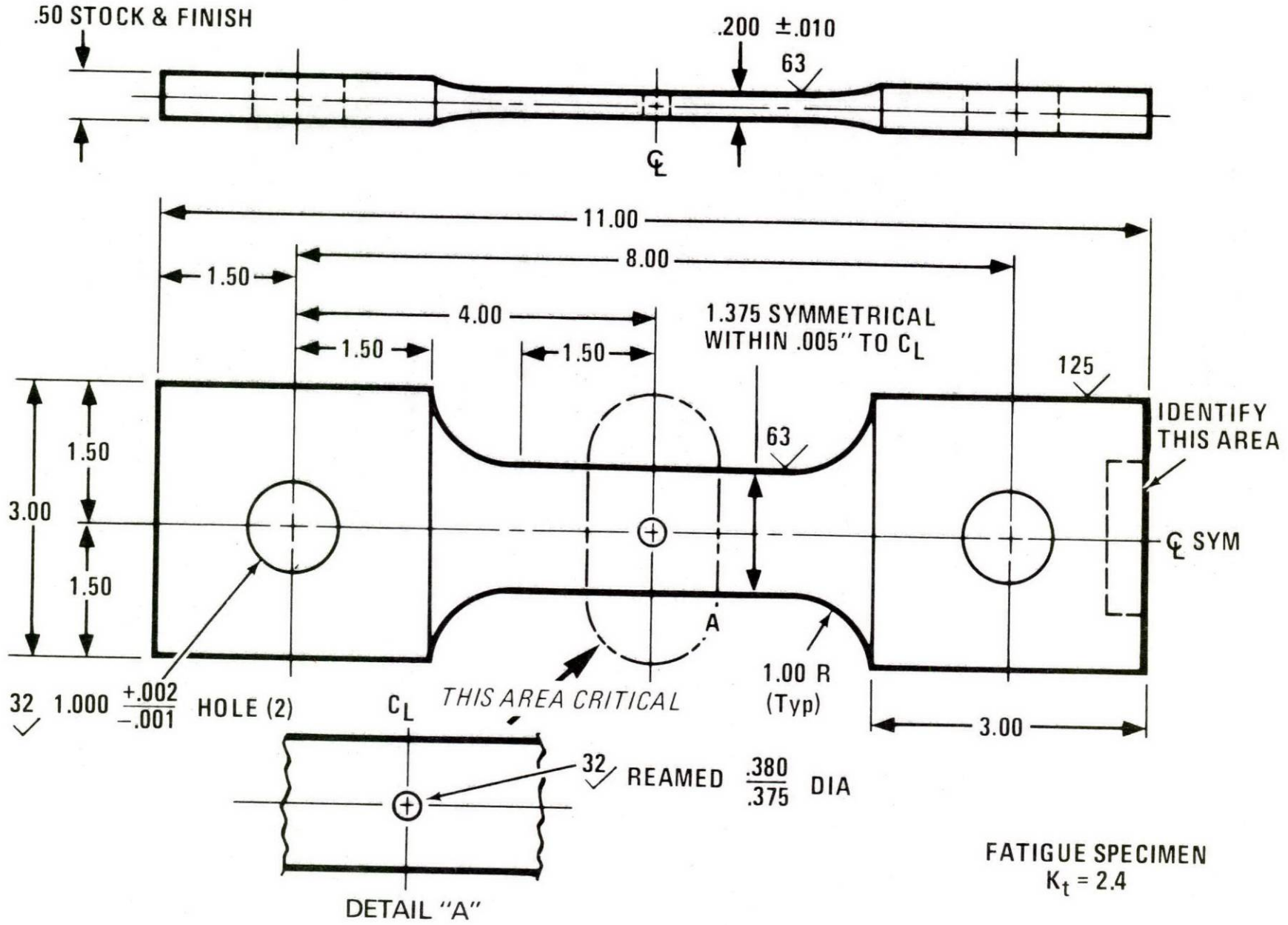


Figure 1 Aluminum Alloy 7475-T7351 Plate Specimens

RESULTS AND DISCUSSION

DEVELOPMENT OF THE 20 VOLT SYSTEM:

A synopsis of the variables and their effect is presented in Figure 2. The coordinates for the five principal alloys have voltage variables on the abscissas and the other ordinate expresses coating weights. Plots of three tank temperatures at the three controlled voltages comprise test data.

By the Process Standard 74.02-3 system which specified 40 volts at 95°F for 1 hour, the high coating weights, e.g., 550 to 850 mg/ft^2, for the 2024-T3 and 2024-T81 aluminum alloys may be seen in Figure 2. Correspondingly low coating weights for the 7000 series in the range of 90 to 400 mg/ft^2 at 40 volts, 95°F were the usual coatings for the overaged 7000 series alloys. Examination of all five alloys at 30 volts revealed little change in coating weights; however, a change to 20 volts anodizing potential had significant effects on coating weights. At 20 volts all coating weights were 300 mg/ft^2 or higher. By raising temperature to 105°F all coating weights were 525 mg/ft^2 or better. Although 20 volts substantially increased coating weight for the overaged 7000 series alloys, the other alloys, (2024-T3 and 2024-T81) coating weights were not increased appreciably. In essence the 20 volt system at 95°F or 105°F

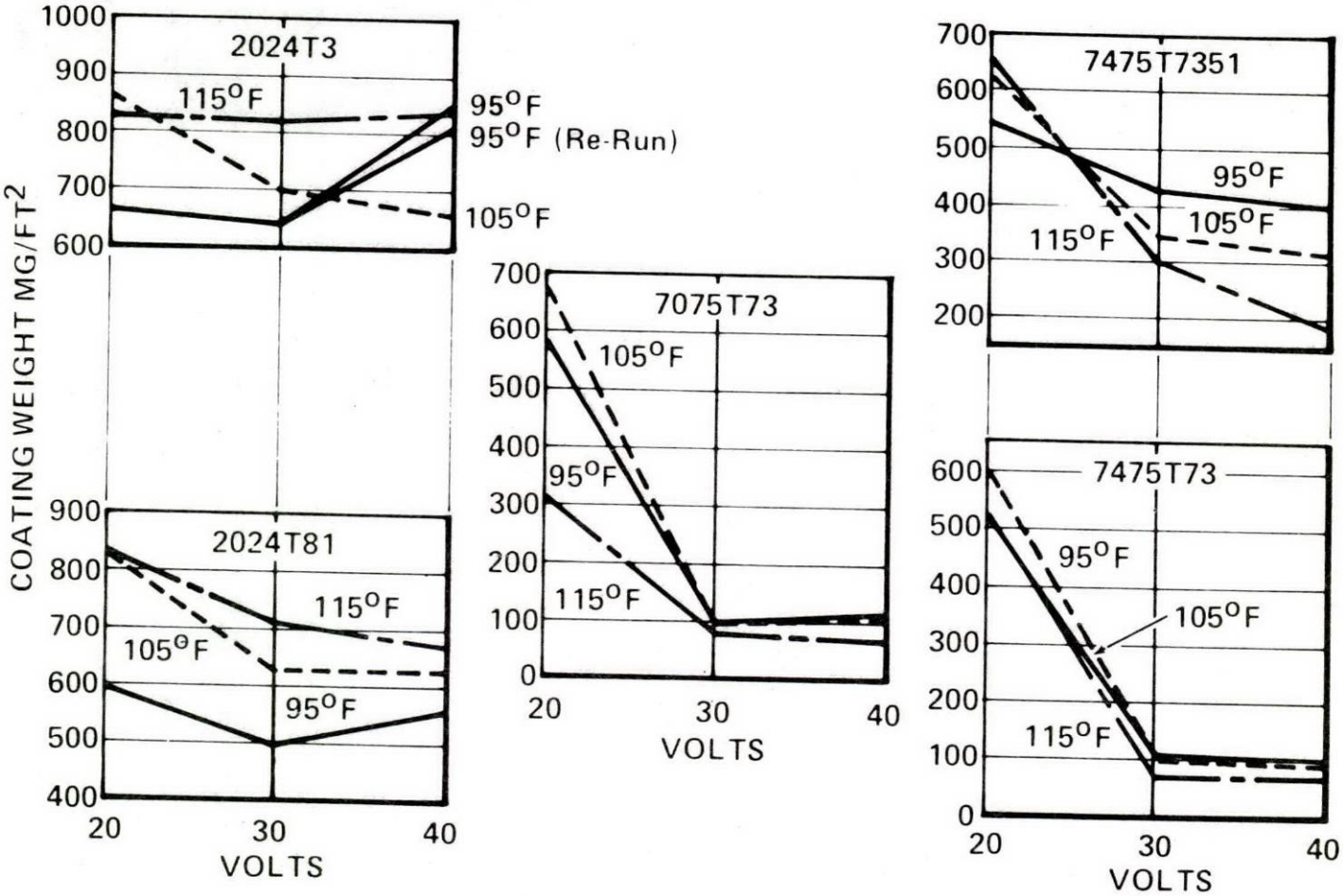


Figure 2 Chromic Acid Anodize – Effects of Process Variables on Bare Aluminum Alloys Per Process Standard 74.02-3 Anodize Time 1 Hour (All)

provides greatly improved coating weights of the overaged 7000 series alloy without undesirably increasing the 2024 alloy coating weights.

Extracting the 20 volt data and expressing it in terms of increasing temperature was accomplished in Figure 3. At 95°F coating weights were generally lower but more uniform or had less variance between the five principal aluminum alloys. Raising the chromic acid anodize process tank temperature to 105°F provided heavier coating weights per unit time. Variance between alloys was also increased but the approximate 250 mg/ft^2 differential was not considered prohibitive. However, at a 115°F tank temperature unacceptable variance occurred and the 7075-T73 alloy coating weight had dropped to approximately 300 mg/ft^2. The Electroplating Engineering Handbook[19] states that 120°F tank temperatures are commonly used when the anodize coating is to be dye impregnated and that powdery coatings are likely to form if tank temperatures exceed 125°F. This suggests that higher temperatures, probably 115°F and higher produce more porous coatings which should have less salt spray corrosion resistance and inadequate paint adhesion.

At this point in the program the topics, best described as "fine tuning at 20 volts" and "what is the electrochemistry involved that allows one to reduce voltage but produce higher

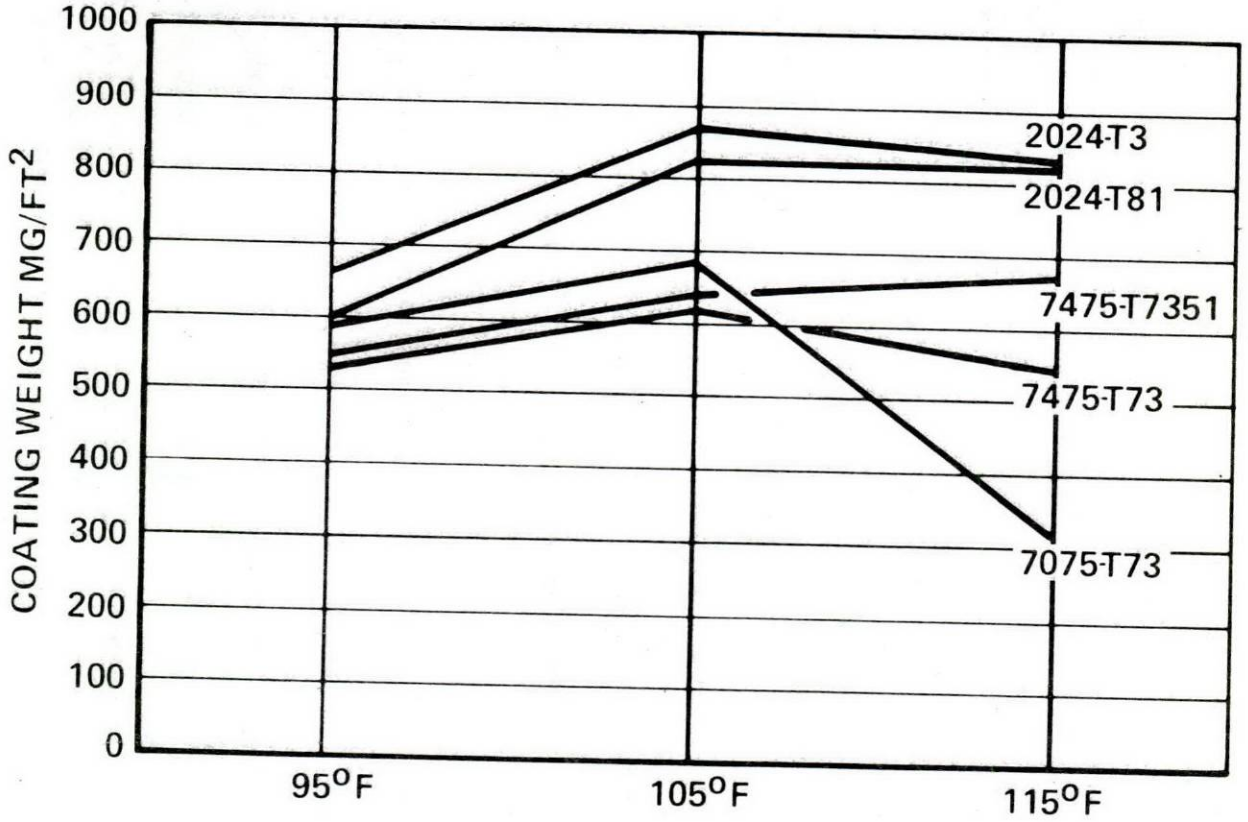


Figure 3 20 Volts at Three Temperatures Per Process Standard 74.02-3 Anodize Time 1 Hour

anodize coating weights", became the principal concern. Figure 4 illustrates more select voltage variations of 18, 20, and 22 volts at 105°F for the unit time of 1 hour. Again, as experienced earlier, higher voltages produce more variance in the five alloys coating weights and actually decreased the coating weight of overaged 7000 series alloys. The military specification for anodizing, MIL-A-8625C,broadly addresses the problem in stating "alloys containing 5% copper and/or those containing 7.5% total alloy elements shall not be chromic acid anodized but sulfuric acid anodized instead". Translating that implication to terms of electrical conductivity as shown in Figure 4, it was apparent the phenomenon was based on inverse conductivity. Related to conductivity of the aluminum alloy, whereby annealed copper is 100%, the overaged 7000 series alloys are more conductive than the 2000 series and the most conductive of the alloys, 7475-T73, typically received less coating weight.

Electrochemically, it is known that the chromic acid anodizing process has the specimen or part as the anode (+) in an aqueous 10% solution of chromic acid. As voltage exceeds approximately 2 volts the water dissociates into oxygen at the anode (specimen) and hydrogen at the cathode. The quantity or rate of oxygen subsequently produced is in a ratio to

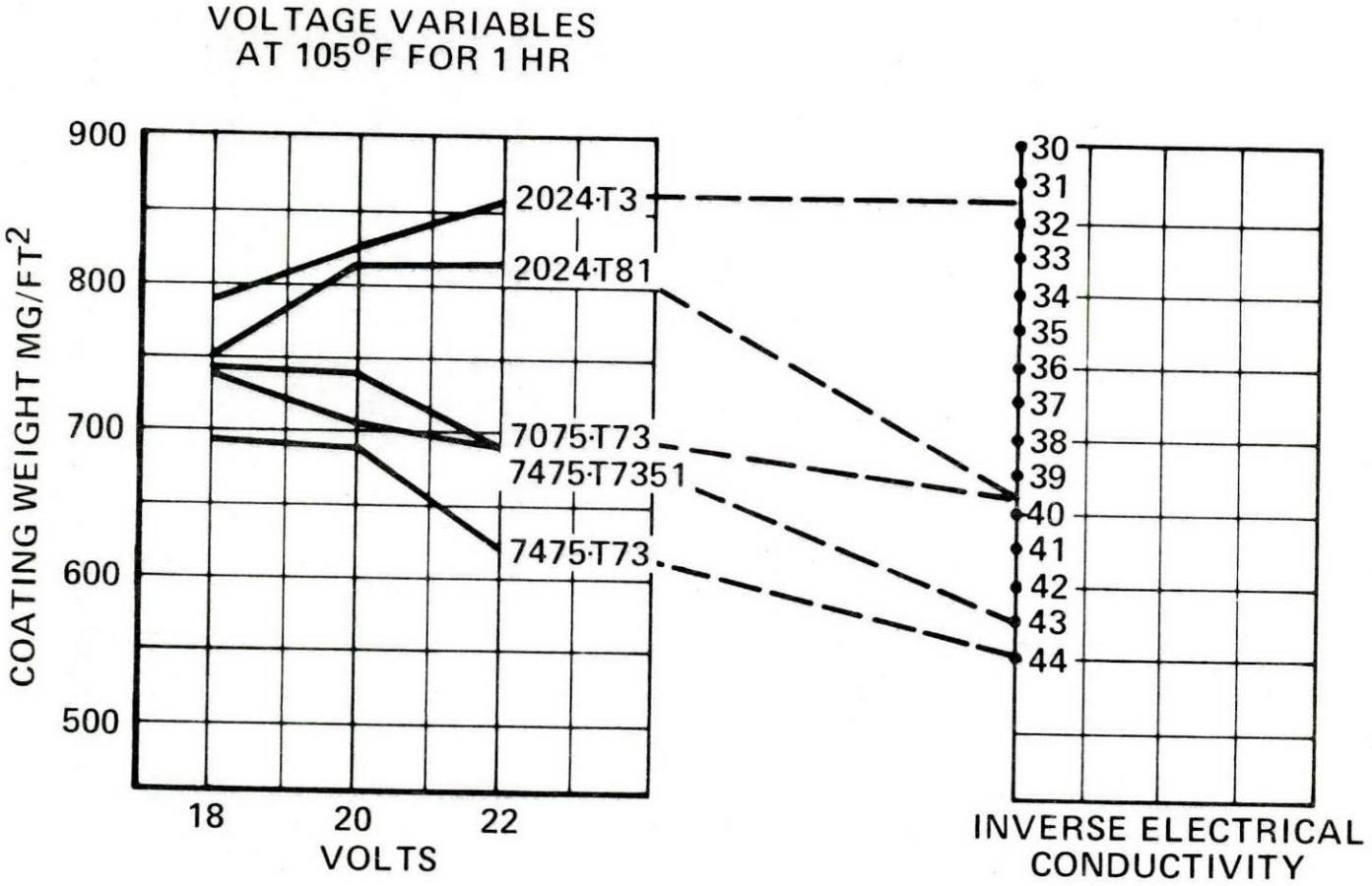


Figure 4 Other Voltage Variables and Their Relation to Alloy Conductivity

voltage. The electrochemically produced oxygen reacts with the aluminum substrate to produce aluminum oxide. Chromic acid serves principally as the electrolyte but small quantities are retained in the oxide film which additionally inhibits corrosion.[20]

It appears that the initial design of the 40 volt system was suitable for the originally studied 2024-T3 aluminum alloy but a more conductive alloy such as 7075 provided too much electrical current conductivity, thus producing an excessive and inhibiting quantity of oxygen on the surface. Rather than lower the voltage to approximately 20 volts which would have had minimal effect in reduced coating weights on 2024 aluminum alloy, the 7075 alloy was directed by specifications to the sulfuric acid anodize process. Ironically, this "successful" sulfuric acid anodize process operated at 14-18 volts as shown in Table 4. Although aluminum oxide coatings were also produced in the sulfuric acid anodizing process, they were not as corrosion resistant; thus requiring coatings of 600 mg/ft^2 to pass equivalent salt spray requirements for chromic acid anodize with a 200 mg/ft^2 minimum coating weight requirement.

The first experiences in a large 8600 gallon production tank of chromic acid are shown in Figure 5. Identical specimens from common sheets of aluminum were selected, aged, precleaned

Table IV ANODIZE PROCESS COMPARISONS

	CHROMIC ACID	SULFURIC ACID
• TEMPERATURE (°F)	95	60–80
• VOLTAGE	40	14–18
• CONCENTRATION % WEIGHT	10	20
• MG/FT^2 MIL-A-8625C	200	600
• CURRENT STABILITY	DECREASE	STABLE

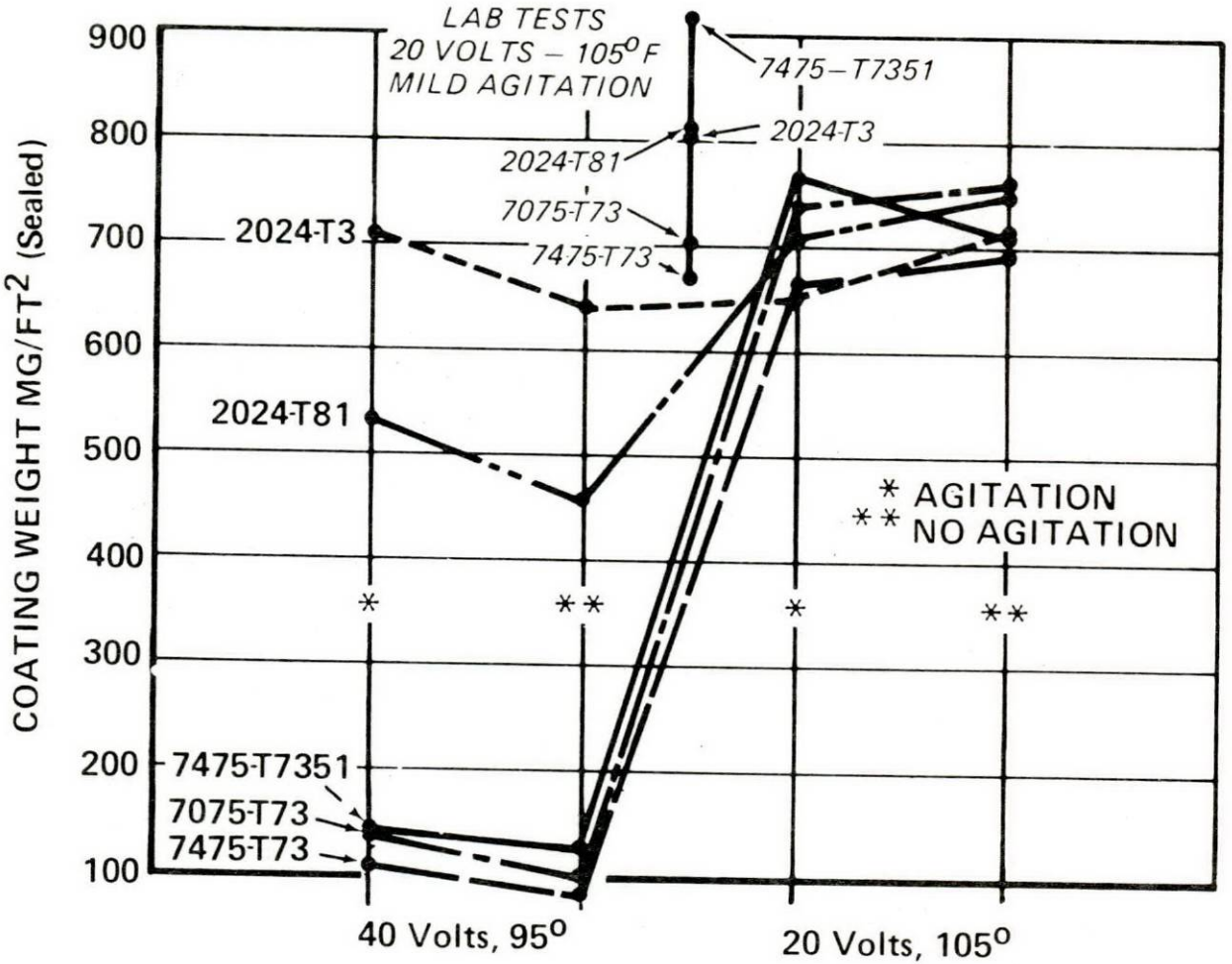


Figure 5 Variables Applied in Shop Tank of Chromic Acid (60 Minutes per PS 74.02-3)*

as reported earlier in Tables I, II and anodized as shown in Figure 5 at either 20 or 40 volts. Data were also taken with and without air agitation. As seen earlier in the laboratory tank, wide variations in coating weights were experienced at 40 volts but very uniform and much higher coating weights occurred at 20 volts. For comparison the lab tests were superimposed in Figure 5. It was obvious the 20 volt system is a distinct and workable improvement in the shop tank.

Having achieved uniform and consistently higher coating weights with the 20 volt system, another control factor, % hydration, which affects corrosion resistance and paint adhesion was studied. These % hydrations using a 170°F hot water seal time of 6-7 minutes with variations of 20 and 40 volts in the preceeding anodize process were determined in the production tank. Figure 6 illustrates the data. In the 40 volt system % hydrations varied from 27 to 70% but at 20 volts the % hydrations ranged from 18 to 25%. The former (40 volts on overaged 7000's) has relatively larger percent hydrations, because these thin coatings hydrate almost completely, thus the higher percents. These data support a conclusion that the 20 volt system will also provide more uniform control of % hydration.

SEALING METHODS INVESTIGATION:

A variety of post anodize sealing methods were investigated for two purposes 1) maximum corrosion resistance and 2) improved paint adhesion, particularly when applied at various

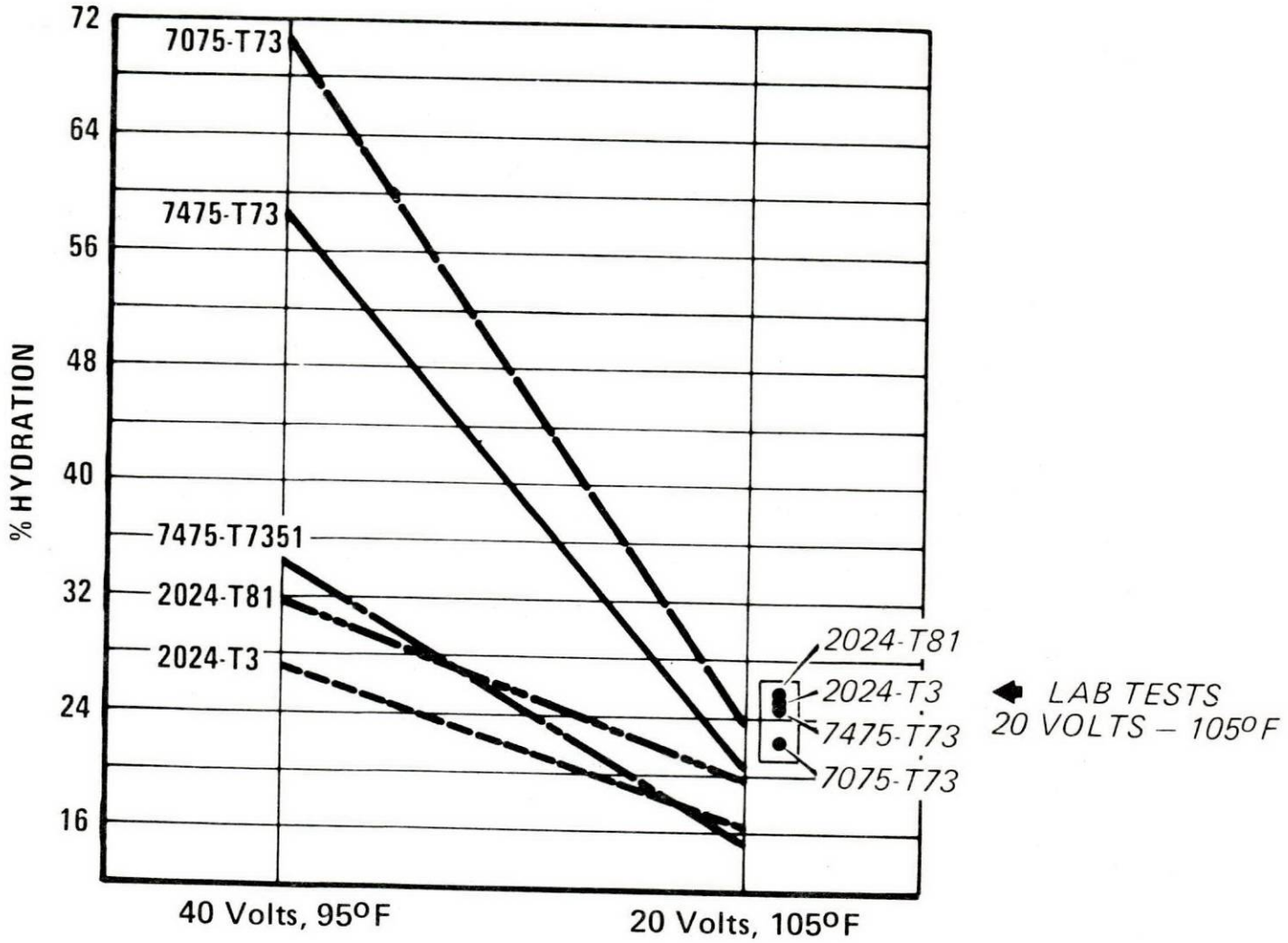


Figure 6 Effects of Variables Applied in Shop Tank on % Hydration
(60 Minutes Per PS 74.02-3 Seal Time 6 to 7 Minutes)

times after anodize.

The first data concerns hot water seal which is the most widely used sealing method for chromic acid anodize.[21] Figure 7 shows 170°F deionized water seals for a variety of seal times, process temperatures and process times. A four minute seal, 95°F, 20 volt anodize for 30 minutes provides the specification required salt spray and wet tape paint adhesion. Concurrent with the hot water seal testing, data were obtained concerning % hydration. Its relation to corrosion resistance and paint adhesion is displayed in Figure 8. The 95°F process provides more corrosion resistance and paint adhesion than the 105°F process. Again, the four minute seal, which provides approximately 21 to 24% hydration for the 95°F process, appears to be the best hot water seal time.

Figures 9 and 10 show the effects of chromic acid seals on the 20 volt chromic acid anodize process operated at 95°F, and 105°F and for 30 and 45 minute anodize process times. There were a multitude of salt spray corrosion and paint adhesion failures which precluded its further consideration as a viable seal media.

Another post anodize sealing method investigated was Alodine 1200S. The data for that task are shown in Figure 11.

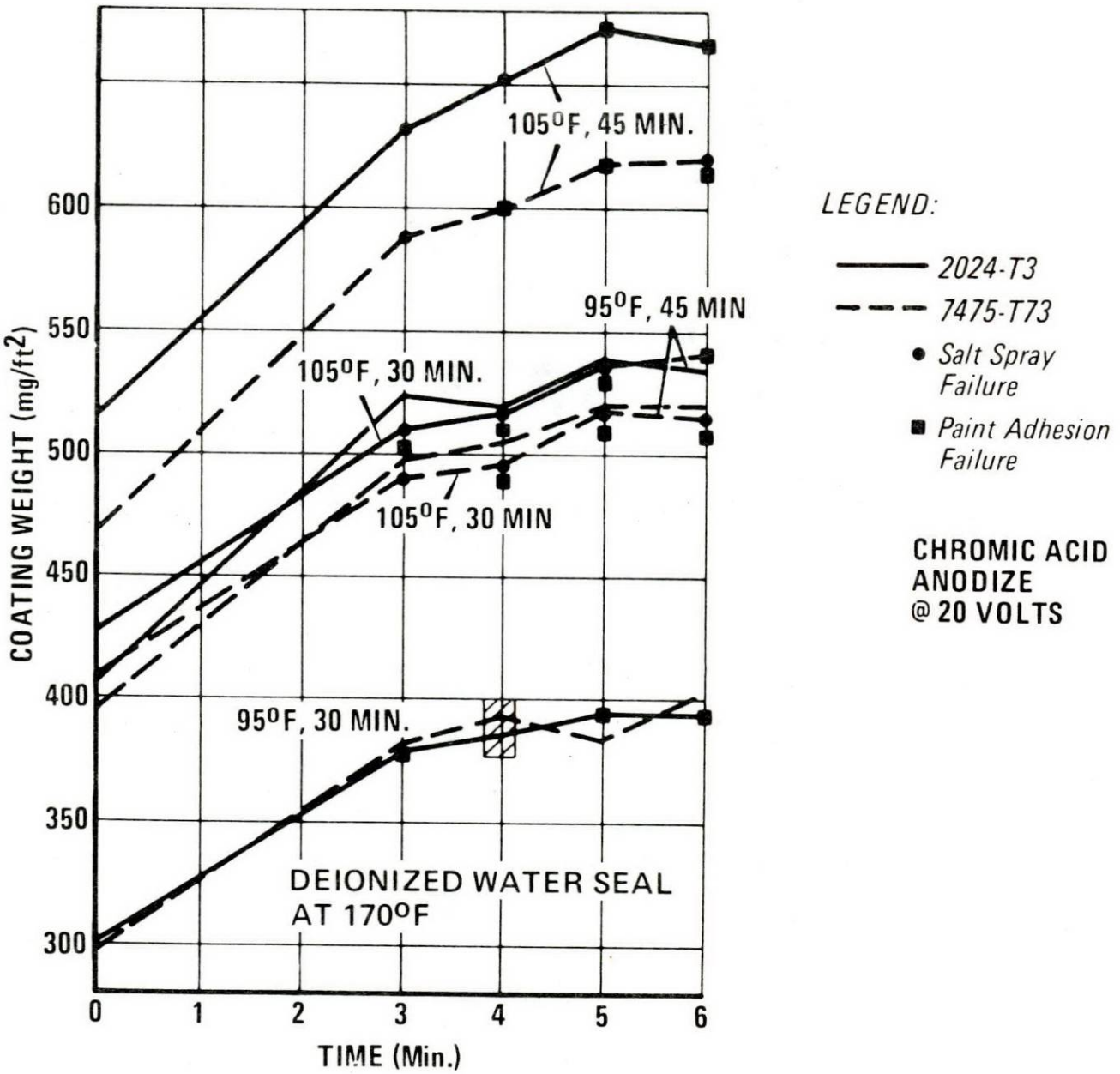


Figure 7 Effect of Water Seal Time on Salt Spray Corrosion and Paint Adhesion

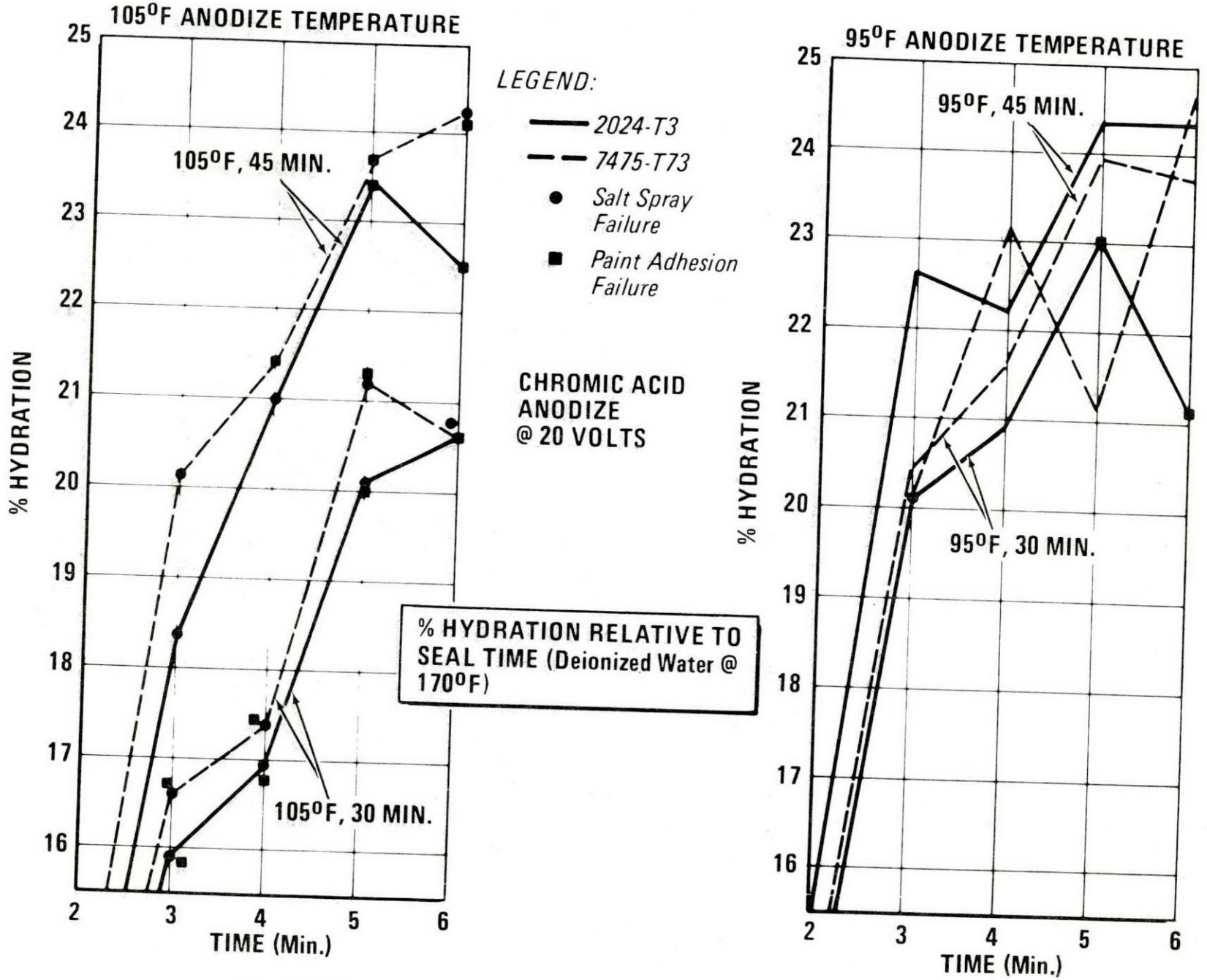


Figure 8 Effects of % Hydration on Paint Adhesion and Salt Spray Corrosion Resistance

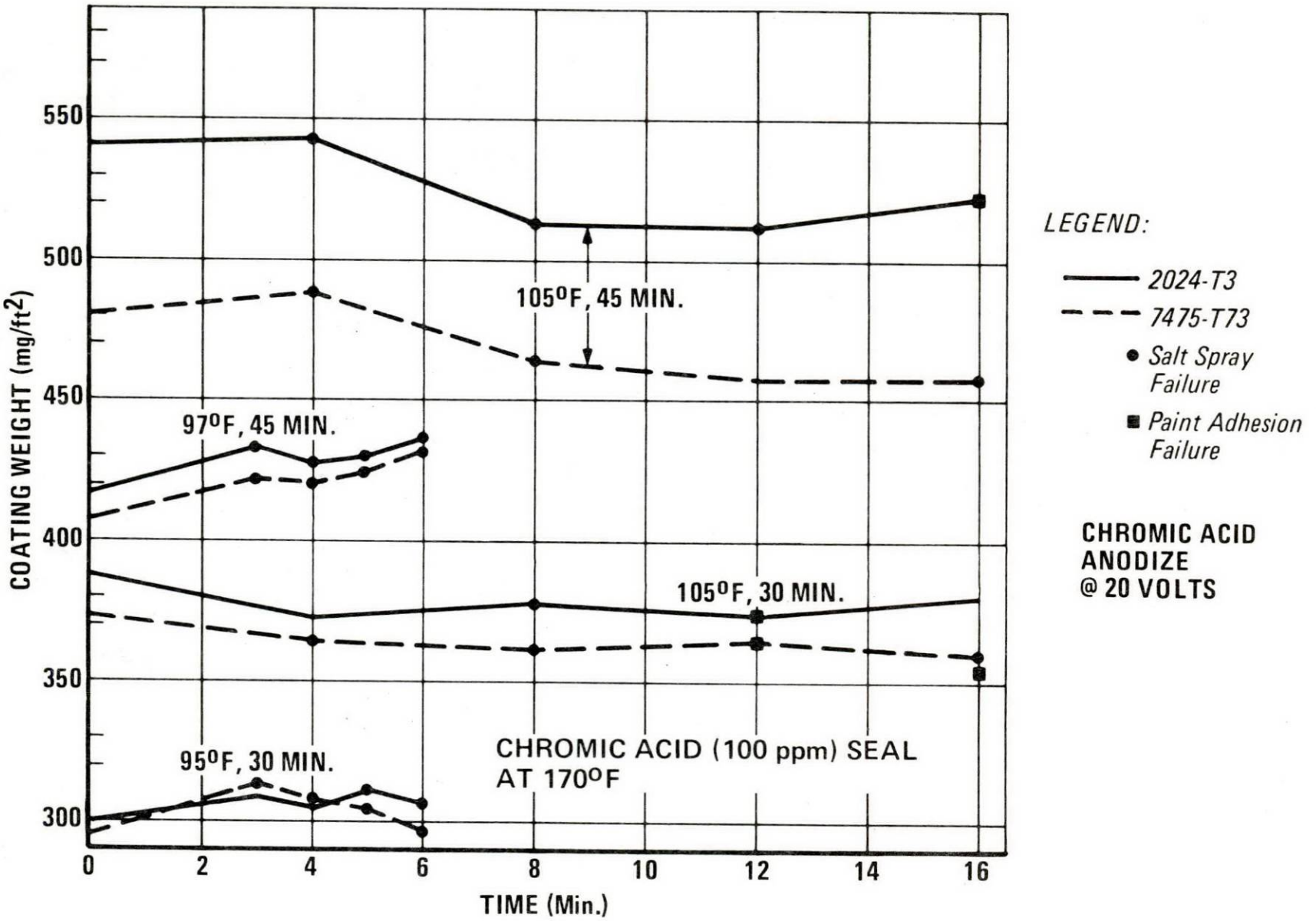


Figure 9 Effect of Chromic Acid Seal on Salt Spray Corrosion and Paint Adhesion

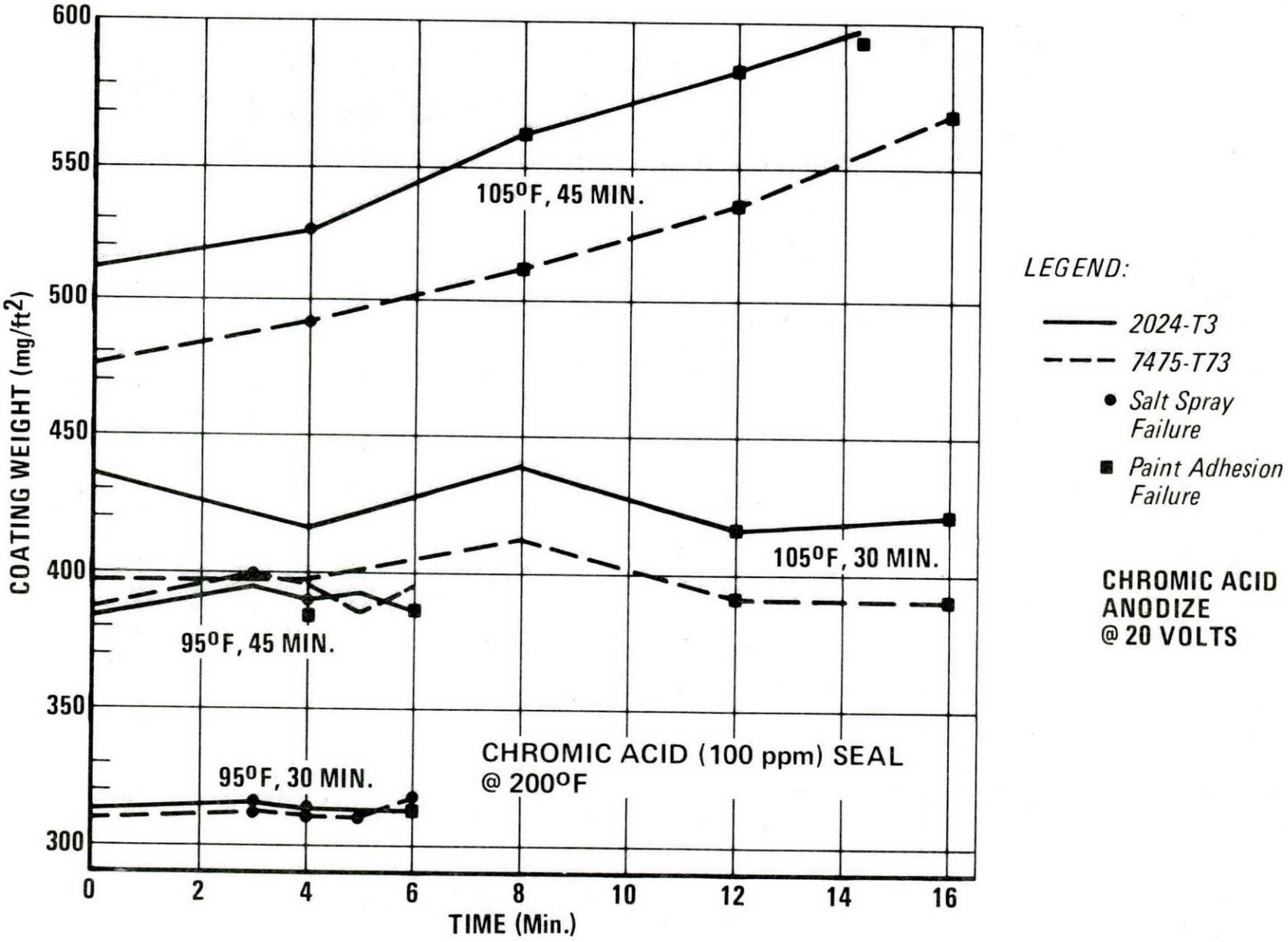


Figure 10 Effect of Chromic Acid Seal on Salt Spray Corrosion and Paint Adhesion

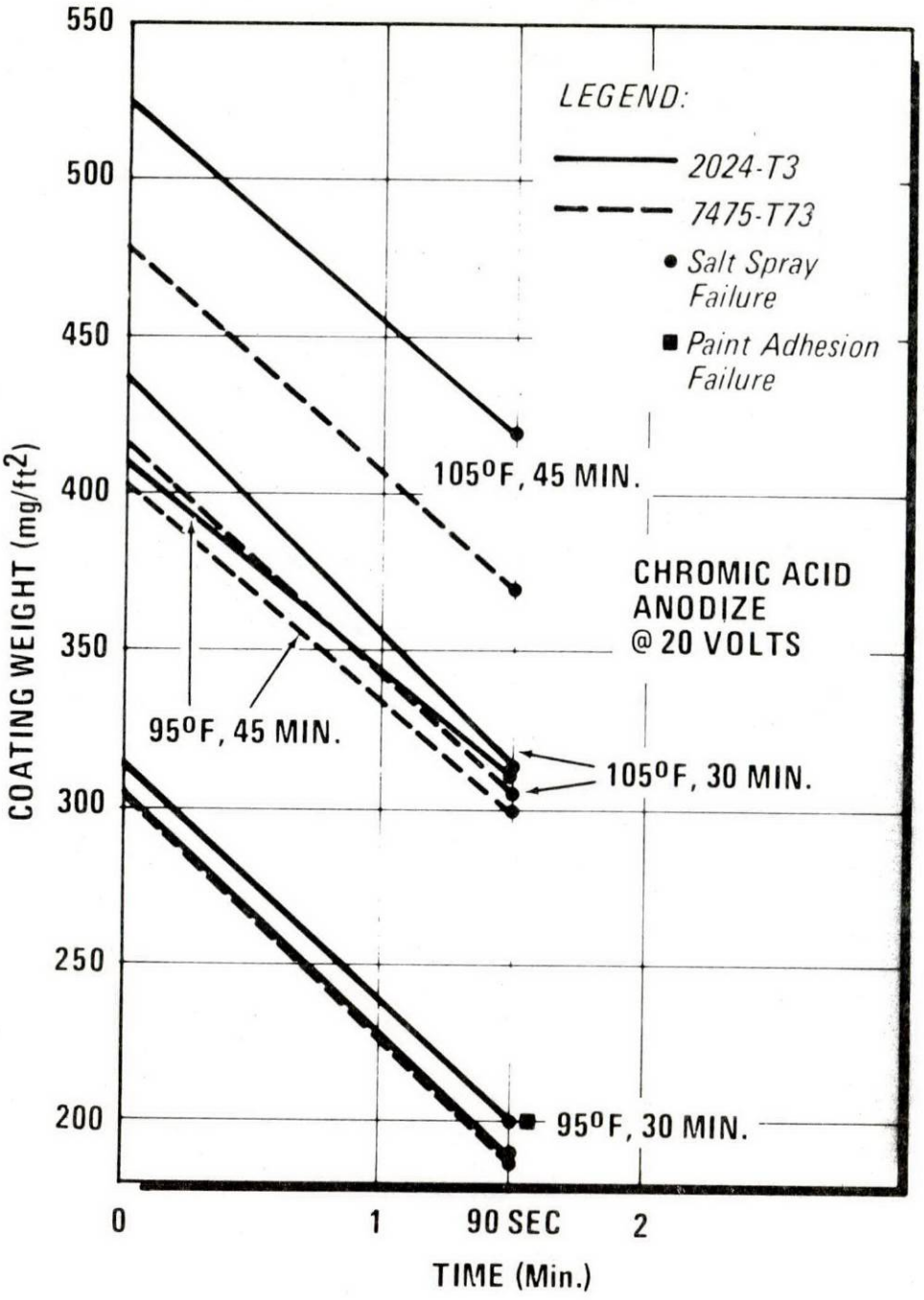


Figure 11 Effect of Alodine 1200S Seal (At 84°F) on Salt Spray Corrosion and Paint Adhesion

At the conventional 90 second application time all processes failed salt spray tests and there was one paint adhesion failure. Because of these failures, the Alodine 1200S was concluded to be an ineffective seal and it was dropped from further considerations.

The final seal investigated was a 5% sodium dichromate seal. Data for that method are shown in Figure 12. It was by far the most effective seal. Only one salt spray corrosion failure and one paint adhesion failure occurred and those were on the 95°F, 30 minute process with the lowest coating weights. Note also by comparing these data to Figure 6 that coating weights do not increase appreciably with time of seal immersion, which suggests that hydration does not occur.

THREE PROCESSES SELECTED:

Based on the previous reported and discussed data the following three 20 volt chromic acid anodize and seal methods were selected for final evaluation:

1. 95°F, 30 MINUTES, 170°F DEIONIZED WATER SEAL FOR 4 MINUTES
2. 95°F, 45 MINUTES, 170°F DEIONIZED WATER SEAL FOR 4 MINUTES

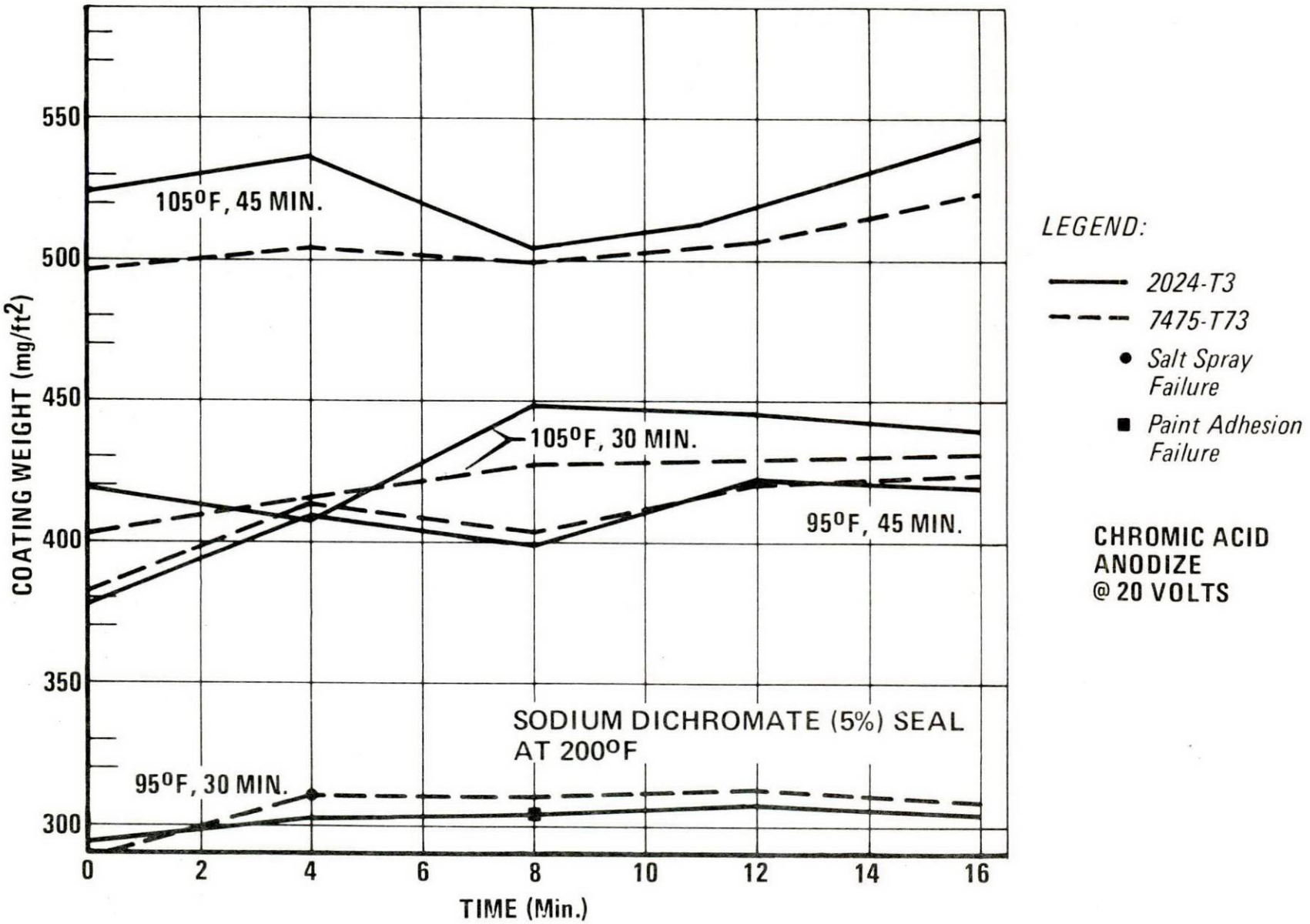


Figure 12 Effect of Sodium Dichromate Seal on Salt Spray Corrosion and Paint Adhesion

3. 95°F, 45 MINUTES, 200°F DICHROMATE SEAL (5%) FOR 10 MINUTES

Final choice to be based on outcome of anodize paint delay interval tests detailed in Table III and the effects on reduced fatigue strength.

Data for the 95°F, 30 minutes anodize with hot water seal are reported in Table V. There were twenty total "wet" tape paint adhesion test failures with the MIL-P-23377 primer system and eleven failures with the MIL-C-27725 polyurethane fuel tank coating. Minimal paint delay times with no post anodize cleanings provide the best adhesion but all things considered this anodize and seal system is marginal.

Data for the 95°F, 45 minute anodize with hot water seal appear in Table VI. The MIL-P-23377 primer system had 12 adhesi failures and the MIL-C-27725 fuel tank coating system had 14 "wet" tape paint adhesion failures. Delay times and subsequent cleanings prior to painting also produced more paint adhesion failures.

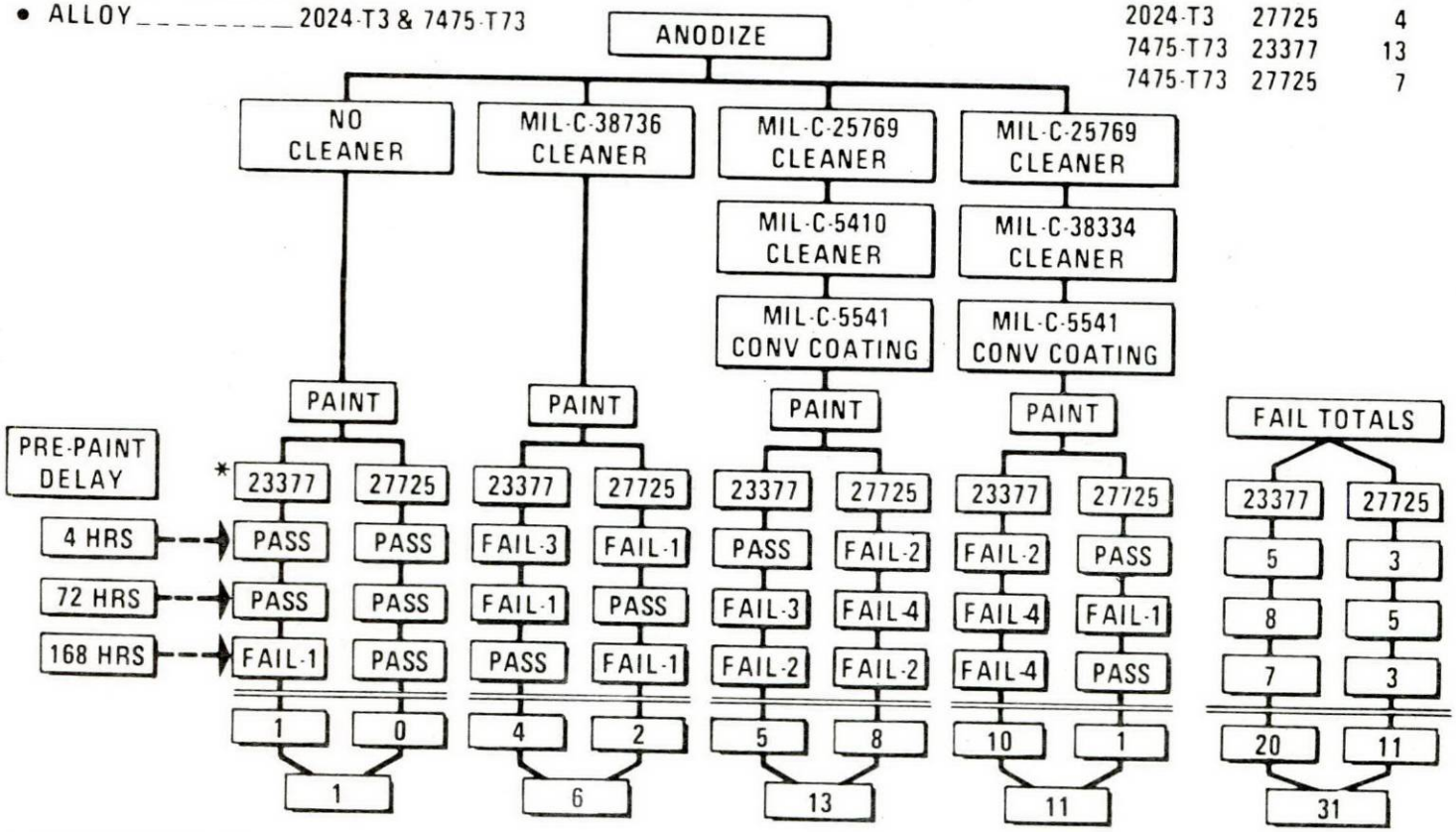
The third candidate process data, 95°F, 45 minutes with a sodium dichromate seal, are displayed in Table VII. There were no wet tape test paint adhesion failures for any condition. Delay times and post anodize, prepaint cleanings did not affect

Table V THREE PROCESS EVALUATION (20 Volt CAA) ANODIZE – TIME DELAY – CLEAN – PAINT – WET TAPE ADHESION TEST

- ANODIZE TIME____30 MIN.
- ANODIZE TEMP____95°F
- SEALING MEDIUM...DEIONIZED WATER
- SEALING TEMP____170°F
- SEALING TIME____4.0 MIN.
- ALLOY_____2024-T3 & 7475-T73

FAILURE BY ALLOY

ALLOY	PAINT	FAILED
2024-T3	*23377	7
2024-T3	27725	4
7475-T73	23377	13
7475-T73	27725	7



EACH PASS/FAIL BOX HAS 4 PANELS REPRESENTED

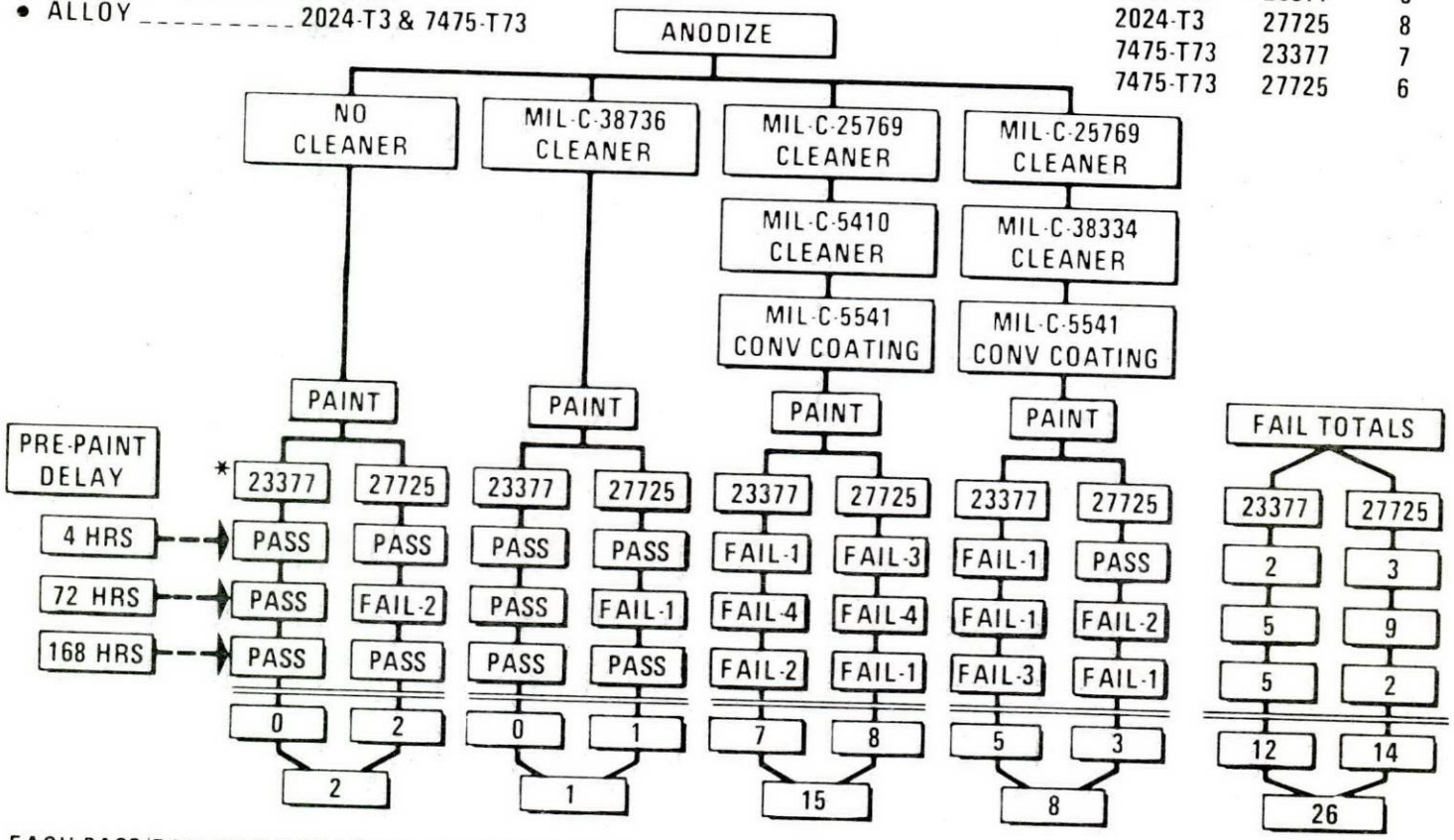
*MILITARY SPECIFICATION NO. (Typ)

Table VI THREE PROCESS EVALUATION (20 Volt CAA) ANODIZE – TIME DELAY – CLEAN – PAINT – WET TAPE ADHESION TEST

- ANODIZE TIME____45 MIN
- ANODIZE TEMP____95°F
- SEALING MEDIUM___DEIONIZED WATER
- SEALING TEMP_____170°F
- SEALING TIME_____4.5 MIN.
- ALLOY _____2024-T3 & 7475-T73

FAILURE BY ALLOY

ALLOY	PAINT	FAILED
2024-T3	*23377	5
2024-T3	27725	8
7475-T73	23377	7
7475-T73	27725	6



EACH PASS/FAIL BOX HAS 4 PANELS REPRESENTED

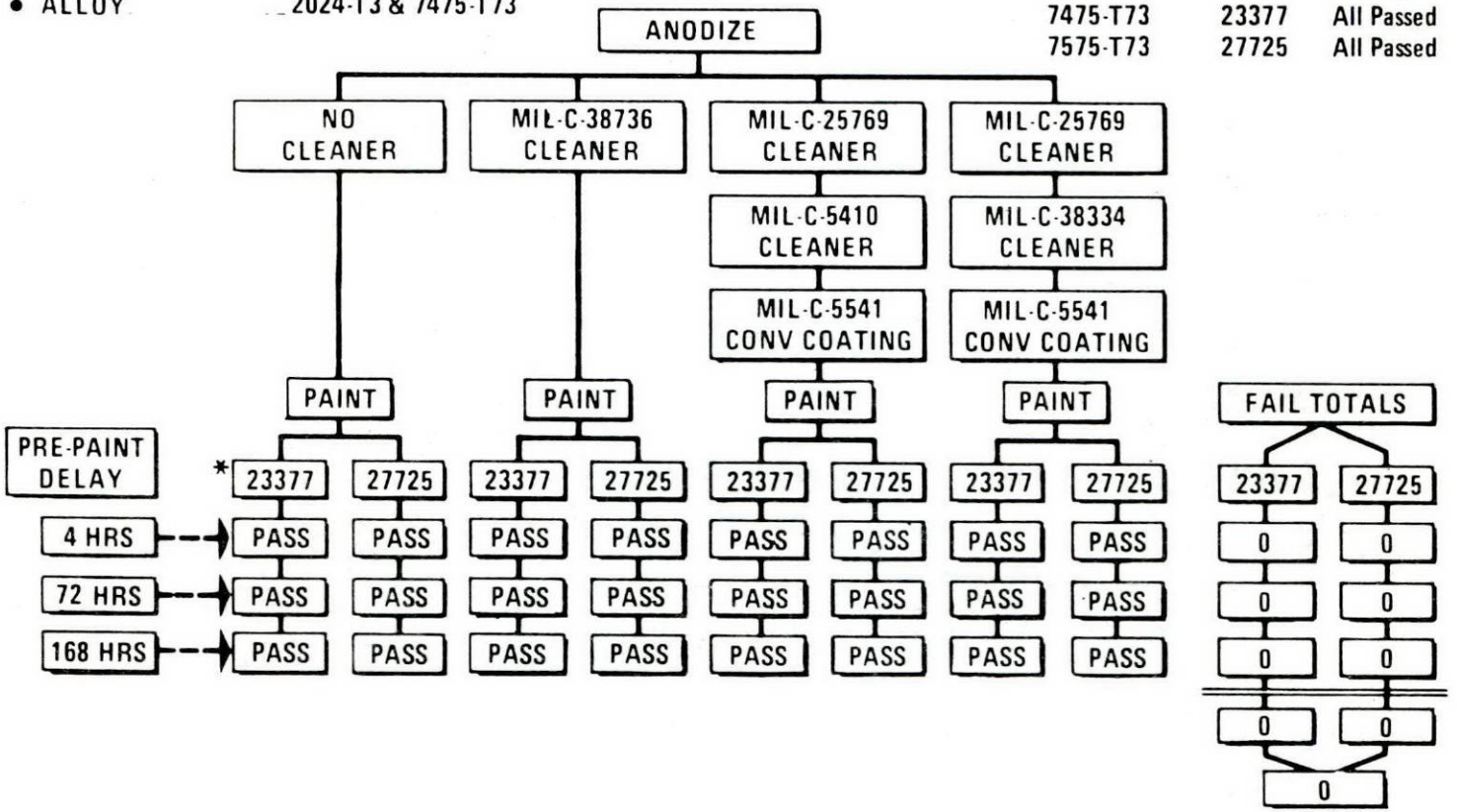
*MILITARY SPECIFICATION NO. (Typ)

Table VII THREE PROCESS EVALUATION (20 Volt CAA) ANODIZE/TIME DELAY/CLEAN/PAINT/WET TAPE ADHESION TEST

- ANODIZE TIME 45 MIN
- ANODIZE TEMP 95°F
- SEALING MEDIUM 5% SODIUM DICHROMATE
- SEALING TEMP 200°F
- SEALING TIME 10 MIN.
- ALLOY 2024-T3 & 7475-T73

FAILURE BY ALLOY

ALLOY	PAINT*	FAILED
2024-T3	23377	All Passed
2024-T3	27725	All Passed
7475-T73	23377	All Passed
7575-T73	27725	All Passed



EACH PASS/FAIL BOX HAS 4 PANELS REPRESENTED

*MILITARY SPECIFICATION NO. (Typ)

paint adhesion. This system of anodize and seal was demonstrated to be superior.

Effect of the three candidate processes on fatigue strengt is shown in Figure 13. The three candidate processes are shown on the left hand side of the bar graph while various control conditions for reference comprise the remaining center and right hand portion. Although some reduction in overall fatigue strength is caused by anodize, the three processes being evaluated have essentially equivalent effects on fatigue. The preferred process, 95°F, 45 minutes with a sodium dichromate seal actually had slightly higher life cycle endurance as shown in Figure 13. This is probably because the sodium dichromate seal does not add water of hydration as do the other two processes which utilize the hot water seal. Figure 7 shows the coating weight increases with hot water seal times whereas Figure 12 concerning sodium dichromate seal displays no appreciable weight gains with longer seal times. The Alcoa Finishing Bulletin[21] states that "fatigue failure also may be hastened by sealing"; presumably by hot water seals.

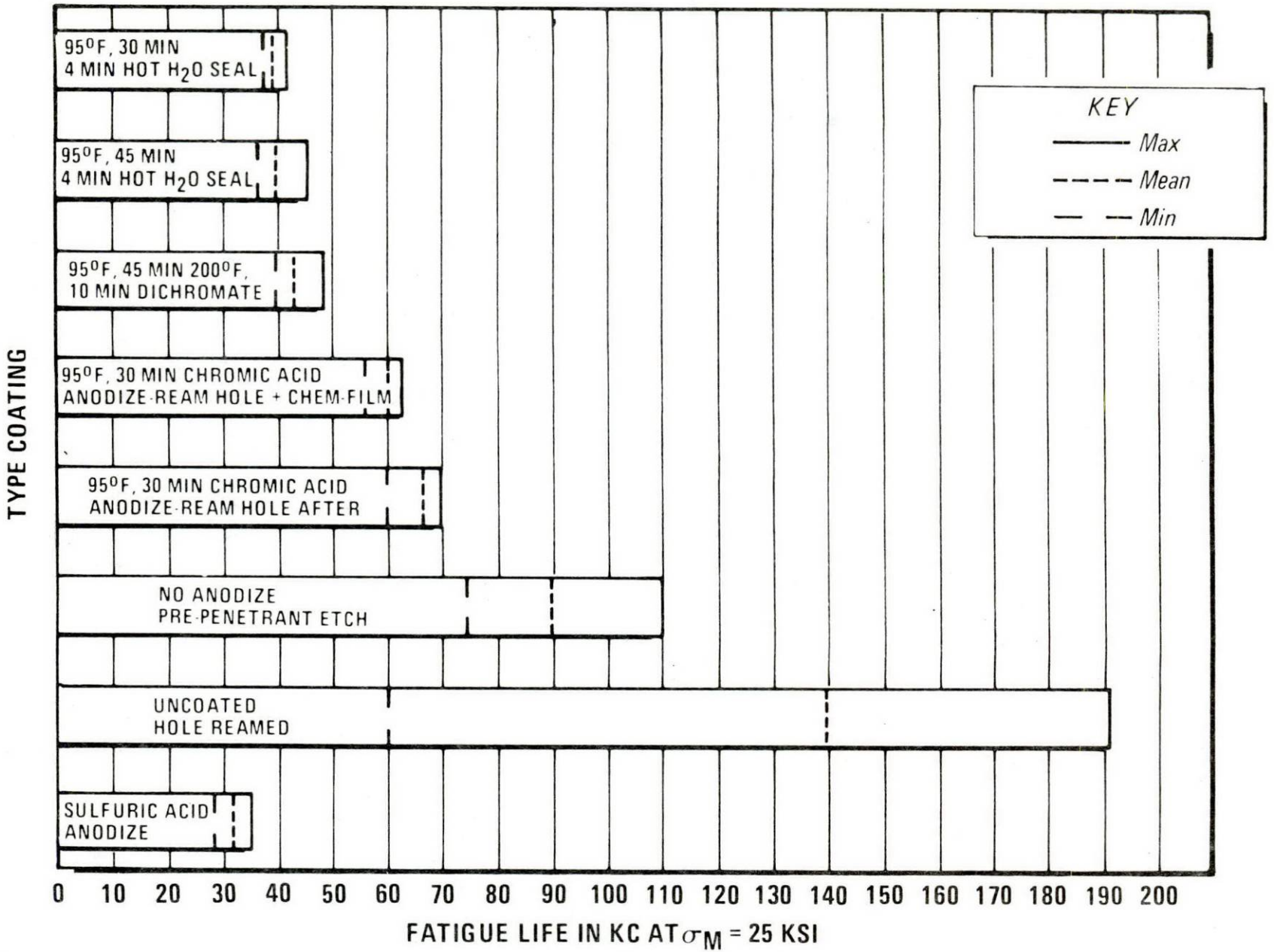


Figure 13. Effects of 20 Volt Chromic Acid Anodize on the Axial Fatigue Life of 7475-T7351 Aluminum Plate, R = 0.1

CONCLUSIONS

1. The 20 volt chromic acid anodize process will provide uniform coating weights for the 2000 and overaged 7000 series aluminum alloys.
2. Coating weights for the overaged 7000 series alloys can be substantially increased with the 20 volt system with little coating weight effect on the 2000 series alloys.
3. With a hot water seal the 20 volt chromic acid anodize process provides a more uniform range of hydration for all alloys.
4. The most nearly optimum 20 volt, hot water seal process is one that anodizes at 95°F for 30 minutes followed by a hot water seal for 4 minutes at 170°F.
5. Chromic acid post anodize seals provide poor corrosion resistance and paint adhesion.
6. Alodine 1200S is an inadequate sealing media.
7. A sealing media of 5% sodium dichromate at 200°F provides the most striking improvements in corrosion resistance and paint adhesion. It is superior for all sealing processes investigated.

8. The sodium dichromate seal media is the only seal investigated which provides good paint adhesion after post anodize delays up to 168 hours and several varieties of prepaint supplemental cleaning.
9. The 45 minute anodize, sodium dichromate seal is slightly better than a 30 minute anodize, hot water seal in terms of reduced fatigue strength.

ACKNOWLEDGEMENTS

A. C. Porter and T. E. Coyle provided the literature survey which indicated a process variables study would provide useful results. R. L. Jones conducted the fatigue tests, reduced the data and provided metallurgical consultation.

PUBLIC RELEASE CLEARANCE

This technical paper was cleared for public release by U. S. Air Force Document ASD/OIP 78-2333. An invention disclosure, Docket Number 7809, was filed with the General Dynamics Patent Counsel on October 12, 1978.

REFERENCES

1. G. D. Bengough and H. Sutton,"The Protection of Aluminum and its Alloys Against Corrosion by Anodic Oxidation", Engineering 122, p. 274 (1926)
2. Robert W. Buzzard, "Anodizing of Aluminum Alloys in Chromic Acid Solutions of Different Concentrations", Journal of Research of the National Bureau of Standards, Volume 18, Research Paper RP975, March 1937.
3. U. S. Navy Department Specification SR19c, 1936.
4. U. S. Government Specification, AN-QQ-6966; April 11, 1941.
5. Military Specification, "Anodic Coatings for Aluminum and Aluminum Alloys", MIL-A-8625C (1), U. S. Government Printing Office, Washington, D.C., 13 March 1969.
6. Metals Handbook, Vol. 2, Eighth Ed., Cleaning and Finishing of Aluminum Alloys, p. 620-627, American Society of Metals, Metals Park, Ohio, 1964.
7. R. W. Buzzard and J. H. Wilson, "Deterioration of Chromic Acid Baths for Anodic Oxidation of Aluminum Alloys", Journal of Research of the National Bureau of Standards, Vol. 18, U. S. Dept. of Commerce, Washington, D.C., 1937.

8. Aluminum Fabrication and Finishing, Vol. III, p. 656-658, American Society of Metals, Metals Park, Ohio.

9. D. R. Clawson, "Anodic Treatment for Aluminum Alloys", Process Standard 74.02-3, General Dynamics Corp., Fort Worth, Texas 24 March 1976.

10. Military Specification, Cleaning Compound, Aircraft Surface , Alkaline Waterbase, MIL-C-25769, U. S. Government Printing Offices, Washington, D.C., July 1977.

11. Military Specification Corrosion Removing Compound, Prepaint, for Aircraft Aluminum Surfaces, MIL-C-38334(USAF), U. S. Government Printing Offices, Washington, D.C., 1 April 1966.

12. Military Specification, "Cleaning Compound, Non-Flame Sustaining", MIL-C-5410B, U. S. Government Printing Office, Washington, D.C., 30 September 1965.

13. Military Specification, "Chemical Conversion Coating on Aluminum and Aluminum Alloys", MIL-C-5541, U. S. Government Printing Office, Washington, D. C., 30 November 1972.

14. Military Specification,"General Purpose Cleaner", MIL-C-38736, U. S. Printing Office, Washington, D.C., 1974.

15. Military Specification, "Primer Coating; Epoxy Polyamide, Chemical and Solvent Resistant", MIL-P-23377C , U.S.

Printing Office, Washington, D.C., 1972.

16. Military Specification, "Coating Polyurethane, Fuel Tank Applications", MIL-C-27725, U. S. Printing Office, Washington, D.C. 1975.

17. Military Specification, "Finishes: Organic, Weapons System, Application and Control Of", MIL-F-18264D, Ammend. 1., U. S. Printing Office, Washington, D.C., 23 April 1971

18. Peterson, R.E., Stress Concentration Design Factors, John Wiley & Sons, 1953, Figure 69.

19. A. K. Graham, "Electroplating Engineering Handbook", Reinhold Publishing Corp., Library of Congress No. 54-1243 1955, p. 378.

20. ibid.,

21. Alcoa Finishing Bulletin No. 22, "Sealing Treatments for Anodic Coatings on Aluminum", Aluminum Corp. of America, Pittsburg, Pa., 15219, p. 7, 1968.

A-4

Light Metals Finishing I
Session A

Phosphoric Acid Anodize
As Pre-Plate Treatment for Aluminum

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Phosphoric Acid Anodize
As Pre-Plate Treatment for Aluminum

by

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ABSTRACT

The phosphoric acid anodic preplating treatment gave poorly adherent nickel plates upon strong aluminum-zinc-magnesium alloys which are presently of intense interest in automotive bumper applications. Excellent adhesion was recently obtained on X7046 alloy when anodized in dilute solutions at high temperatures, voltages and current densities. Slow filling of the anodic coating pores with nickel plate was essential. Additional requirements with X7021 alloy were an abnormally acidic nickel plating solution and an acidic pre-plating rinse. High copper content of the X7021 alloy improved adhesion stability.

As a pretreatment for electroplating, phosphoric acid anodizing is unusual since deliberate growth of an oxide film takes place. Some advantages are: The method is free from the requirement to deposit specific and perhaps undesirable foreign metals. Cyanide plating solutions are not needed. The procedure is simple, consisting of cleaning, anodizing, and the initial plating. The anodic oxide may even improve corrosion performance, as earlier investigations suggest (Refs 1 and 2).

The principal disadvantage to phosphoric acid anodizing is that different optimum anodizing conditions exist for various aluminum alloys. Another objection is that an extra power supply may be needed. Finally the deposit adhesion is rarely as great as that from complete metal-to-metal bonds.

Fischer obtained the original patents over forty years ago, while Spooner and Seraphim thoroughly described the anodizing process and Bunce developed procedures for various aluminum alloys (Refs 3-6). However, two important alloy classes, the 2XXX and 7XXX series,* remained especially intractable to phosphoric acid anodizing.

Adhesion on alloys of the aluminum-copper-magnesium type such as 2024 alloy was greatly improved by addition of sulfuric acid to the phosphoric acid anodizing electrolyte (Ref 7). This modification was not effective on alloys in the 7XXX series, which recently were desired for their high strength and formability in automotive bumper applications.

Initial results on X7046 alloy, Table I, were discouraging. Maximum peel adhesion (Ref 8) was about 32N/cm (18 lb/in.) for a sulfamate nickel deposit. Three times greater adhesion was obtained by applying the full anodizing voltage suddenly at the start of anodizing (Refs 9 and 10).

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* Aluminum Association designations for alloys in which the principal alloying additions are copper and zinc, respectively.

One problem was occasional "burning" - a greatly excessive current in localized areas. Another objection was the high initial current surge, necessitating power supplies with otherwise excessive capacities.

A new examination of anodizing and initial plating variables was obviously needed. The goal was simply to obtain satisfactory nickel electrodeposit adhesion upon the aluminum alloys of interest.

Acceptable Adhesion

The method for determining adhesion was the peel test (Appendix) somewhat refined from that described earlier (Ref 8). Originally devised by Jacquet (Ref 11), the test was recently more precisely specified and mechanized by Klingenmaier and Dobrash (Ref 12).

How much adhesion is enough is not known. With a strong ductile coating the best one might expect in a peel test would be a rupture within the weaker substrate. Upon commercially pure aluminum, this ultimate was reached with a peel adhesion of 240 N/cm (Ref 8). Stronger aluminum alloys probably would permit greater peel adhesions.

Would some peel adhesion less than the ultimate be satisfactory? Adequate attachment is needed to resist mechanical stresses imposed during normal service from impact, flexing, vibration or thermal shock. The plate should also resist peeling from bulky corrosion products at points of plate penetration. An earlier investigation showed an adhesion of 50 N/cm was adequate (Ref 2), hence, a present goal of about twice that value seemed reasonable.

Procedure

The finishing and testing procedure for each sample consisted of the steps outlined in Figure 1, with details supplied in the Appendix.

Substrate Aluminum

The main effort was directed upon X7046-T53 alloy extrusions and X7021-T63 alloy sheet, plus some work on X7029-T53 alloy extrusions and sheet and 6010-T6 alloy sheet. Nominal and actual compositions are given in Table I.

The aluminum extrusions for plate-adhesion testing were all 3.8 cm (1-1/2 in.) wide, 0.95 cm (3/8 in.) thick and 15 cm (6 in.) long, with plating extending to 12.5 cm (5 in.). The aluminum sheet samples were the same length and were either 3.8 or 2.5 cm (1-1/2 or 1 in.) wide and 0.3 cm (1/8 in.) thick.

X7046 Alloy

Filling of Pores

Phosphoric acid anodizing produces an oxide coating with well-defined pores (Ref 9). Nickel plating must obviously fill such pores, but this operation must be carried out carefully. Sudden passage of the full plating current produces hydrogen evolution with catastrophic break-up of the anodic coating. A rough electrodeposit and poor adhesion result.

Preliminary tests quickly showed that visible gas evolution was avoided by following a rigid schedule for plating start-up:

1. Immerse the anodized and rinsed aluminum sample into the nickel plating bath connecting to the power supply set at zero.
2. Gradually increase current density to 8.6 ma/cm^2 (8 amp/ft^2) in two minutes and hold for five additional minutes.
3. Increase current density to 69 ma/cm^2 (64 amp/ft^2) in two minutes and maintain for remainder of plating period.

Anodizing Voltage

In an early experiment the anodizing voltage was varied from ten to sixty volts. Only the sixty-volt sample had an appreciable adhesion of 58 N/cm.

Anodizing Temperature and Total Current

These were varied on a series of samples which were all anodized at sixty volts in the same electrolyte as in the previous experiment, i.e., 20% by volume (290 g/l) phosphoric acid. Temperature ranged from 29-46°C and total current was 4, 10 or 20C/cm^2. All conditions gave about 50 N/cm nickel adhesion except for two samples. The sample run at 35°C and only 4 C/cm^2 gave zero adhesion. At the other end of the range, one of several samples run at 46°C and 20 C/cm^2 gave an adhesion of 80 N/cm well above average. The samples with anodic coatings produced in 10 C/cm^2 were all about average.

A similar survey in a 10% by volume phosphoric acid solution with total currents held constant at 30 C/cm^2 gave the results shown in Figure 2. While the lowest temperature gave the highest adhesion, this was accompanied by a four-fold increase in anodizing time over that at the highest temperature, 52°C. The effect is clearly evident in a plot of adhesion versus anodizing time (Figure 3) which shows a levelling off after about 20 minutes.

Another set of samples was run in a 5% solution, at high temperature, with total current held at 15 C/cm^2, only half that in the previous survey. The 60 and 70 volt runs gave the best adhesion and used less than 5 minutes of anodizing time:

Voltage	Temp.,°C	Current Density ma/cm^2	Time, min.	Adhesion N/cm
60	57	56	4.8	103
70	52	60	4.5	107
70	54	69	3.8	105

Later, two samples anodized in the 10% solution at 60 volts, 38°C, 10 ma/cm^2 and for 26 minutes had adhesions of about 150 N/cm.

Clearly, X7046 alloy may be nickel plated adherently by means of phosphoric acid anodizing under a broad range of conditions: 5-10% by volume phosphoric acid, temperatures 50-60°C, voltages 60-70, current densities 50-70 ma/cm^2, total currents 15-30 C/cm^2 and anodizing times 3.5 to 10 minutes.

X7021 Alloy

The empirical search for optimum phosphoric acid anodizing conditions upon X7021 alloy (Table I, Lot 61) proved much more difficult. The earliest work was encouraging since a fair degree of adhesion, 50 N/cm, was immediately obtained. However, this was not repeatable at will. Acid concentrations were varied from 1 to 20% by volume, temperatures from ambient to 70°C, voltages from 30 to 60, and total currents from 4 to 35 C/cm^2. Apparently, a solution to the problem existed but one or more of the anodizing or plating conditions was out of control.

One of the earliest observations was the need to maintain the boric acid content in the nickel plating solution near saturation, but this precaution was not of itself sufficient to assure good adhesion.

Spooner and Seraphim explored the current-voltage relationships for different acid concentrations and temperatures (Ref 5). During phosphoric acid anodizing at constant voltage, the current also remains essentially constant, thus permitting a plot of steady-state current density vs. voltage. Figure 4 illustrates the curves for two different acid concentrations at several temperatures. Clearly, the current densities increase with voltage, temperature and acid concentration. The curves are steeper at higher temperatures and acid concentrations, reaching their steepest point just below the voltage where burning occurs.

The flat curves, obtained at the lowest temperatures, invariably represent conditions of very poor plate adhesion. Frequently, after peeling, the aluminum was black and shiny indicating very tiny pores, weak nickel tentacles filling the pores, and unroughened aluminum surface.

On the other hand, anodizing under conditions of a steep curve might give good adhesion, but the tendency to burn was also strong. Slight increases in temperature perhaps caused by inadequate stirring, poor regulation of a heater, or a slight variation in the applied voltage could initiate the burn. Consequently, the intermediate conditions were the ones sought after.

To reduce anodizing time one would look for the maximum current density with the least slope of the curve. The more dilute electrolytes satisfied this need better than the more concentrated ones.

Table II lists anodizing conditions for the samples giving the best adhesion for each concentration of phosphoric acid used. The actual adhesion values were nearly the same. But the higher anodizing current densities developed with the dilute solutions permitted significantly lower anodizing times. This was the result of higher temperatures. The best of all the samples had been anodized in a 3% by volume solution. The fact that the anodizing time was relatively short and the tendency to burn was well removed made it seem worthwhile to intensify the study in this area.

During this effort the discovery was made that operating the nickel plating electrolyte at a lower pH of 2.5 doubled the adhesion and improved the quality of the deposit. The need for more frequent pH adjustment was somewhat bothersome but seemed worthwhile in view of the advantages gained.

No direct correlation was developed between the aluminum content of the anodizing bath and the nickel plate adhesion. However, it was easier to maintain the anodizing solutions at or near saturation with aluminum. For the 3% by volume electrolyte an aluminum content near 0.8 g/l seemed to represent a stable condition.

As mentioned earlier, the sudden application of the full anodizing voltage was helpful in developing good adhesion on X7046 alloy. With a better understanding of the problem of burning, it became feasible to examine the effect of sudden full voltage application upon X7021 alloy.

Several variations of full voltage application are conceivable: hot or cold anode entry, rate of hot anode entry, imposition of an instantaneous current limitation, and the magnitude of this limitation. Also, sudden application of a fraction of the full anodizing voltage should give somewhat similar results. So should controlled, rapid but not instantaneous voltage rise to full voltage.

Since hot anode entry at high dc voltages presents a shock hazard as well as the possibility of shorting the load to ground, cold anode entry appears operationally more attractive. In the best case with cold anode entry, an adhesion of 99 N/cm was obtained on X7021 alloy, Lot 81. Anodizing took place in a 3% by volume phosphoric acid, 66°C, 60 volts preset and steady-state, a limiting current density 200 ma/cm^2, and 16 C/cm^2 total current.

Adhesion Stability

Peel adhesion was normally measured within about one hour after completion of the plating. No question was raised whether the adhesion would be the same after varying delays.

Lashmore at the National Bureau of Standards found that heating of nickel plated X7021 alloy (Table I, Lot 31) at 150°C for two hours drastically reduced the peel adhesion (Ref 13). His observation was quickly confirmed. Peel adhesion samples retained from earlier tests were also available for further peeling, thereby indicating adhesion stability without resort to heating. Results on typical samples of four alloys are shown in Table III.

In all cases, the initial adhesion was fair to excellent. After room-

temperature storage from one day to over a year, the alloys behaved quite differently. X7021 alloy (Lot 81) showed a marked decline in adhesion in only 24 hours; in six months adhesion on Lot 61 had dropped to unsatisfactory levels. By contrast, the two other 7XXX alloys gave substantially increased adhesion; and 6010 alloy gave only a slight decrease.

With heating, the adhesion on the better of the two X7021 alloy samples dropped to unsatisfactory levels, while the other older sample remained at that low level. X7029 alloy gave a slight adhesion increase with heating. But X7046 and 6010 alloys showed a dramatic increase.

One approach to solving this problem on X7021 alloy was to modify the finishing process. Another approach was to see what made the otherwise similar 7XXX alloys so different.

In the first approach the method was to prepare the sample and determine the adhesion immediately, and then after heating for two hours at either 175° or 150°C. The techniques tried were those that might affect the structure, hydration or thickness of the anodic coating, such as: prior heating, drying in various ways, soaking in water at various temperatures and pH's. No satisfactory improvement was found.

One variation that appeared useful, however, was a soak of the anodic coating in acidulated water. This technique gave the best initial adhesion but did not improve adhesion stability.

The effect of heating temperature from 60-175°C was relatively slight. On the early X7021 alloy samples, a decline in adhesion always occurred.

A comparison of the compositions of the four alloys tested revealed a factor that conceivably could explain the difference in behavior between X7021 alloy and the others, viz. the copper content:

Alloy	X7046	X7029	X7021	6010
Cu,%	0.12	0.50	0.025	0.22

The copper content of X7021 alloy was about one-fifth of that of the lowest of the other three alloys.

Accordingly, adhesion and stability tests were carried out on special compositions of X7021 alloy (Table I) with the same copper content as the X7046 material. Results are illustrated in Figure 5.

The anodizing and plating were all done identically by the process outlined in the Appendix for reproducible high adhesion on X7021 alloy. The only difference was that the three samples subject to heating at 150°C were anodized to 16 C/cm^2, which gave better adhesion than a similar set anodized twice that long. On the other hand, the sample allowed to age at room temperature was anodized for the longer period.

The sample from Lot 33 was outstanding in that it showed no adhesion decline either due to aging or heating. Lot 42 declined slightly but recovered, all the while remaining at satisfactory levels of adhesion. But Lot 81 with the lowest copper content lost half its adhesion in only two hours of heating. While some recovery occurred, adhesion never returned to a satisfactory level.

In conclusion if the copper content of the X7021 alloy is high enough, the adhesion will improve with aging. Otherwise, some decline must be expected.

Acknowledgement

Thanks are extended to John Riordan for carrying out the experimental work, especially the careful preparation of the many peel adhesion test specimens. Thanks to Kaiser Aluminum & Chemical Corporation for permission to publish this paper.

REFERENCES

1. R. C. Spooner and D. P. Seraphim, Metal Finishing 58, 40-44, 47 (Dec., 1960); 59, 37-41 (Jan., 1961).
2. H. J. Wittrock, Tech. Proc. A.E.S. 48, 52 (1961).
3. Fischer, J., Metallwirtschaft 11, 473 (1932).
4. Fischer, J., U.S. patents 1,947,981; 1,968,483; 2,036,962; 2,095,519 (1934-7).
5. R. C. Spooner and D. P. Seraphim, Trans. Inst. Met. Finishing 31, 29 (1954).
6. B. E. Bunce, Electroplating and Metal Finishing 6, 317 (1953).
7. H. J. Wittrock, U.S. patent 3,098,804 (1963).
8. H. J. Wittrock and Larry Swanson, Plating 49, 880, (1962).
9. H. J. Wittrock, "Plating on Aluminum: How Voltage Application Affects Phosphoric Acid Anodizing," paper presented at the 62nd annual technical conference of the American Electroplaters' Society, June 26, 1975.
10. H. J. Wittrock, U.S. patent 3,943,039 (1976).
11. P. A. Jacquet, Trans. The Electrochemical Society, 66, 393(1934).
12. O. J. Klingenmeier and S. M. Dobrash, Adhesion Measurement of Thin Films, Thick Films and Bulk Coatings, ASTM STP 640, K. L. Mittal, Ed., 1978, pp 369-390.
13. Private communication.

TABLE I

COMPOSITION OF ALUMINUM ALLOYS*

Alloy		Lot	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Zr	V
X7046	Nominal**		0.20	0.40	0.25	0.30	1.0-1.6	0.20	6.6-7.6	0.06	0.10-0.18	-
	Actual		0.09	0.16	0.12	0.17	1.2	0.11	6.4	0.007	0.12	-
X7029	Nominal		0.10	0.12	0.50-0.9	0.03	1.3-2.0	-	4.2-5.2	0.03	-	0.05
	Actual		0.04	0.04	0.50	0.001	1.6	0.000	4.6	0.013	-	-
X7021	Nominal		0.25	0.40	0.25	0.10	1.2-1.8	0.05	5.0-6.0	0.10	0.08-0.18	-
	Actual	61	0.07	0.20	0.013	0.006	1.4	0.001	5.6	0.017	0.10	-
	"	81	0.08	0.18	0.025	0.065	1.3	0.025	5.9	0.037	0.10	-
	"	31	0.08	0.15	0.005	0.086	1.5	0.001	5.2	0.008	0.10	-
	"	33	0.08	0.17	0.12	0.10	1.2	0.047	5.3	0.036	0.11	-
	"	42	0.07	0.17	0.12	0.10	1.3	0.046	5.3	0.022	0.09	-
6010	Nominal		0.8-1.2	0.50	0.15-0.6	0.20-0.8	0.6-1.0	0.10	0.25	0.10	-	-
	Actual		0.95	0.25	0.22	0.34	0.69	0.00	0.04	0.01	-	-

* Percentage of foreign elements, balance aluminum.

** Aluminum Association Registration Record, March 1, 1978. Single nominal value indicates maximum; double nominal value indicates range.

TABLE II

BEST NICKEL PLATE ADHESION UPON X7021 ALLOY*
AS FUNCTION OF ANODIZING ACID CONCENTRATION

% by Vol. H_3PO_4	°C	V	ma/cm^2	C/cm^2	Min.	N/cm
1	63	60	18	17	16	70
2	66	60	33	17	9	65
3	57	50	21	17	14	81
5	52	40	19	34	30	67
10	38	50	16	17	18	61
15	38	50	19	34	30	72
20	32	50	14	34	40	60

* Lot 61, see Table I

TABLE III

TYPICAL NICKEL ADHESION STABILITY

UPON VARIOUS ALUMINUM ALLOYS

Alloy	Peel Adhesion, N/cm		
	Initial	After Storage	After Heating*
X7021 (Lot 81)	107	82 (1 day)	40
X7021 (Lot 61)	81	32 (148 days)	28
X7029	100	131 (418 days)	154
X7046	135	170 (202 days)	236
6010	95	84 (23 days)	254

* Two hours at 150°C

APPENDIX

Anodizing, Plating and Adhesion Testing Procedure

1. Buff: Polish and buff the aluminum to decorative brightness.
2. Rack: Attach to aluminum plating rack.
3. Clean: Soak in -

Oakite NST or equivalent	10% by volume
Temperature	55°C
Time	5 min

Rinse in cold water. Deoxidize in 1:1 nitric acid at room temperature for 1 minute. Rinse in cold water.

4. Anodize using regulated DC power supply*, two units coupled in series when greater than 60 volts are required.

Usual Procedure:

a. Twenty liter glass jar, thermostatted electrical resistance heating, mechanical stirring and lead cathodes for all runs. Acid concentration and temperature as desired for individual run.
b. Cold anode entry.
c. Turn ON power supply set at zero volts and 15 amp limiting current, equivalent to 60-205 ma/cm^2 current density depending upon sample size.
d. Increase voltage to that desired for individual run. Time to reach full voltage controlled as desired but in most cases from 1 to 5 minutes. Current not regulated.
e. Maintain constant full voltage to desired total anodizing time, usually calculated from desired total passed current divided by actual current.
f. Turn OFF power supply, remove sample from anodizing electrolyte and rinse in cold water.

---

* Harrison Model 6274A, 0-60V, 0-15 a; mfg by Hewlett-Packard

Optimum Procedure for X7021 Alloy:

g. Equipment as in a. above. Acid concentration and temperature as specified below.

h. Preset power supply at 60 volts, preset limiting current at double the steady state current calculated from a steady state current density of 33 ma/cm^2 (31 amp/ft^2).

i. Cold anode entry

j. Turn power supply ON.

k. Electrolytic details:

Phosphoric acid (85% by weight)	40 g/l (≃ 3% by vol)
Aluminum in solution	0.7 g/l
Temperature	65°C
Voltage	60 volts
Current density	33 ma/cm^2
Total current	32 C/cm^2
Time	16 min

l. Turn current OFF. Remove work from tank and rinse in cold water.

5. Acid Rinse: In this investigation used only on X7021 alloy. Immerse in water acidulated by addition of ≃ 2 g/l sulfamic acid to pH ≃ 2, temperature 60°C, time 1 min. Remove work and transfer directly to nickel plating electrolyte.

6. Nickel Plate: Immerse in nickel plating electrolyte with DC power OFF.

Nickel sulfamate* (600 ml/l concentrate)	330 g/l
Nickel chloride*	6 g/l
Boric acid	37 g/l
AP 12*	0.15% by vol
pH (for all work except latest work on X7021 alloy)	3.5-4.2
pH (for all recent work on X7021 alloy)	2.5 ± 0.1
Temperature	60°C
Heating	External, thermostatted
Tank, 4 liters	Glass
Agitation	Mechanical
Anodes	Depolarized, bagged

---

* M&T chemicals

Time, min	
0	Soak anodized aluminum in nickel plating solution with power to zero volts.
1	Gradually increase applied DC voltage to 1.5 volts in one minute. Current density permitted to float but will reach about 15 ma/cm^2.
2	Continue plating at 1.5 volts for five minutes.
7	Gradually increase applied DC voltage so that current density reaches 65 ma/cm^2. Final voltage will be about 3 to 4 volts.
9	Continue plating at 65 ma/cm^2 for 120 minutes. Remove, rinse and dry.

7. Test for Adhesion. Using the basic method described in Reference 8, prepare sample for peel test. Cut off plated end of sample with band saw. Undercut nickel plate from exposed end as close beneath plate as possible exercising care not to cut into the nickel plate. Sand off plated edges of sample, carefully trim with file to remove burrs and other irregularities. Insert opposite end of sample into vise. At undercut make tab consisting of nickel plated aluminum by bending back and forth until aluminum substrate breaks but before nickel plate breaks. Attach clamp to nickel tab and fish scales to clamp. Pull back on fish scales making certain that force is exerted perpendicular to unpeeled plated surface. Measure force required to maintain slow, steady rate of peel. Measure exact width of peeled plate and calculate peel adhesion as force per unit length of peel front (N/cm or lb/in.).

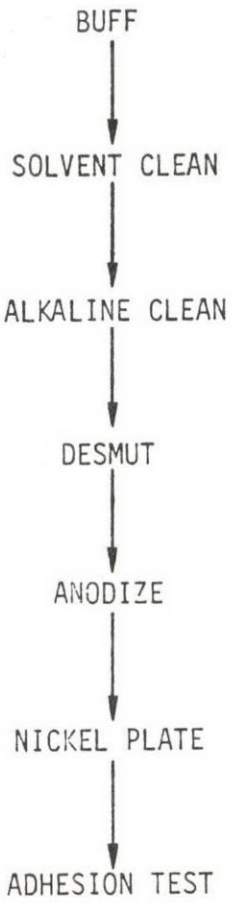


FIG. 1 - OUTLINE OF FINISHING AND TESTING PROCEDURE

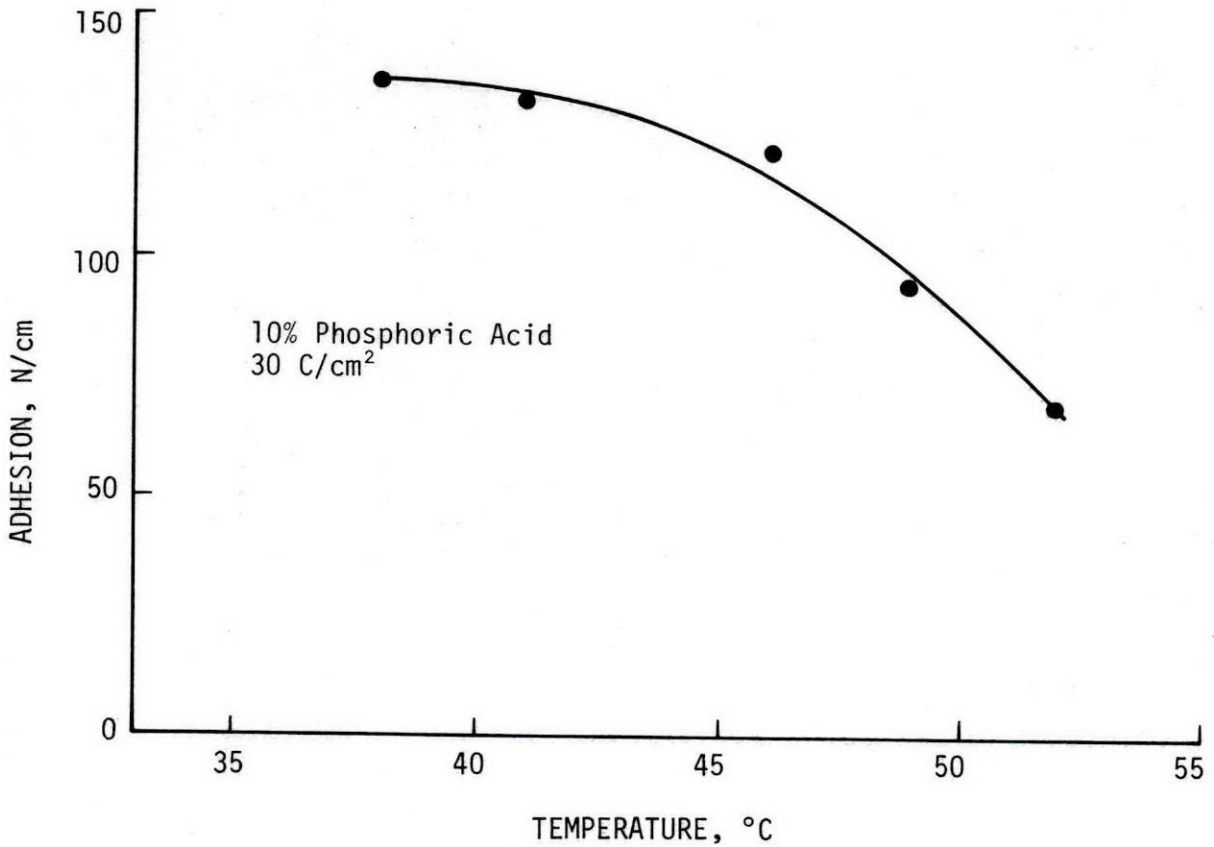


FIG. 2 - ADHESION OF NICKEL PLATE UPON X7046 ALLOY ANODIZED AT SIXTY VOLTS AND VARIOUS TEMPERATURES

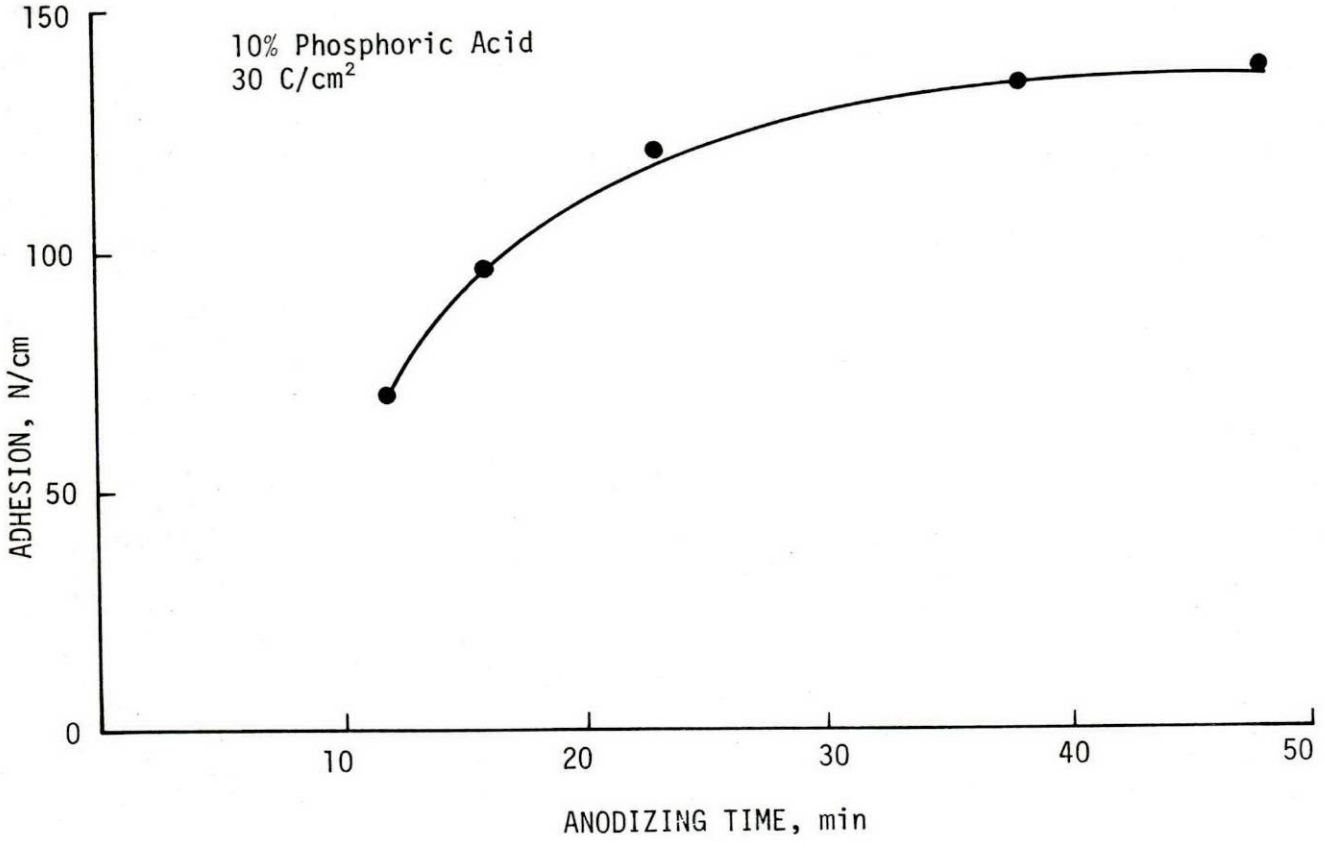


FIG. 3 - ADHESION OF NICKEL PLATE UPON X7046 ALLOY AT VARIOUS ANODIZING TIMES AT CONSTANT TOTAL CURRENT

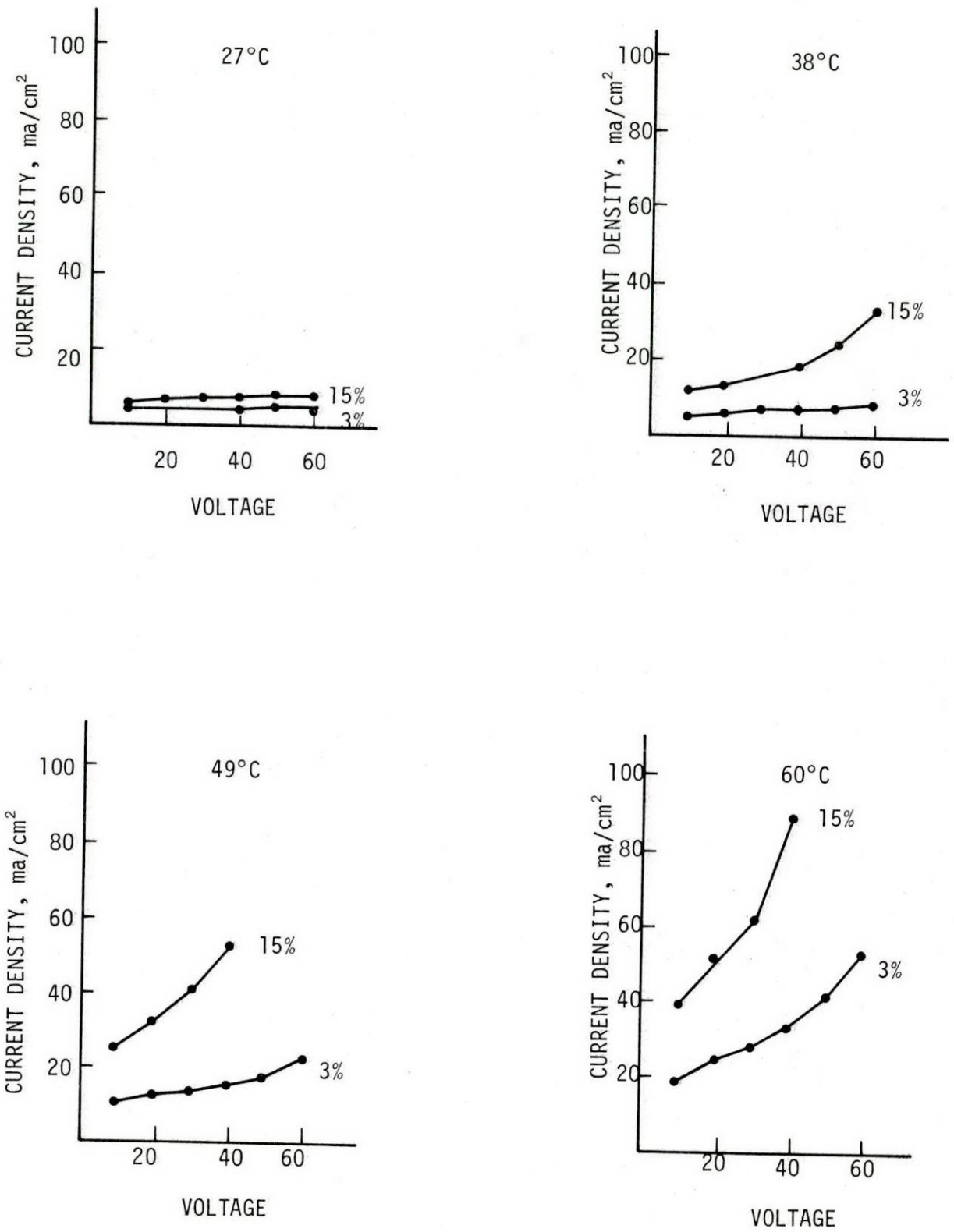


FIG. 4 - CURRENT DENSITY VS. VOLTAGE

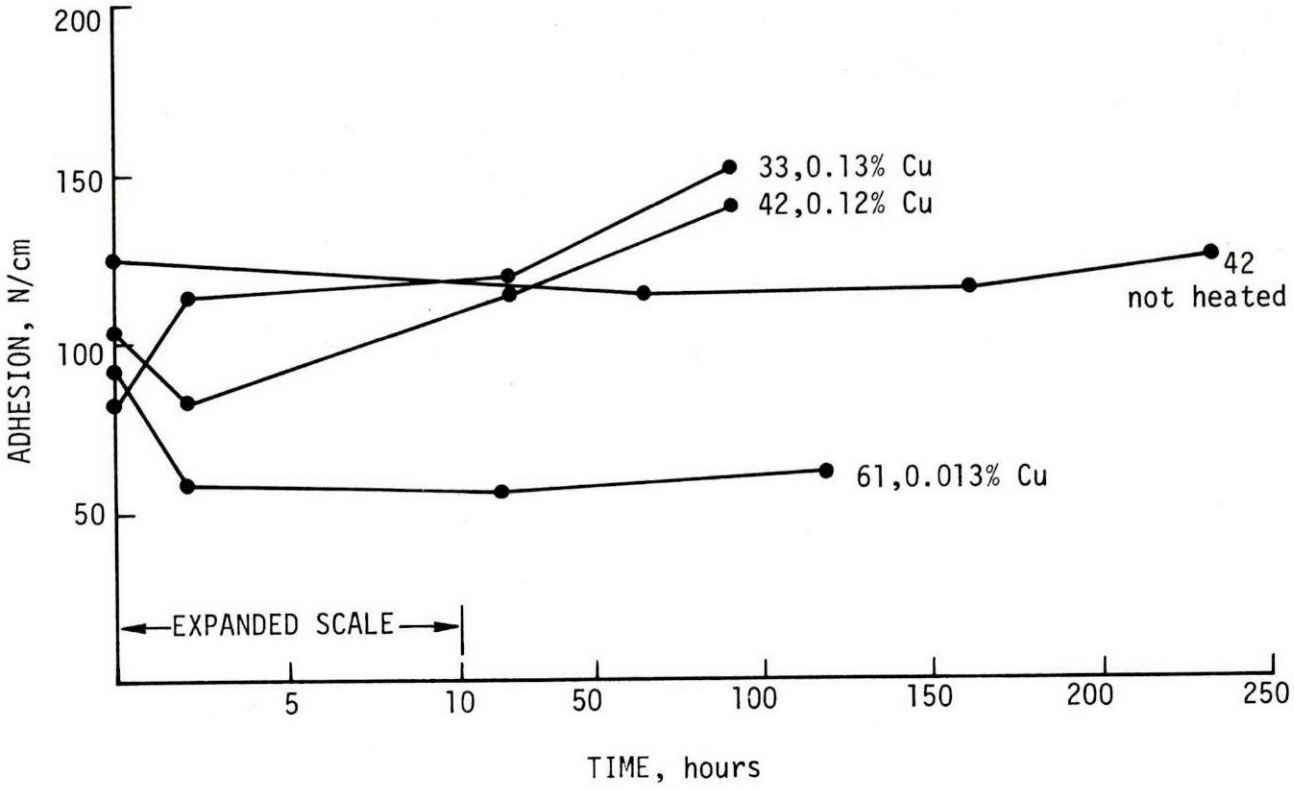


FIG. 5 - NICKEL PLATE ADHESION UPON X7021 ALLOY AFTER AGING OR HEATING

B-1

General Interest Session B

High Speed Continuous Nickel Plating From Sulfamate Solutions

T. Inagaki
Hudson Wire Co.
Ossining, New York

HIGH SPEED CONTINUOUS NICKEL PLATING FROM SULFAMATE SOLUTIONS

T. Inagaki

Hudson Wire Company
Ossining, N.Y. 10562

ABSTRACT

High speed continuous nickel plating of copper wire from a sulfamate solution at high current densities is described. The mechanical properties of these deposits are related to the traditional plating parameters as well as to several unique process modifications. Microstructural analysis of the deposits has also been conducted to correlate the mechanical properties with the plating parameters. By the variation of these parameters, a thick nickel deposit up to 30% by weight of the basis metal exhibiting good ductility has been obtained at current densities as high as 108 A/dm^2.

1.0 INTRODUCTION

Nickel plated copper wires are being used extensively in the conductor industry for their excellent resistance to corrosion at elevated temperatures. These applications include hookup and interconnecting wires in the aerospace industry as well as in the appliance industry where exposure to elevated temperatures is common.

Due to economic considerations, the standard manufacturing processes include electrodeposition of the nickel at a large diameter followed by cold drawing to the final size rather than electrodepositing the nickel on size. This economic constraint makes the production of a ductile deposit not only desirable but mandatory. In most production sequences the plated wire is cold drawn to over 95% reduction in area without any intermediate anneals.

Electrodeposited nickel from a sulfamate solution in a continuous plater has been employed by Hudson Wire Company for a number of years because of the excellent combination of high deposition rates and mechanical properties obtained. Generally, these baths have been operated at up to 32 A/dm^2 producing deposits with an excellent ductility.

However within recent years, the demand for nickel plated copper conductors has seen an unprecedented rise such that serious efforts to increase the deposition rates and thus the production capacity have been initiated. Since the deposition rate is a direct function of the current density, electrodeposition at a higher current density is desirable. However, deposition at current densities above 32 A/dm^2 using the standard bath formulation and operating conditions produces a relatively brittle deposit such that severe cracking results during the drawing operation.

In the present investigation this ductile to brittle transition of the nickel deposit with increasing current density has been evaluated with respect to the plating parameters. Further, the continuous multiple pass wire plating process as it relates to these properties is also discussed. Through this investigation a process has been developed for high speed continuous plating of a ductile nickel deposit at current densities up to 108 A/dm^2.

2.0 EXPERIMENTAL PROCEDURES

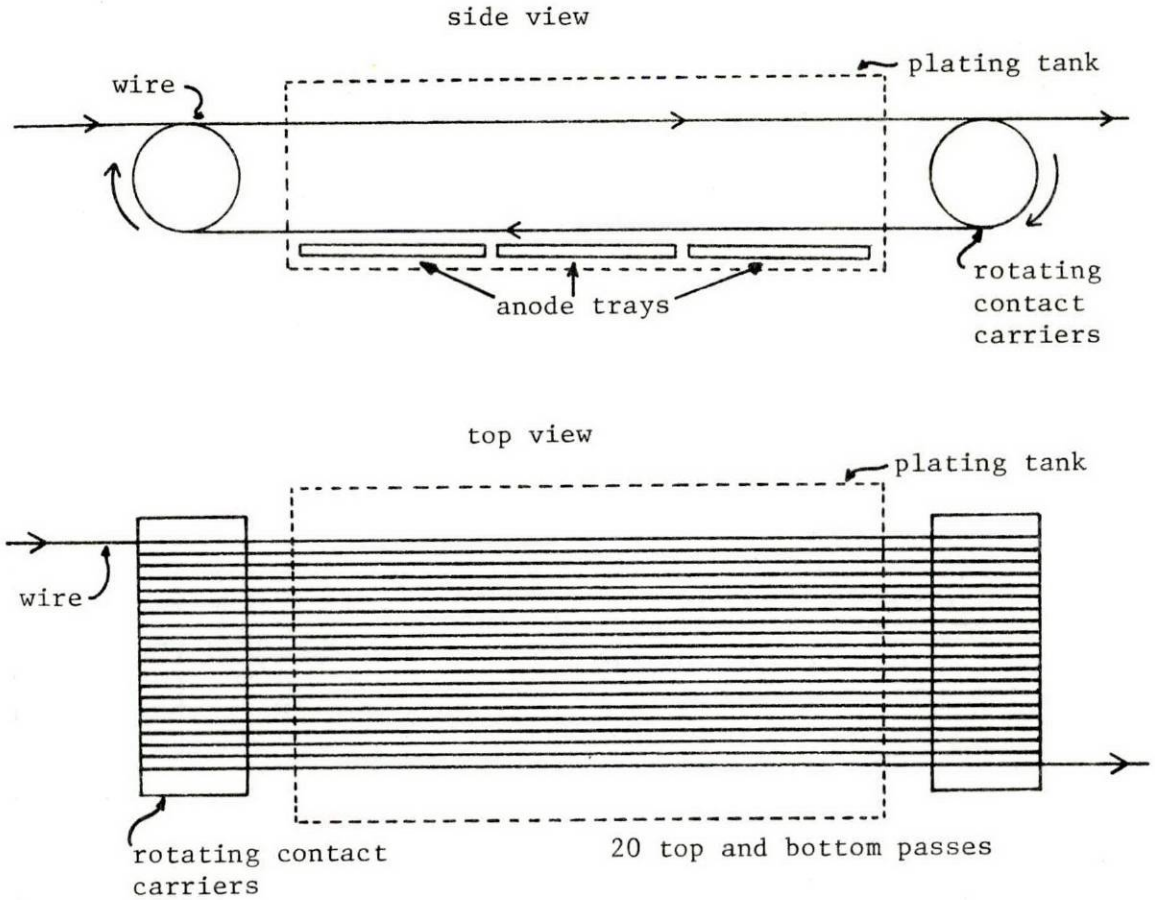
All the nickel plated copper wire samples were prepared in a continuous single line multiple pass plater as seen in figure 1. Nickel was deposited from a 1700 liter nickel sulfamate solution using SD* electrolytic nickel as the anode material. 1.0 mm diameter CDA 102 copper wire was plated to a thickness of up to 0.10 mm at compositions and operating conditions as listed in table 1.

Table 1.

	Standard Bath	Modified Bath
Nickel Sulfamate	320 g/l	675 g/l
Nickel Chloride	15 g/l	20 g/l
Boric Acid	38 g/l	38 g/l
pH	4.0	4.0
Temperature	54°C	71°C
Cathode Current Density	24 - 84 A/dm^2	48 - 108 A/dm^2
Anode Current Density	4 - 13 A/dm^2	8 - 17 A/dm^2

* trademark INCO

Figure 1



Tensile tests were performed on the nickel plated wire samples to study the mechanical properties of the deposits. Tests were conducted at room temperature on an Instron tensile testing apparatus using a gauge length of 254 mm and a crosshead speed of 25.4 mm/min. By interpolating these results in terms of a composite material, the tensile properties of the nickel deposit were calculated.

The hardness of the nickel deposits were also measured to study the mechanical properties. All tests were conducted on a Micromet microhardness tester utilizing a Vickers indentor and a load of 50 g.

Microstructural analysis of the surface and cross-section were conducted on an AMR 1200 SEM and a Reichert Metallograph at magnifications as noted. EDAX studies were also conducted to qualitatively analyze the nature of the deposits.

3.0 EXPERIMENTAL RESULTS

3.1 MECHANICAL PROPERTIES

The mechanical properties of the nickel deposits as a function of the cathode current density are listed in table 2. Utilizing the standard bath, nickel deposits produced at a relatively low cathode current density exhibited excellent ductility with a 0.2% yield strength of 222 MPa (32.2 ksi) and an elongation of 20%. However, as the cathode current density was increased, a gradual degradation of these properties occurred. As seen in figures 2 and 3, the 0.2% yield strength increased to 413 MPa (60.0 ksi) while the elongation decreased to less than 1% at a cathode current density of 84 A/dm^2.

Table 2

Standard Bath				
Current Density (A/dm^2)	Elongation (%)	0.2% Yield Strength (MPa)	(ksi)	Hardness (VHN)
24	20	222	32.2	232
36	17.4	232	33.6	265
48	3.8	280	40.7	270
60	1.0	307	44.5	286
72	1.0	345	50.3	297
84	0.5	413	60.0	312
Modified Bath				
48	18.5	234	34.0	232
60	17.8	232	33.7	220
72	12.2	244	35.4	239
84	10.5	257	37.3	235
96	5.0	266	38.6	242
108	3.2	269	39.0	250

Figure 2

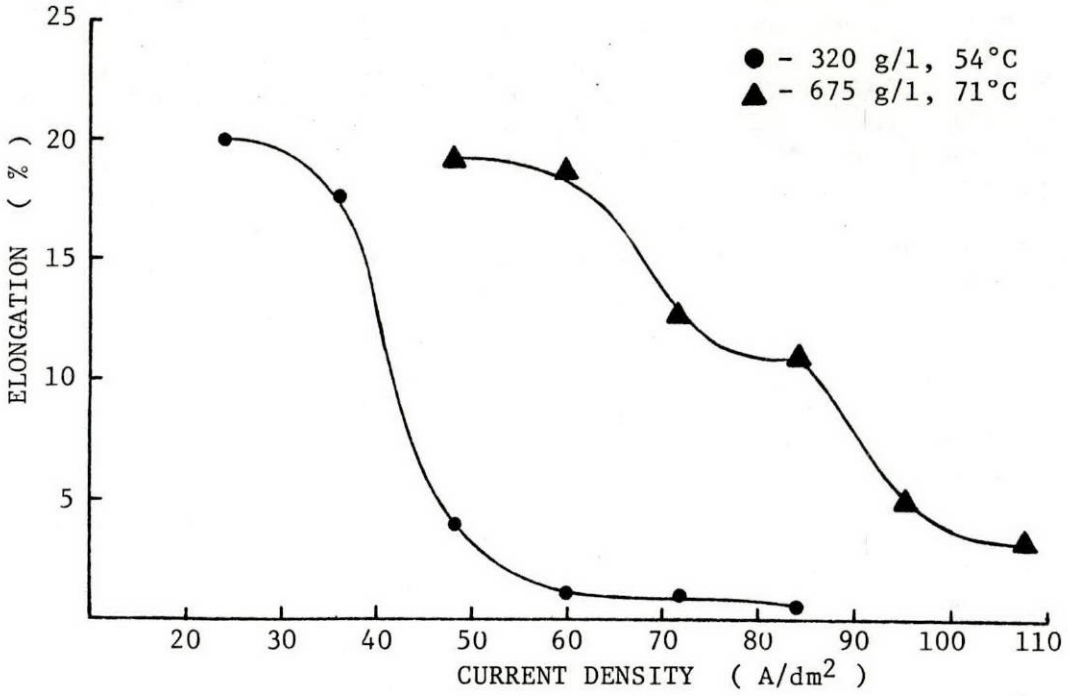
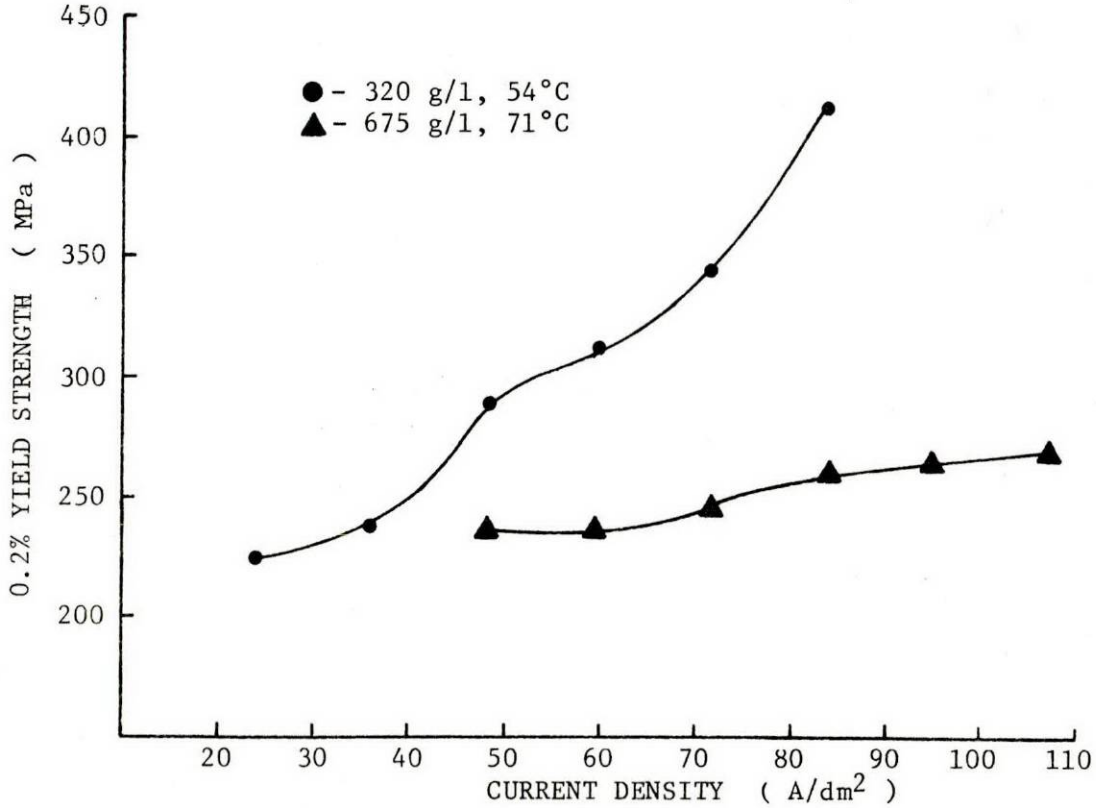


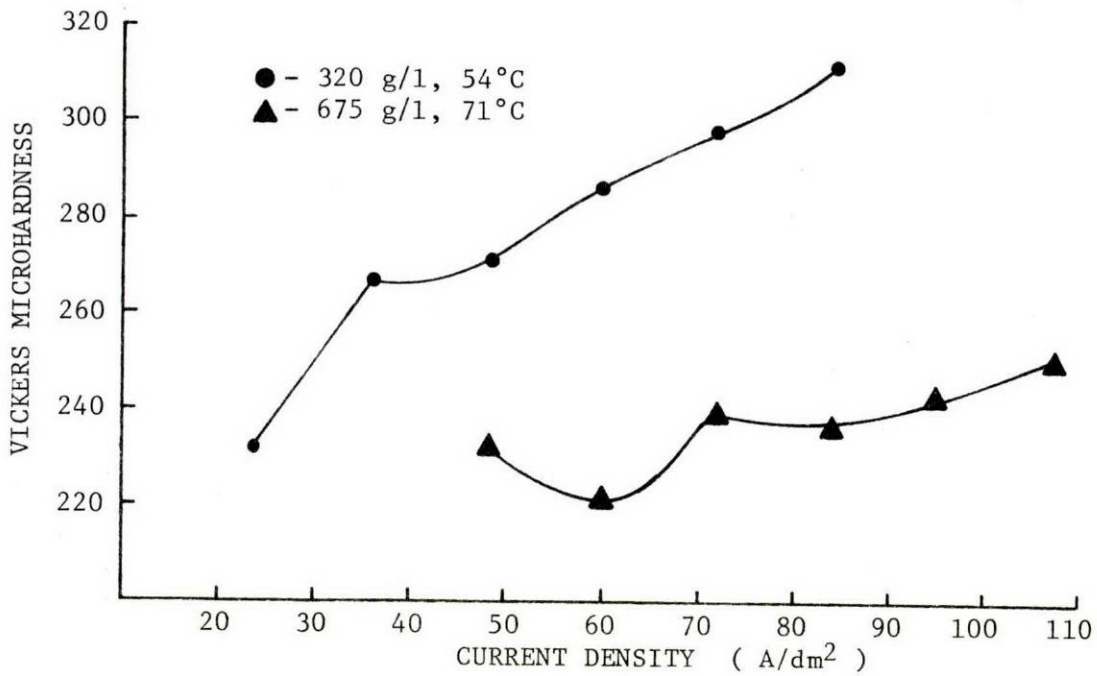
Figure 3



By modifying the operating conditions of the plating solution to those listed in table 1, a significant recovery of the ductility of the nickel deposit was observed. At 60 A/dm^2, adjusting the parameters resulted in a dramatic increase in the elongation from 1% to 17.8% as well as a substantial decrease in the yield strength from 307 MPa (44.5 ksi) to 232 MPa (33.7 ksi). However, upon further increasing the cathode current density a gradual decrease in the ductility was again observed. Although a significant decrease in the elongation and an increase in the yield strength was observed, the extent of the degradation was not as severe as in the nickel deposits prepared in a lower temperature, concentration bath.

As seen in figure 4, the hardness was also a direct function of the cathode current density. In a standard bath, upon increasing the current density from 21 A/dm^2 to 84 A/dm^2, a change in the hardness from 232 VHN to 312 VHN was observed. Increasing the temperature and sulfamate concentration of the bath had the effect of stabilizing the hardness. Within the above range of current densities, the hardness was generally around 230 VHN with little variation even at high cathode current densities.

Figure 4



3.2 MICROSTRUCTURAL ANALYSIS OF THE NICKEL DEPOSITS

Microstructural analysis revealed considerable differences in the nature of the nickel deposits as a function of the plating parameters. Nickel deposits that were electrodeposited in a standard bath at a relatively low cathode current density of 21 A/dm^2 exhibited a fine equiaxed grain structure with an average grain size of 10 µm. As seen in figure 5, the structure is lamellar with evenly spaced bands of alternating thick and thin deposit layers. Further the matrix as well as the lamellar interfaces appeared coherent with no evidence of voids or inclusions. As seen in figure 6, EDAX scans of the thick and thin regions revealed only the presence of nickel. No other elements were observed to suggest selective codeposition in the specific layers.

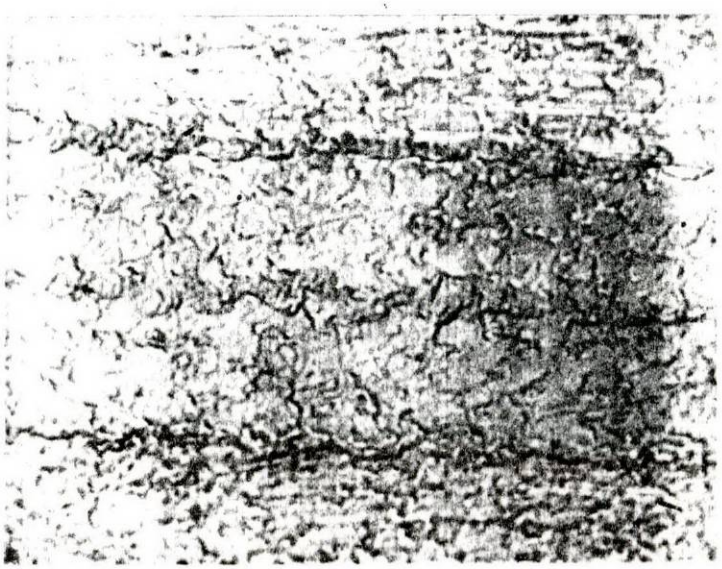


Figure 5 As deposited structure of nickel

Longitudinal cross-section

1000 X

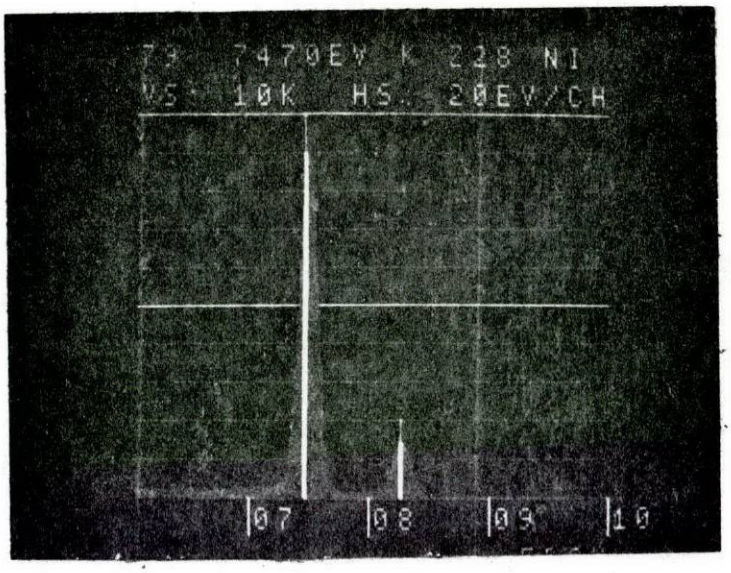


Figure 6. EDAX scan of region shown in figure 5 revealed only the presence of nickel

As the cathode current density was increased, a refinement of the grain structure was observed with an average grain size of .2μm at 84 A/dm^2 (see figure 7). Further, at relatively high current densities, inclusion particles from 1 to 3μm in size and randomly dispersed were also observed as seen in figure 8. These inclusion particles caused a distortion of the lamellar structure such that severe surface roughness was exhibited. The extent of this surface roughness is revealed in the comparative surface scans of nickel deposited at high current densities and at low current densities where no inclusion particles were present as seen in figures 9 and 10.

EDAX analysis of these particles revealed the presence of two distinct types of particles. As seen in figure 11a and 11b, particle A appears to be nickel while particle B appears to be a compound of nickel and sulfur.

Increasing the temperature and sulfamate concentration of the plating solution resulted in a coarsening of the grain structure. As seen in figure 12, by increasing the parameters from 54·C and 320 g/l to 71°C and 675 g/l respectively, an average grain size of 10μm was observed at a cathode current density of 84 A/dm^2. However, the inclusions were still present in the nickel deposits at higher cathode current densities.



Figure 7. Longitudinal cross-section of nickel deposited from a standard bath at 84 A/dm^2

1000 X



Figure 8. Nickel deposited at high current density exhibits inclusion particles

150 X

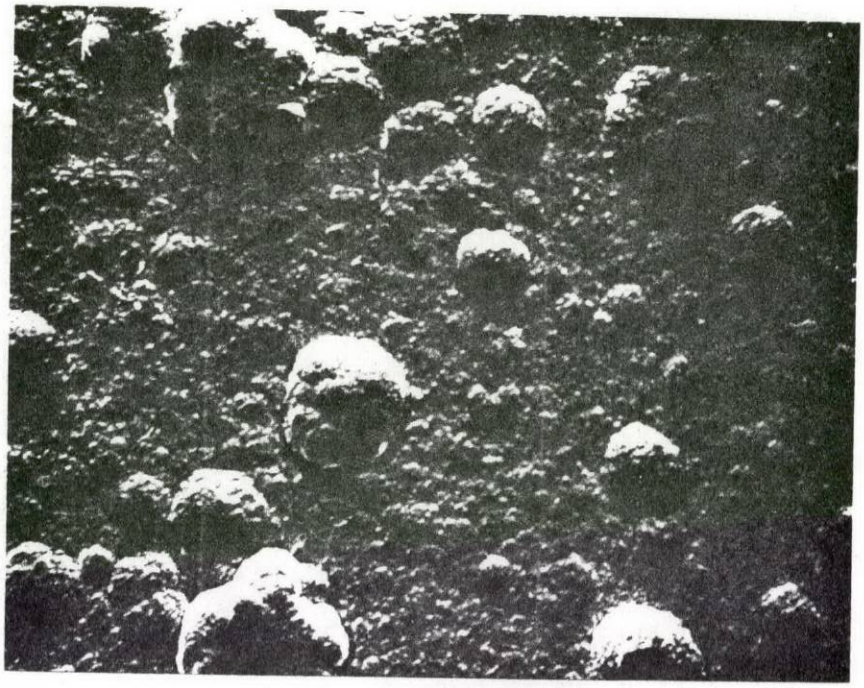


Figure 9. Surface of nickel deposited at a high current density

SEM 200 X

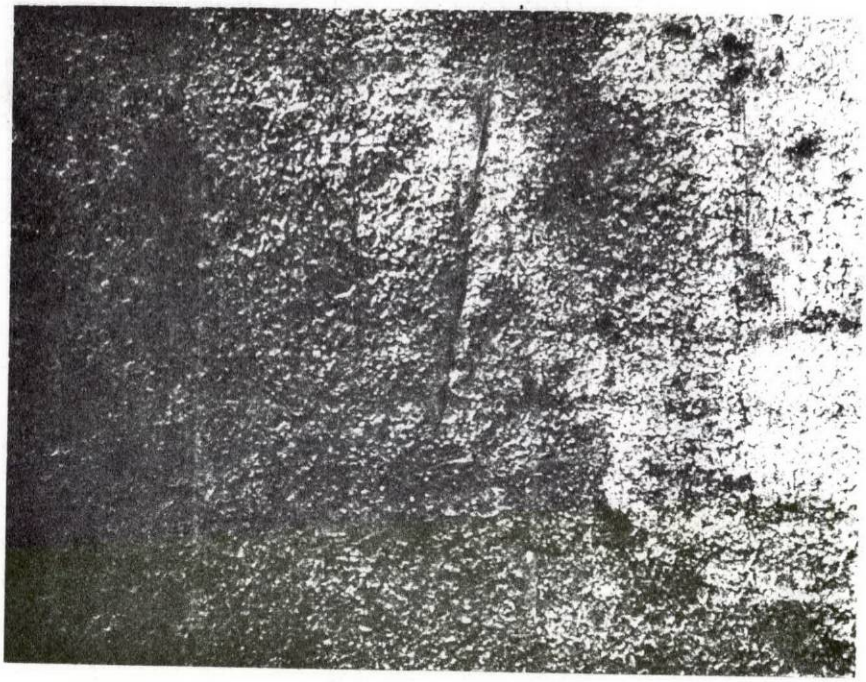


Figure 10. Surface of nickel deposited at a low current density

SEM 200 X

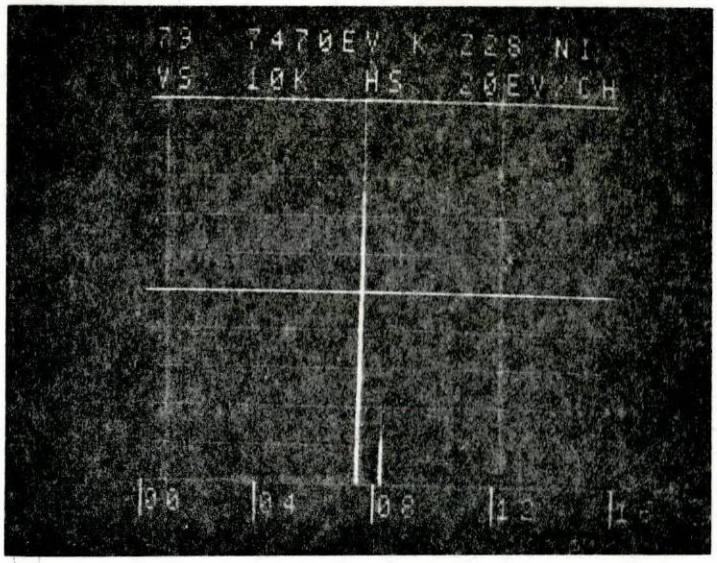


Figure 11a. Spot scan of particle A revealed only the presence of nickel

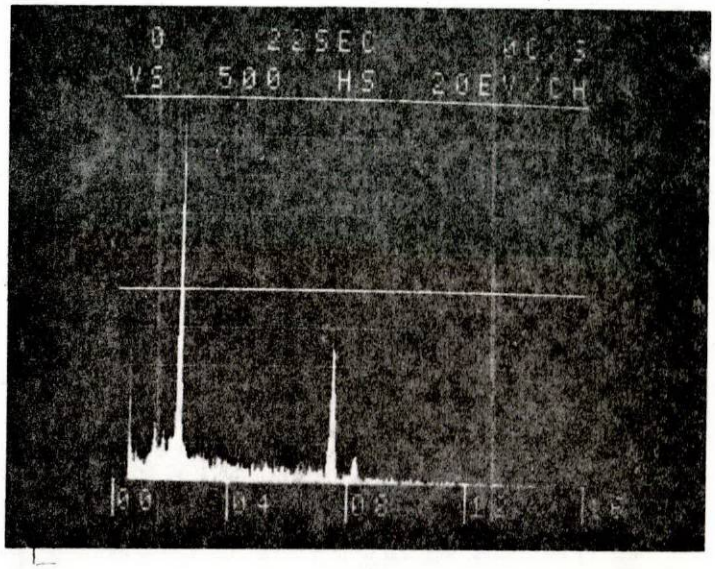


Figure 11b. Spot scan of particle B revealed the presence of both nickel and sulfur.

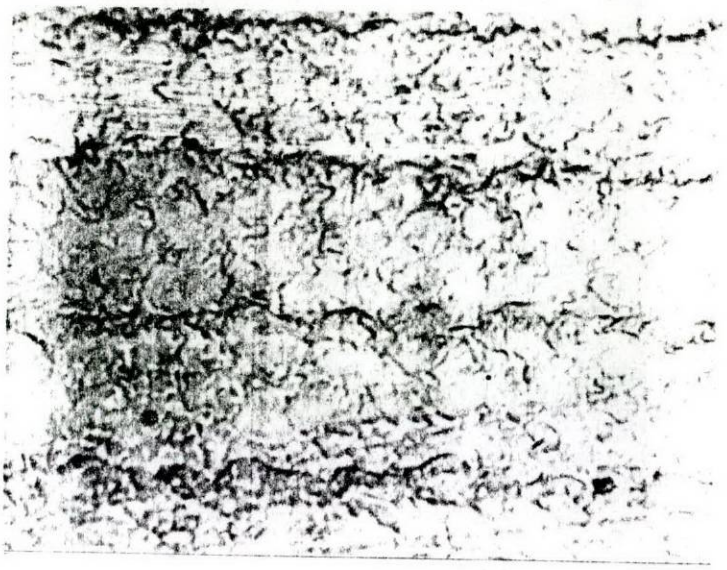


Figure 12. Longitudinal cross-section of nickel deposited from a modified bath at a current density of 84 A/dm^2

1000X

4.0 DISCUSSION

Electrodeposition of nickel at high current densities significantly alters the mechanical properties of the deposits. As the cathode current density is increased, a gradual change from a ductile to brittle behavior is observed. From microstructural analysis this change in properties may be related to the nature of the nickel deposit. Two distinct changes in the microstructure occur as a function of increasing cathode current density; a) refinement of the grain structure and b) presence of inclusions in the plate. The first appears to be a consequence of the plating parameters while the latter a result of the continuous plating process.

4.1 EFFECT OF PLATING PARAMETERS ON THE MECHANICAL PROPERTIES

It appears an increase in the current density results in a decrease in the ductility of the deposit as well as an increase in the hardness.

At high current densities it appears that the rate of nucleation of new crystal orientations (formation of nuclei) occurs more rapidly than the growth of existing ones resulting in a finer grain structure. From internal energy considerations alone this mechanism seems unlikely. However, at high current densities a concentration polarization of the cathodic surface occurs where a large difference develops between available electrons and metal ions. This difference may act as the driving force for this type of deposit formation. Further, the higher the current density the greater is the polarization accounting for the observed dependence of grain size on the cathode current density.

A change in the grain structure as a function of the cathode current density has also been observed by Knapp (3). However, an increase rather than a decrease in the grain size as reported in the present investigation was observed with increasing cathode current density. The range of current densities investigated by Knapp was much lower than in the present investigation. It appears that in this range of current densities, polarization of the cathodic surfaces had not occurred. Therefore, increasing the current density increased the rate of growth of existing nuclei rather than the rate of nucleation.

The increase in hardness of the nickel deposit with increasing current density may also be attributed to the polarization at the cathodic surfaces. Due to the polar-

ization, a deposit with a high defect concentration is produced. These defects are probably in the form of microvoid formation due to the entrapement of excessive gaseous hydrogen produced at the cathodic surface or a high vacancy concentration due to the depletion of metal ions at the cathodic surface. The greater the polarization the higher is the defect concentration accounting for the increase in hardness with increasing current density. Jacobson and Sliwa also observed evidence of such defect formation in nickel deposits produced from a sulfamate solution (1).

By increasing both the temperature and the sulfamate concentration of the solution, a significant increase in the ductility and a decrease in the hardness was observed. The microstructures of these deposits exhibited a larger grain size. Increasing the temperature and concentration appeared to effectively decrease the concentration polarization by increasing the diffusion rate and the supply of ions respectively to the substrate resulting in the larger grain size and a lower hardness.

4.2 EFFECT OF CONTINUOUS PLATING PROCESS ON THE MECHANICAL PROPERTIES

In the continuous single line multiple pass plating process, 40 successive passes are made through the plating solution by wrapping the wire around two rotating contact carriers. The wire is passed horizontally over the anode trays such that a constant distance of 5 cm is maintained in the lower pass and a distance of 60 cm in the upper pass. Since the wire is continuously passed in and out of the plating solution a lamellar type structure is produced rather than a columnar grain structure. The effects produced are similar to pulse plating. Whereas in pulse plating the applied current is electronically pulsed the multiple pass process achieves this on and off time mechanically by passing the wire in and out of the solution.

As the cathode current density is increased the presence of inclusions are observed in the plate. These inclusions were obtained even after increasing the bath temperature and sulfamate concentration and appeared to be responsible for the loss of ductility under these conditions. EDAX analysis of these inclusions revealed the presence of both nickel and sulfur in significant quantities. It appears these inclusions are nickel sulfide particles which formed at the anodes during dissolution and subsequently deposited on the surface during plating.

Because of the high dissolution rate of the anodes

needed at higher current densities, the solution is vigorously circulated in the plating tank by three transfer pumps with a total capacity of 570 l/min. Further, to decrease anodic polarization, bags are not placed aroung the anode trays. At high current densities the rate of formation of nickel sulfide is greatly accelerated and due to the large turbulence in the tank is dispersed into the solution. The particles subsequently deposit onto the surface of the wire during electrodeposition. These inclusion particles act as stress raisers during deformation and results in embrittlement.

5.0 SUMMARY

The brittle nature of nickel deposits produced from a sulfamate solution at high current densities may be attributed to the microstructure of the nickel deposit. Due to increased polarization at higher current densities, an extremely fine grain structure with a high defect concentration is exhibited. Further, the high rate of anode reactions incorporates nickel and nickel sulfide particles in the deposit resulting in embrittlement. By controlling the plating parameters and the continuous plating process responsible for the observed microstructure, a ductile nickel deposit may be obtained.

By increasing the temperature and sulfamate concentration from 54°C and 320 g/l to 71°C and 675 g/l, the polarization at the cathodic surface was reduced such that a moderate grain size structure with a relatively low defect concentration was obtained. This substantially increased the ductility and decreased the hardness of the deposit.

To eliminate the particle deposition two modifications in the plater were made: a) increase the anode area, b) installation of finer filters for filtration down to 1µm. By increasing the anode area the anode current density was reduced such that the rate of formation of nickel sulfide was reduced. Through the use of finer filters, particles which would otherwise be passed back into the solution were collected.

Utilizing these modifications a ductile nickel deposit was obtained at current densities as high as 108 A/dm^2. Metallographic examination of the deposits revealed an average grain size of 10µm with no evidence of inclusions. Deposits exhibited excellent mechanical properties with an elongation of 20%, a 0.2% yield strength of 220 MPa (31.5 ksi) and a hardness of 225 VHN.

REFERENCES

1. B. E. Jacobson and J. W. Sliwa, "65th ANNUAL AES TECHNICAL CONFERENCE" Washington D.C. (June 1978)

2. G. S. Petit, R. R. Wright, T. Kwasnoski and C. W. Weber "COPLATING OF OXIDE DISPERSIONS IN NICKEL FROM HOMOGENEOUS SOLUTION" Plating and Surface Finishing (October 1977)

3. B. B. Knapp "NOTES ON NICKEL PLATING FROM SULFAMATE SOLUTIONS" Plating (December 1971)

4. L. Gianelos "TROUBLESHOOTING OF NICKEL PLATING SOLUTIONS" Plating and Surface Finishing (August 1977)

5. F. X. Carlin "PREVENTION OF POOR ADHESION BETWEEN LAMELLAE IN THICK NICKEL DEPOSITS AND ELECTROFORMS" Plating (February 1968)

6. R. E Reed-Hill "PHYSICAL METALLURGY PRINCIPLES" D. Van Nostrand Co. 1973

B-2

General Interest
Session B

Peptone Control in Solder Electroplating

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ABSTRACT

The ultra-violet spectral analysis of peptone in the solder plating bath has been studied. Observations of the grain structures of solder alloys plated from solder baths at various peptone concentrations are also presented. The Hull Cell Test and the solder alloy composition analysis support the results of this study.

It has been found that peptone can be determined quantitatively by a UV spectral analysis. This analytical method supplies a simple and quick way to control peptone in solder plating. It can also be applied as a control for the carbon treatment schedule to prevent the accumulation of the peptone decomposition products in the plating bath. The inspection of the grain structure of the plated solder is recommended as an aid to peptone control for those plating laboratories which have no UV spectrophotometer facilities.

1. INTRODUCTION:

The solder coating plated on copper deposits of printed wiring boards (PWB) functions as an etch mask and as a corrosion resist. It also serves as an inhibitor for whisker growth and an aid to solderability. A good solder deposit must conform to quality standards, since problems with solder deposit normally become apparent after reflow when the board is almost 100% finished; fixing problems at this stage is very costly. Therefore, solder plating is one of the most important and critical steps in PWB's manufacturing process.

High throw fluoborate solder plating baths are commonly used in solder plating. Solder alloys plated from these baths have a high degree of uniformity and a fine-grained solder structure with excellent solderability characteristics. Bath parameters, except peptone, can be properly controlled by wet chemical analysis or instrumental analysis.

Peptone is one of the important ingredients in the solder fluoborate electroplating bath. It is an organic additive that promotes the formation of fine-grained structure of solder deposits. Peptone also affects the composition of the solder deposit. Lack of quantitative analysis for peptone, coupled with its decomposition and removal by carbon treatment, make it extremely difficult to control its concentration in a solder bath. Inadequate or excessive peptone additions cause wide varieties of problems.

Paunovic and Oechslin[1] had found that peptone can be determined by chronopotentiometry. However, the measurement (i.e., transition time) is a function of concentrations of all bath components. Separate calibration curves are necessary for a particular composition of the plating bath. Since all chemical constituents in the production solder bath change from time to time, the chronopotentiometric method is not practical.

This paper describes a very simple and quick method to control peptone in solder plating. The grain structure of the deposit, plated at different peptone concentrations, are also presented for discussion.

2. ULTRA-VIOLET SPECTROPHOTOMETRY - BEER'S LAW:

Spectrophotometry in the UV region of the spectrum has been practiced for a long time. Widespread analytical use began after World War II. The UV Spectrophotometric method is generally rapid and is adaptable to the determination of small concentrations of species. It involves the measurement of the absorption of radiant energy by a chemical species as a function of the wavelength of the radiation. When light passes through a transparent material, small wavelengths of light may be absorbed. This selective absorption of radiation forms the basis for the application of UV Spectrophotometry to qualitative analysis. The intensity of the transmitted light is related to the concentration of the material and, therefore, can be used for quantitative analysis. The calculation of the intensity of an absorption band involves the use of Lambert's and Beer's Laws [2,3]. Lambert's Law states that the absorbance of a homogeneous sample is directly proportional to the thickness of the sample in the optical path. Beer's Law is analogous to Lambert's Law. The amount of light absorbed is proportional to the number of absorbing molecules through which the light passes. The combined Beer-Lambert Law can be formulated mathematically by (4,5):

$$T = \frac{I}{I_0} = 10^{-abc}$$

or

$$A = -\log T = \log \frac{I_0}{I}$$

Where A is defined as absorbance or optical density, T is transmittance which is the ratio of the transmitted light intensity I to the incident light intensity I_0 through a path length of b (in centimeters), c is the concentration of sample absorbing species (usually in grams/liter or mole/liter) and the constant a is called the absorptivity. The Beer-Lambert Law in the form A = abc is widely used in quantitative analysis because

absorbance is directly proportional to concentration. The absorptivity, a, is a characteristic of a given substance only under precisely defined conditions of wavelength, solvent, temperature and other parameters.

As a practical matter, spectrophotometric measurements usually are made in dilute solution ($\leq 10^{-3}$ M), and practically all solutes exhibit ideal behavior in the absence of specific chemical effects [6]. There are several graphical presentations of spectrophotometric data[7] depending upon the problem, one may use the preferable way to plot the data. When the plot of absorbance vs. concentration for an absorbing species at a particular wavelength is linear, the substance is said to obey Beer's Law. Such a plot is known as a calibration curve or working curve. Concentration of the unknown sample can be determined from this graph.

3. EXPERIMENTAL:

The solder plating solutions used for this study consisted of a low metal, high throw fluoborate bath identical to the production bath at Photocircuits, Kollmorgen Corporation. Tin content was supplied as tin fluoborate (Harstan, industrial grade). Fluoboric acid (Allied Chemical, purified grade) was added to maintain the high conductivity of the bath. Boric acid (Kurts & Wolfe Company) was added at saturation level. Peptone concentration was controlled on the basis of dry peptone powder (American Laboratories Inc.).

Tests were run in a one-gallon tin-lead solution with variations of peptone concentrations ranging from 0 g/l to 20 g/l. All other constituents were held constant. Bath solutions which were one-hundredths diluted were taken as the sample solutions for the UV spectrophotometric study of peptone. The solder deposits plated at 20 amp/ft^2 in the solder solution at increasing peptone concentration were analyzed for tin and lead contents by atomic absorption spectrophotometer. Alloy deposit and Hull cell panels were also plated for observations of the grain structure and the qualtiy of solder.

Beckman DBG-T UV-Visible Spectrophotometer was used for UV spectral studies. Perkin-Elmer Atomic Absorption Spectrophotometer 360 was used for alloy content analysis. Unitron NEC-P-155 metallograph with Model PB camera attachment was used for the grain structure observations of the solder deposit.

4. RESULTS AND DISCUSSION:

A. UV Spectra

A low metal, high-throw fluoborate solder bath with peptone as the grain refiner shows a broad peak at 205-225 mμ. There are two peaks overlapped at the foot of the broad peak and they show as shoulders at 245 and 275 mμ (Figure 1A). These peaks appear as additive peaks of the individual components of the solder bath shown in Figures 1B, 1C and 1D. The peak listings for the bath components are summarized in Table I. It is evident that the broad peak at 205-225 mμ of the solder bath solution is the sum of the individual composite. Additionally, this broad peak is pretty close to the vaccum UV range, it is of little importance analytically.

The UV peak at 275 mμ of peptone was studied. In order to obtain a better defined peak for peptone in the solder bath, the UV spectrum was taken under the compensation of solder bath without peptone in the reference cell of a double beam UV Spectrophotometer. A series of solder bath solutions were made at various peptone concentrations. These UV spectra are shown in Figure 2. The first peak (Peak I) becomes more well-defined and its absorbance increases as peptone concentration increases. The second sharp peak (Peak II) shows the same characteristics. The compilation of wavelength maxima and absorbance of the two peaks are shown in Table II. Peak I stays constant at 275 mμ as peptone concentration increases. Peak II also shows relatively constant wavelength maxima within experimental errors. The absorbance of both peaks increases in direct proportion to the peptone concentration. The proportionality is evident in Figure 3. This is the calibration curve from a series of peptone standard solutions under optimum solder plating conditions. These

standards cover a reasonable range of peptone concentration in the solder plating bath. Curve I corresponds to Peak I at 275 mμ of peptone. It obeys Beer's Law perfectly. However, Curve II which corresponds to Peak II at 233 mμ, deviates from Beer's Law at lower concentration of less than 1.0 g/l. Curve I fully demonstrates that the UV peak at 275 mμ is due to peptone absorption, and that it obeys Beer's Law. The UV spectral analysis can be applied for peptone control in the solder plating.

In practical solder plating, bath composition changes from time to time, analysis of peptone by compensation of tin and lead absorption in the reference cell would be tedious. Therefore, solder bath samples are investigated at various peptone concentrations without compensation of tin and lead absorption (in other words, with solvent water in the reference cell). These UV spectra are shown in Figure 4. The peptone peak at 275 mμ is affected by the absorption of tin and lead. The peak is not very well-defined and shows as a shoulder. The peak maxima shifts about $\pm$ 5 mμ. However, the absorbance of the peak still can be determined from the spectrum. The calibration curve of absorbance vs. peptone concentration in Figure 5 again follows Beer's Law perfectly. It is very interesting to note that the absorbance of the tin peak (i.e., tin concentration in the bath) at 244 mμ increases as peptone concentration increases and finally is merged with the peptone peak in Figure 4. This phenomenon supports and explains the fact that peptone addition increases the amount of tin deposited in the solder alloy as reported earlier[8,9]. Actually, it is found that in the low metal solder bath, tin increases by 1-5% in the solder deposit with increased peptone addition from 1.0 to 5.0 g/l.

B. Grain Structure of Solder Deposit:

Hull cell panels had been used for the test of solder bath performance with respect to peptone levels[9]. Estimation is fairly satisfactory based on observed Hull cell results. Without peptone in the solder bath, the Hull cell panel shows treeing on the high current density edge; no plating on the low current density edge. Peptone at 3.0-7.0 g/l range shows smooth and light grey Hull cell panels covering from the high to low current density edges. Peptone at 10 and 20 g/l shows darkening on the high current density edges. In addition to the Hull cell tests, grain structure of solder deposits plated from solder bath at different peptone concentration were observed. At 0.0 g/l peptone, an unacceptable high lead alloy and poor fusing deposit is observed. The grainy and dark surface can be easily inspected visually. The grainy solder crystals are magnified in Figure 6A. A slight increase in peptone concentration makes a marked change in the crystal structure of solder. Better mutual solubility of tin and lead are noticeable upon addition of peptone. In other words, the tin-lead is finer-grained. At 1.0 g/l of peptone, many wet look solder particles of 1.5-2.0 mil size are observed on a uniform solder base, as shown in Figure 6B. As peptone increases to 3.0 g/l, more uniform solder crystals with a few flat and wet solder particles (about 2.5 mil) is observed in Figure 6C. The grain structure is much improved. At 5.0 g/l of peptone, the microstrucutre of the tin-lead alloys (Figure 6D) shows a typical eutectic structure with a high degree of uniformity. This fine-grained tin-lead alloy shows good fusing without any particle formation and surface residue. When the peptone concentration is 7.0 g/l or higher in the plating bath, particles start to reappear. The particles become larger and more numerous with higher peptone concentrations as can be seen in Figures 6E and 6F. At extremely high peptone levels of 20 g/l, brownish particles, the size of

5.5-6.0 mil, are noticed and less uniform solder is obtained. (See Figure 6G). Although the content of these brown particles is not identified, it is believed that the codeposition of peptone (brown in color) is highly possible. Another indication of codeposition of peptone is the brown holes (Figure 7) observed in the solder microsection deposit plated from the solder bath with overdosaged peptone.

5. CONCLUSION:

Based on the test results of this study, it is found that peptone in the solder plating bath can be determined quantitatively by a simple and quick UV spectral measurement. The calibration curve for a set of standard peptone solutions as in Figure 5 can be established in any plating laboratory. The UV absorption is measured at 275 mμ for the diluted sample plating bath solution. The peptone concentration can be read directly from the calibration curve.

Peptone decomposition products have a deteriorative effect on the quality of solder. Accumulation of excessive amounts of the organic breakdown products of peptone can cause darkening of the solder deposit. Carbon treatment is the normal operation to remove the organic compounds. It is found that the UV spectrum of the solder bath is very useful in predicting the necessity for carbon treatment. Figure 8 is the UV spectrum of a solder bath which has been plated for quite a while (water in reference cell). Many organic impurities, although not identified, are indicated by many overlapping peaks in 330-260 mμ region. Routine UV spectral analysis for the solder plating bath can determine not only the peptone concentration but also the scheduling of the bath carbon treatment.

For those plating laboratories where no UV Spectrophotometer is facilitated, observations of the grain structure of panels plated in the plating bath can be used as a helpful aid for troubleshooting. Establishment of these practices at Photocircuits has resulted in reduced plating problems and a greater confidence in the solder electroplating process.

ACKNOWLEDGEMENT

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REFERENCES

(1) Paunovic, M., and R. Oechslin, Plating, 58(6), 599 (1971).

(2) Malinin, D.R., and J.H. Yoe, Journal of Chemical Education, 38, 129 (1961).

(3) Pfeiffer, H.G., and H.A. Liebhafsky, Journal of Chemical Education, 28, 123 (1951), 30, 450 (1953).

(4) Lohman, F.H., Journal of Chemical Education, 32, 155 (1955).

(5) Holleran, E.M., Journal of Chemical Education, 32, 636 (1955).

(6) Van deHulst, H., "Light Scattering by Small Particles," Wiley, New York, p. 270 (1957).

(7) Mellon, M.G., Ed., "Analytical Absorption Spectroscopy," Wiley, New York, p. 104 (1950).

(8) Rynne, G.B., Plating, 58(9), 867 (1971).

(9) Spiliotis, N.J., Insulation/Circuits, June, 33, (1978).

TABLE I: UV PEAKS FOR THE CONSTITUENT COMPONENTS OF THE SOLDER BATH

Sample[(a)]	λmax_1 μm	λmax_2 μm
Peptone	275	205
Tin Fluoborate	244	217
Lead Fluoborate	-	207

a. Concentrations of sample solutions are:

Peptone : 0.05 g/l

$Sn(BF_4)_2$: 0.15 g/l

$Pb(BF_4)_2$: 0.07 g/l

TABLE II: UV PEAK PARAMETERS OF PEPTONE IN SOLDER BATH[a]

CONCENTRATION OF PEPTONE IN SOLDER BATH g/l	PEAK I		PEAK II	
	λmax μm	ABSORBANCE	λmax μm	ABSORBANCE
1.0	275	0.0039	235	0.0044
3.0	275	0.012	233	0.031
5.0	275	0.020	231	0.074
7.0	275	0.026	232	0.080
9.0	275	0.033	231	0.102
11.0	275	0.038	232	0.128

(a) All measurements are with the compensation of solder bath at 0.0 g/l of peptone in the reference cell. Samples for UV spectra are one-hundredth dilution of the bath solution.

FIGURE 1: UV Spectra of the Solder Bath and Its Composite

FIGURE 2: UV Spectra of Peptone at Various Peptone Concentrations

FIGURE 3: Absorbance vs. Peptone Concentration

FIGURE 4: UV Spectra of the Solder Plating Bath Solutions at Various Peptone Concentrations

FIGURE 5: Calibration Curve for Peptone in Solder Plating Bath

FIGURE 6: Microstructure of Solder Deposit Plated from Solder Baths with Variation of Peptone Concentrations.

FIGURE 7: Codeposition of Peptone in the Solder Deposit

FIGURE 8: UV Spectrum of the Solder Plating Bath with High Accumulation of Peptone Decomposition Products

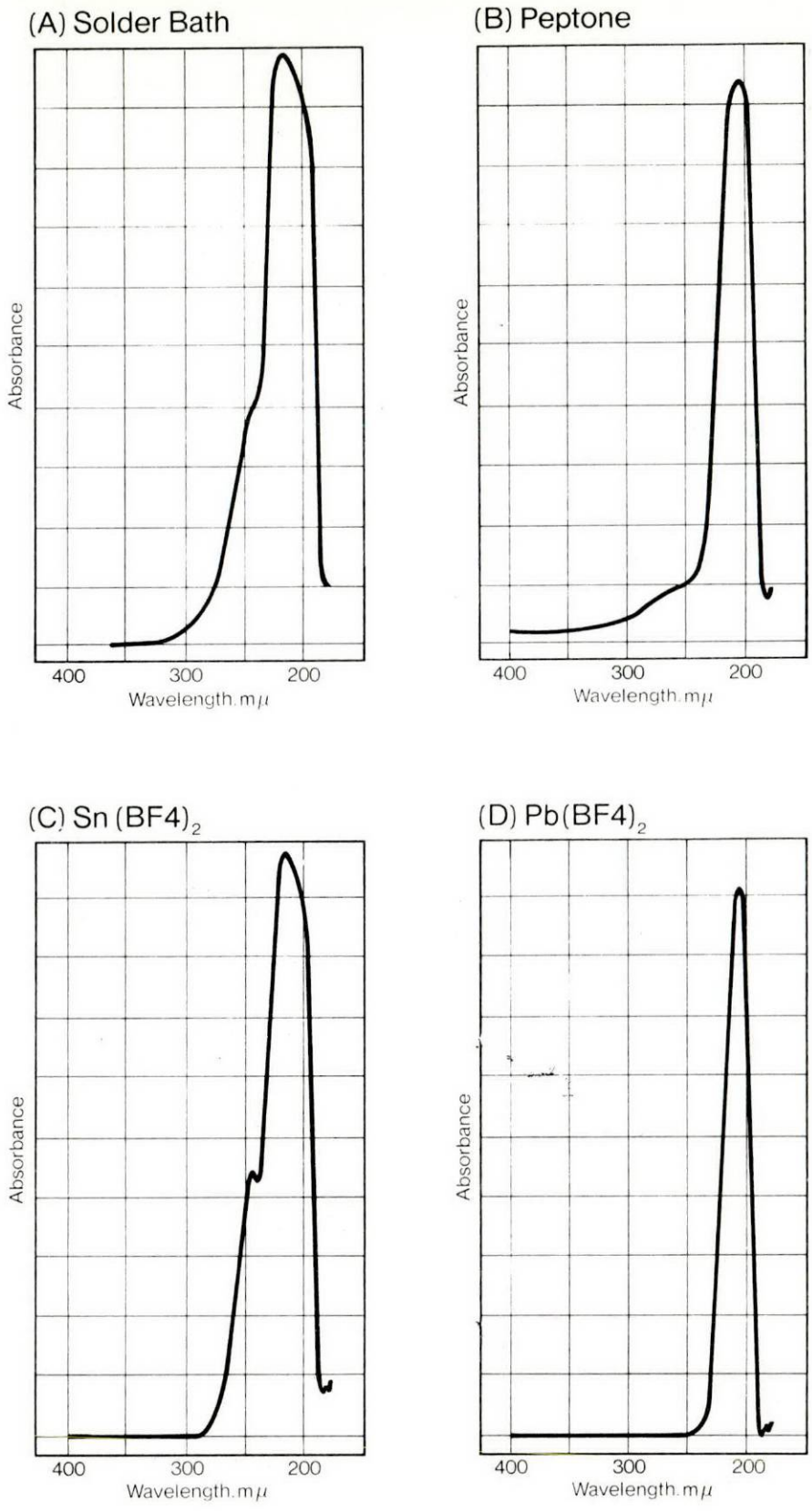


Figure 1. UV Spectra of Solder Bath and Its Composite

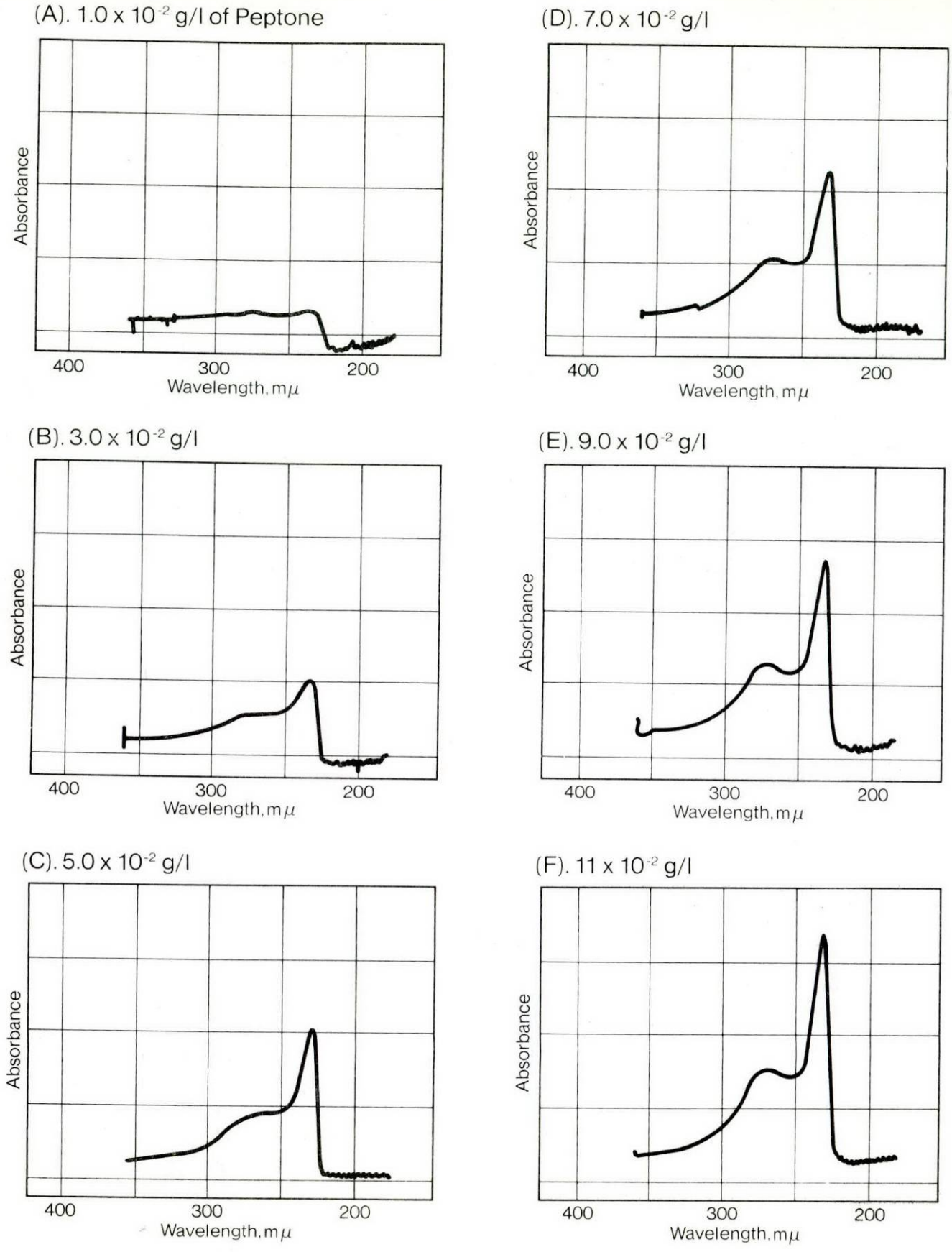


Figure 2. UV Spectra of Peptone
(Tin and Lead Absorptions are Compensated)

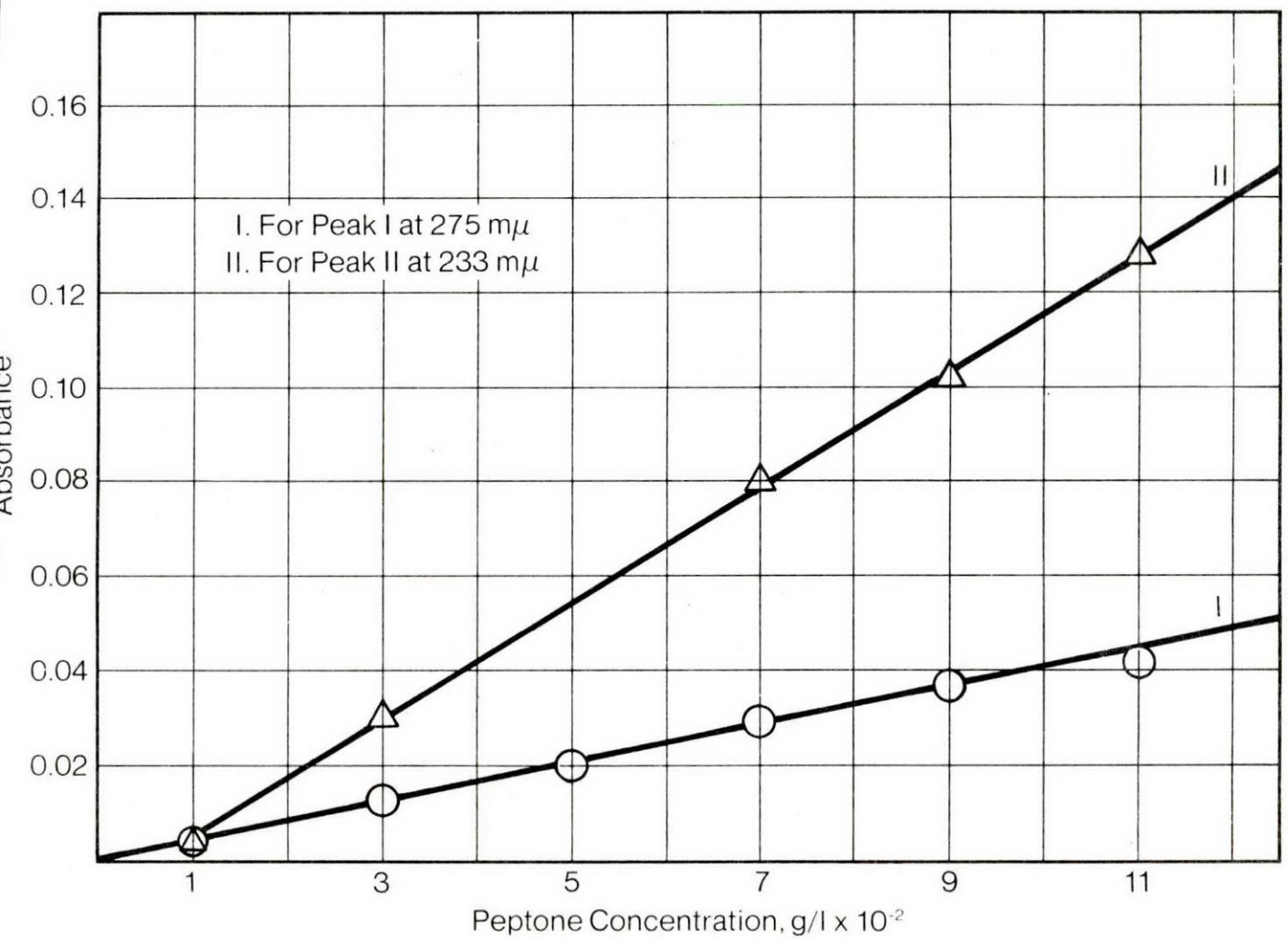


Figure 3. Absorbance vs. Peptone Concentration

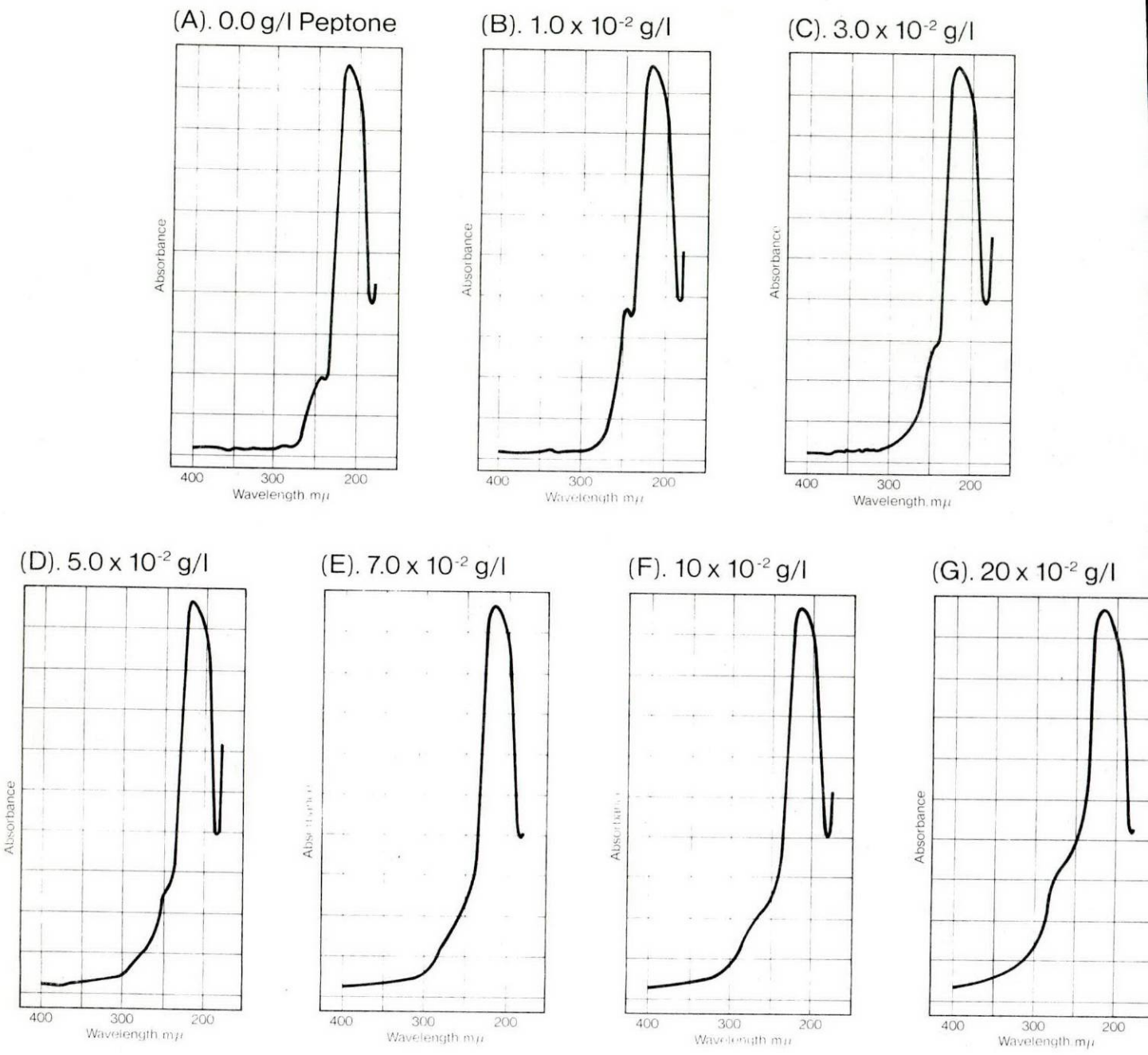


Figure 4. UV Spectra of the Solder Plating Bath Solutions at Various Peptone Concentrations

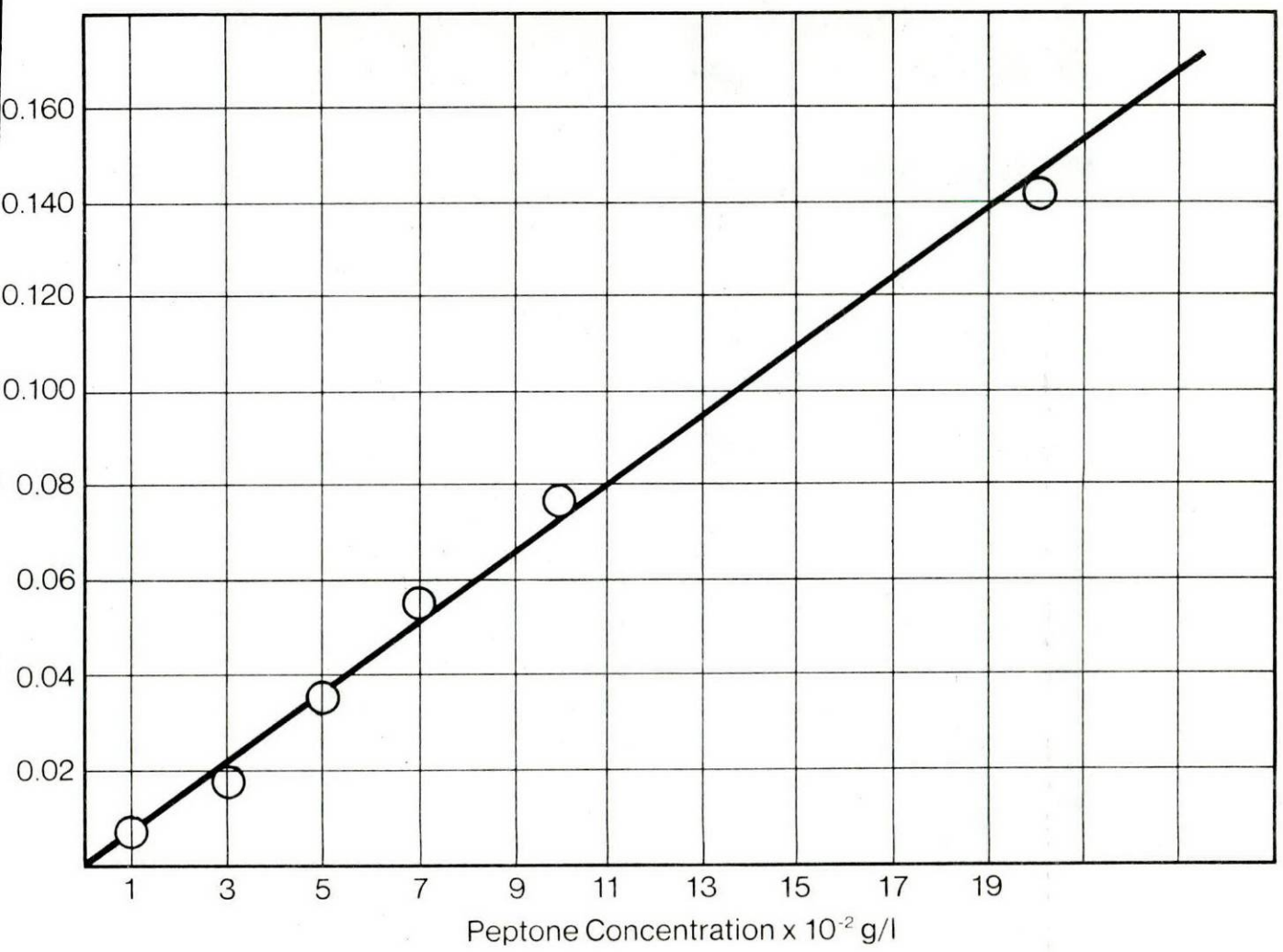
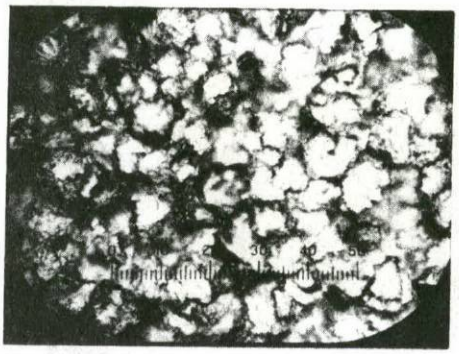
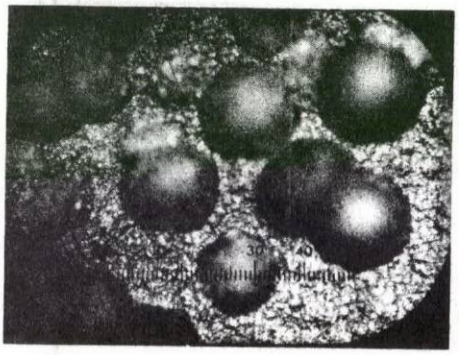


Figure 5. Calibration Curve for Peptone in Solder Plating Bath

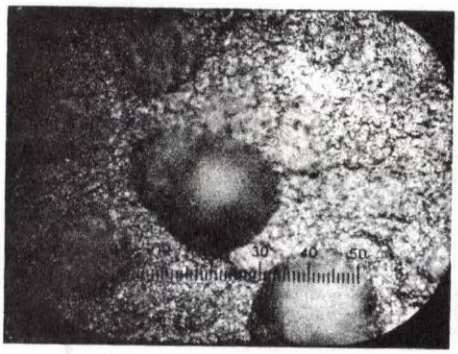
(A) 0.0 g/l Peptone



(B) 1.0 g/l



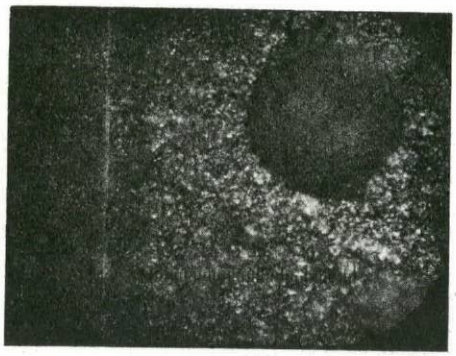
(C) 3.0 g/l



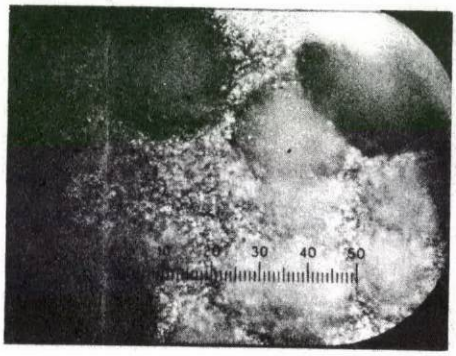
(D) 5.0 g/l



(E) 7.0 g/l



(F) 10 g/l



(G) 20 g/l

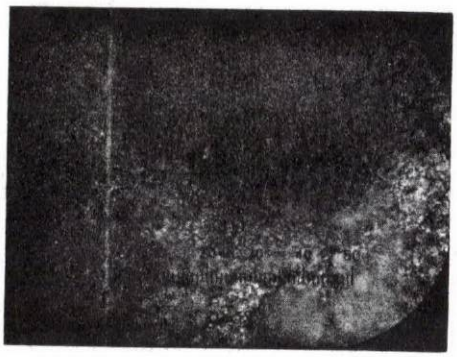
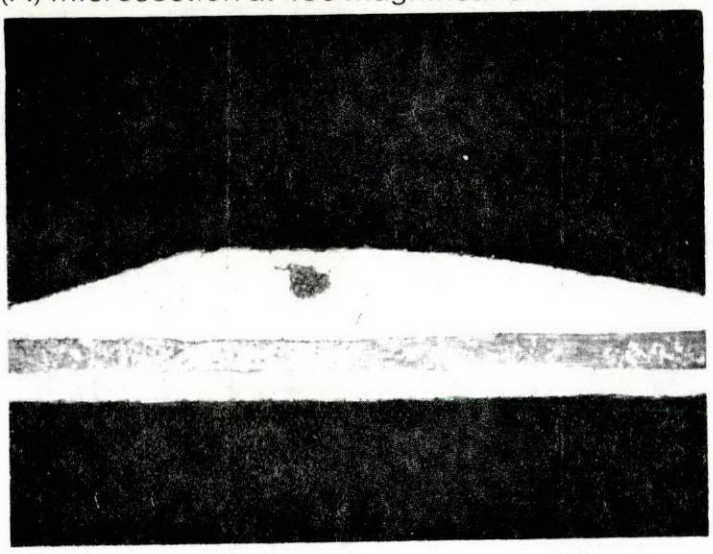


Figure 6. Microstructure of Solder Deposit Plated from Solder Baths with Variation of Peptone Concentrations (400 Magnification)

(A) Microsection at 400 Magnification



(B) Microsection at 1000 Magnification

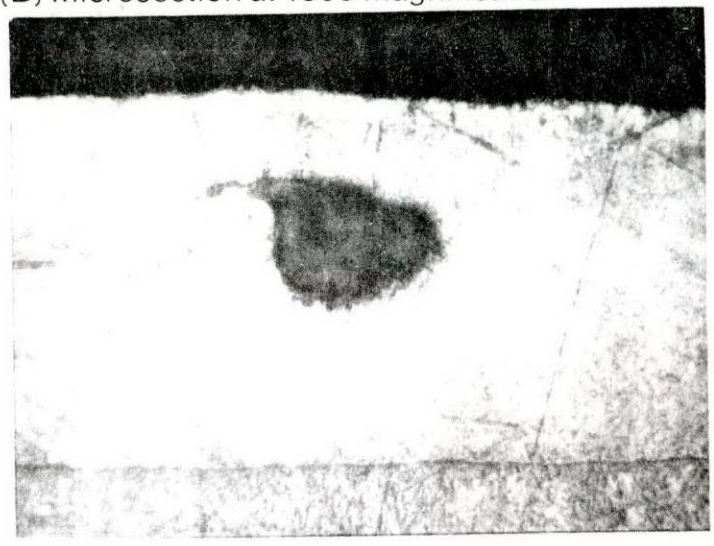


Figure 7. Codeposition of Peptone in Solder Deposit

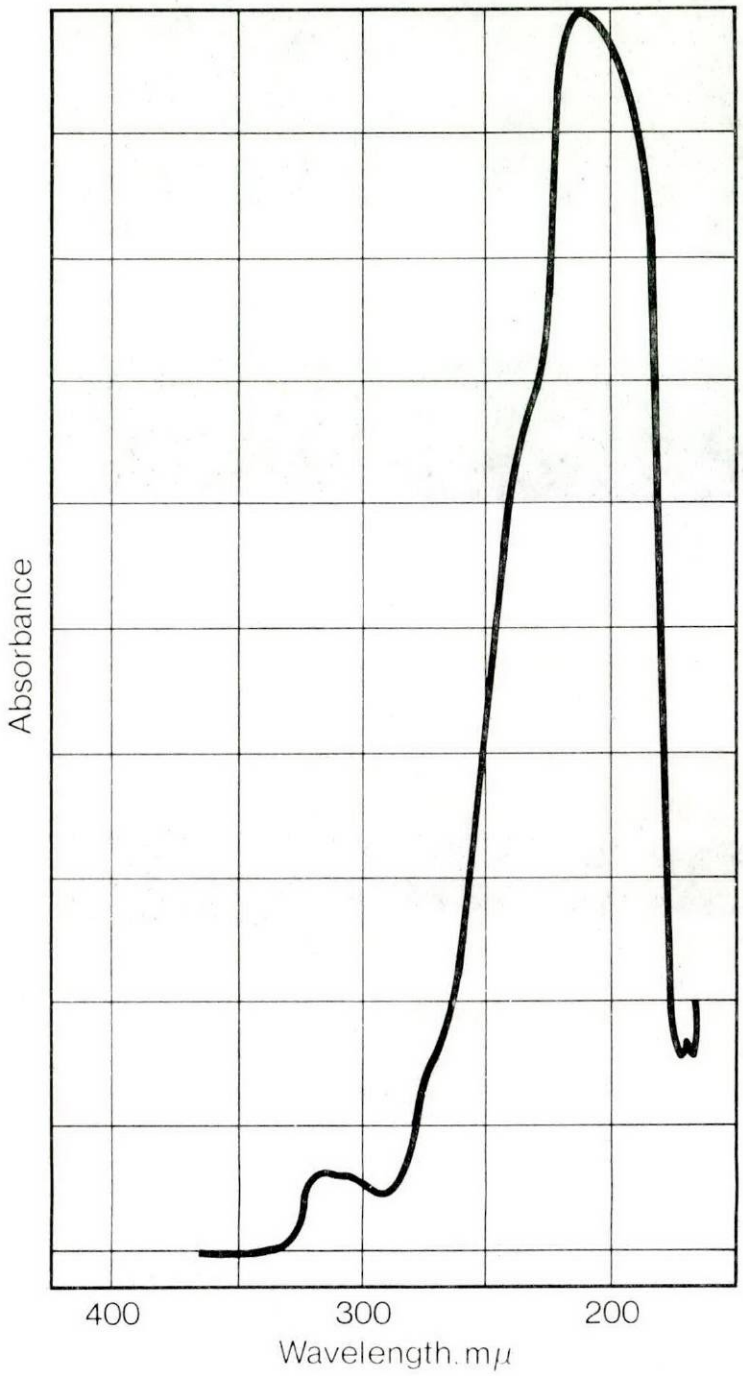


Figure 8. UV Spectrum of the Solder Plating Bath with High Accumulation of Peptone Decomposition Products

B-3

General Interest
Session B

Bright Cadmium Deposits from Sulfate Baths

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BRIGHT CADMIUM PLATING FROM SULFATE BATHS

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Introduction:

During the past decade, discharge of harmful and toxic chemicals into the environment has been greatly restricted. In the 1980's the discharge limits on many chemicals will approach zero, and in some cases they will be zero. Thus, research in the 1960's was directed to develop non-polluting chemical processes. In the plating industry, this research brought forth the alkaline zinc baths[1] and the chloride zinc baths, which do not contain cyanides. Both of these non-cyanide processes are in use today and are rapidly replacing cyanide zinc baths. The chloride zinc baths also provide substantial electrical energy savings[2].

As stricter cyanide discharge limits were imposed, the plater had the option of either installing expensive waste treatment facilities or changing from the cyanide zinc bath to either the alkaline or chloride bath. Changing to the chloride bath usually required equipment modification, since the chloride bath is slightly acidic and corrosive. Where cost was a deciding factor, the alkaline bath was chosen since it could be used with the same equipment as required for the cyanide bath. However, advantages of the chloride bath over the alkaline bath often justified the additional cost[3] of equipment modification. The plater who had other cyanide baths such as brass, copper and cadmium was required to meet cyanide effluent discharge limits either by diluting his discharge with water or by treating the cyanide.

Many plating shops that zinc plate also cadmium plate because some customers that require zinc plating also may have a smaller requirement for cadmium plating. The need for a non-cyanide cadmium bath became apparent when a plater chose to install either the alkaline or chloride zinc if he desired to eliminate cyanide from his plant. Since non-cyanide cadmium baths that plated bright deposits were not available until recently, he was either faced with the problem of going out of the cadmium plating business or finding a way to treat the cyanide from his cadmium plating operation.

Development of a satisfactory non-cyanide cadmium bath that plated bright lagged behind that of zinc. The reason was obvious in that total zinc gallonage may be at least twenty times that of cadmium. Most research dollars were channeled into the development of non-cyanide zinc baths.

The evolution of the non-cyanide cadmium plating bath followed a track similar to that of the chloride zinc. An alkaline cadmium bath is not feasible since the cadmium metal would precipitate out of solution. The zinc chloride bath[4] evolved through various bath types. One of the first was a chelated bath[5, 6, 7] which was followed by an ammoniated bath[8] containing no chelators. These types of baths were not desirable because once the metal was chelated, its removal by conventional precipitation methods was nearly impossible. The ammonium ion will complex copper and nickel in effluents making their removal difficult. The potassium chloride zinc bath[9] does not contain chelators or ammonium ions, thereby eliminated the related waste treatment problems associated with chelators and ammonium compounds.

One of the early non-cyanide cadmium bath[10, 11] that plated bright deposits was a chloride bath that was both ammoniated and chelated. Its use has diminished in past years because of the problems associated with ammonium and chelators in waste treatment processes. In the past, other acid baths have been introduced, but deposits were not bright or fine grained. Throwing power was also poor.

The parameters for a new non-cyanide cadmium plating bath were established. It must not contain chelators nor ammonium ions. A highly alkaline bath was not possible because the metal would precipitate as a hydroxide. In an acid sulfate system, it was found that the anode efficiency was close to 100%, while the cathode efficiency was less. This difference caused the metal in the solution to climb out of range resulting in an undesirable electroplated deposit. A method was required to keep the metal in the bath within the operating range. Bath control should be by conventional means such as chemical analysis and Hull cell evaluation. Organic additives should have a reasonable consumption rate. Cadmium removal from rinse water effluent should be simple.

As development progressed, it was found that the chloride system would not be satisfactory because insoluble anodes, such as carbon, would be required to keep the metal concentration in balance. The use of carbon anodes in a chloride bath results in the evolution of chlorine gas at the anodes. Taking this into consideration, the obvious choice was a sulfate bath, being less expensive than a fluoborate system. It was found that if all carbon anodes were used, a higher voltage was required, which caused the bath temperature to rise. A combination of cadmium and carbon anodes proved satisfactory.

The non-cyanide cadmium bath[12, 13, 14] that is presented here can be termed an acid sulfate bath. A variation of this bath which utilized a mixture of sulfuric and anoboric acids is also covered. Two organic proprietary additives are used. The

deposits are fine grained and bright over a wide current density range. The deposit may be clear or iridescent chromated to impart further corrosion resistance. The bath is suitable for both rack and barrel plating. A high throw formulation is available for rack plating parts with deep recesses. Substrates that are plated in the cyanide bath can be plated in the sulfate bath. Stainless steel can be plated without the use of a nickel strike.

The sulfate fluoborate bath is recommended for surfaces that may not plate in the sulfate bath. In the sulfate bath, instead of cadmium depositing, hydrogen is evolved at the cathode. Some carbo-nitrided parts have to be plated in the sulfate fluoborate bath. Operation of both baths is similar. Control of the sulfate fluoborate bath is somewhat more critical and make-up costs higher.

Bath Make-Up and Composition:

The acid sulfate cadmium bath is made up as follows:

	Barrel	Rack
Cadmium Oxide	17 g/l	17 g/l
Sulfuric Acid, Sp. Gr. 1.84	31 ml/l	62 ml/l
Primary Additive	30 ml/l	30 ml/l
Secondary Additive	3 ml/l	3 ml/l
Water to make	1 liter	1 liter

The additives are proprietary and are aqueous solutions containing organic compounds.

The sulfate fluoborate bath is similar and utilizes the same proprietary additives. The make-up for both barrel and rack plating is as follows:

Cadmium Oxide	17 g/l
Fluoboric Acid (49%)	55 ml/l
Sulfuric Acid, Sp. Gr. 1.84	25 ml/l
Primary Additive	30 ml/l
Secondary Additive	3 ml/l
Water to make	1 liter

The composition of the cadmium sulfate bath is shown in Table I.

TABLE I

COMPOSITION OF THE CADMIUM SULFATE BATH

	Preferred Ranges	
	Barrel	Rack
Cadmium (as metal)	11.25 - 18.75 g/l	Same
Free Sulfuric Acid	18.5 - 31.2 ml/l	31.2 - 62.4 ml/l
Primary Additive	20 - 30 ml/l	Same
Secondary Additive	2 - 3 ml/l	Same

The operating conditions are shown in Table II.

TABLE II

OPERATING CONDITIONS OF THE CADMIUM SULFATE BATH

	Barrel	Rack
Temperature	18 - 27°C	Same
Cathode Current Density	0.5 - 1.5A/dm^2	0.5 - 2.5A/dm^2
Voltage	12 - 18 volts	6 - 12 volts
Filtration	Periodic	Required
Agitation	None	Cathode Rod 1-Meters/Minute

The composition of the cadmium sulfate fluoborate bath is similar to the sulfate bath except fluoboric acid is added. Composition is shown in Table III.

TABLE III

COMPOSITION OF THE CADMIUM SULFATE FLUOBORATE BATH

	Barrel and Rack Preferred Range
Cadmium (as metal)	11.25 - 18.75 g/l
Volume Ratio of Free Fluoboric to Free Sulfuric Acid 2.2:1	45 - 80 ml/l
Primary Additive	20 - 30 ml/l
Secondary Additive	2 - 3 ml/l

The operating conditions of the sulfate fluoborate bath are the same as for the sulfate bath shown in Table II.

Plating Rate:

The plating rate and efficiency for both sulfate baths is shown in Table IV.

TABLE IV

CADMIUM ACID SULFATE BATH

A/dm^2	Microns	Minutes	Efficiency
0.5	2.5	12	96%
1.5	2.5	4.9	80%
2.5	2.5	3.9	60%

CADMIUM SULFATE FLUOBORATE BATH

A/dm^2	Microns	Minutes	Efficiency
0.5	2.5	12	96%
1.5	2.5	4.4	90%
2.5	2.5	2.9	80%

Cathode Efficiency:

The cathode efficiency of the sulfate fluoborate bath compares favorably with a conventional cyanide cadmium bath. The sulfate bath has slightly lower efficiency as shown in Figure I.

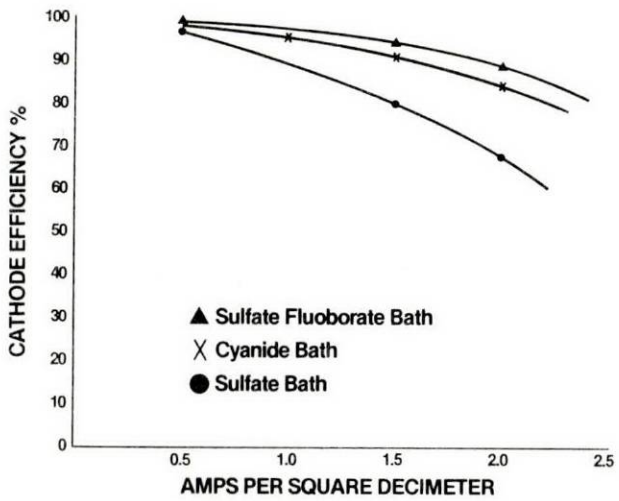

Fig. 1 Cathode efficiencies of bright cadmium electroplating baths.

Disadvantages:

The primary disadvantage from a cost viewpoint is that acid resistant equipment is required. Bare steel tanks that were suitable for the cyanide bath have to be lined, and any bare metal that may be contacted or be splashed upon by the solution must be protected to prevent corrosion.

A combination of carbon and cadmium anodes must be used to keep the metal in the bath within the recommended range. Titanium anode holder baskets cannot be used, necessitating the use of cadmium anodes in slab form.

Cooling is required to keep the solution below 27°C.

Part cleaning and pickling is more ciritcal than that required when plating from the cyanide bath.

Some chromating solutions suitable for deposits plated from the cyanide bath may not be satisfactory. A clear chromate is recommended to keep deposits bright under some long term storage conditions. Plated parts may exhibit bleed-out from seams causing discoloration.

Operation and control of the bath initially is more difficult until its particular working parameters are determined.

Cost of operation is higher than the cyanide bath (excluding waste treatment costs).

Advantages:

The primary advantage from a cost viewpoint is that waste treatment is simple and economical. The bath contains no cyanide, no ammonium ions, no chelators, and no complexing agents.

The acid sulfate bath contains less cadmium metal per gallon than the cyanide bath. Therefore, there is less metal dragout into the rinses during plating.

Since it is an acid bath, there is no carbonate formation as in the cyanide bath. Therefore, there is no shutdown period required to either freeze out the carbonates or to cut the bath to reduce the carbonate level below the critical point where high current density problems occur.

The acid sulfate bath will plate directly onto stainless steel that has been properly activated without the necessity of a nickel strike.

Process Cycle:

The acid sulfate plating bath does not have the cleaning ability that the alkaline cyanide bath does. Since it is more susceptible to organic contamination, the cleaning cycle must be adequate to remove alkaline and acid soluble contaminants that could find their way into the plating solution.

The requirements for the cleaning and pickling portion of the plating line are identical to that of the chloride zinc plating line. Ferrous alloy parts that are heavily contaminated with oil or grease should be first soak cleaned, followed by an anodic electro cleaner. A water rinse is only required between the two cleaners if they are not compatible.

The electro cleaner is followed by an adequate water rinse in order to eliminate drag over into the acid pickle. Where two or more rinses are required after a chemical processing step, it is a good practice to use counterflow tanks to conserve water.

Parts are pickled in 50% by volume hydrochloric acid to remove smut, rust, and scale. An inhibited acid must not be used since it may result in poor adhesion of the plate to the substrate. A surfactant compatible with the cadmium bath may be used in the acid to promote faster penetration into the rust and scale by the acid and to emulsify oil that has not been adequately removed by the alkaline cleaner. A counterflow rinse should be used after the acid.

The parts are cadmium plated until the required plate thickness is obtained, rinsed and usually chromated. Chromates have been developed that are suitable for cadmium plated from the acid sulfate bath. Chromate previously used on deposits plated from the alkaline cyanide bath may not be suitable. Indications of an unsuitable chromate include dullness, non-uniformity, or flaking of the chromate film.

Equipment:

Plating tank and equipment requirements are similar to those specified for chloride zinc plating. Acid resistant equipment is required where the solution may contact it. In most plating installations, a capital expenditure is required when converting from the alkaline cyanide bath to the acid sulfate bath. The alkaline bath is not corrosive and may be contained in a bare steel tank.

Tanks:

Steel tanks must be lined. Materials suitable to contact the solution are PVC, polypropylene, polyethylene, rubber, and some grades of fiberglass reinforced plastic. However, fiberglass should be avoided with the sulfate-fluoborate bath.

Following good plating practice, new tanks as well as those previously used for other solutions should be scrubbed clean and then leached for at least 24 hours. The leaching solution consists of 3% by volume sulfuric acid to which is added 0.1% by volume of the primary additive. The leaching solution should fill the tank to the brim and should be circulated through the filter chamber, pumps, and heat exchanger. After leaching, the tank is drained completely and flushed with clean water. Leaching of tanks previously used for cyanide solutions must be done with extreme caution and with adequate exhaust ventilation.

Filter:

All components of the filter chamber and its pump must be constructed of acid resistant materials. Flat membrane, wound cartridge, and bag type filters are suitable. Diatomaceous earth may be used as a filter aid. The filter should be capable of turning the solution over at least once an hour and preferable twice when filter aid is used.

To optimize solution filtration and provide solution agitation, the intake and discharge of the filter or circulating systems should be at opposite ends of the tank with the discharge counter to work flow.

Heating:

Heating is not required unless bath temperature is below 60°F., which is unlikely in the average plating installation. However, heating may be done by steam passing through Teflon* tubes, graphite heat exchangers, or electrically isoluted titanium coils. Titanium coils are not recommended for the sulfate fluoborate bath. In barrel installation, the solution temperature may be brought up to the optimum range by processing several dummy loads or part types that are not critical as to appearance.

*Registered Trademark of E. I. duPont deNemours and Company, Inc.

Cooling:

One of the keys to the successful operation of this bath is adequate cooling to maintain it at the optimum of 22°C. Barrel plating operations requiring high voltage operation for successful plating will quickly raise the temperature above the recommended maximum resulting in unsatisfactory deposits and no plate. Cooling is recommended both for barrel and rack operations.

A chiller is best for large installations. Water from a deep well with water temperatures of 10 to 15°C., is adequate for small tanks and rack plating operations. Materials of construction for cooling coils may be the same as for heating coils. Components of the chiller must be resistant to sulfuric acid or sulfuric fluoboric acid depending upon the bath used.

Bus Bars:

Anode and cathode bars should be solid copper and with a diameter large enough to carry the required current. Corrosion of the copper may be minimized by wrapping the bars with vinyl tape or covering with PVC shields or tubing. At anode or rack contact points, the plastic is cut away to expose the copper. This precaution will minimize copper contamination of the solution from this source.

Anodes:

The operation of this bath differs from other plating baths in that both soluble and insoluble anodes are used simultaneously. The soluble anodes are made of cadmium and the insoluble anodes are carbon, both in slab form. Cadmium ball anodes are not used because titanium baskets are attacked by the acid sulfate solution.

If all cadmium anodes were used, the metal concentration in the solution would quickly rise above the recommended operating level due to the difference in anode and cathode efficiencies. Thus, less metal is plated out than dissolves from the anode. The difference at the cathode is made up by hydrogen which evolves as a gas. The purity of the cadmium anodes should be at least 99.9% meeting specification ASTM B-440 or MIL QQ-A-671. Standard cadmium slab anode size is 3-1/2" x 1-1/4" x 18" long. No bags are used on the anodes.

The anode surface area ratio between carbon and cadmium is approximately one to one. The ratio may be varied periodically to keep the metal in range by adding or replacing cadmium anodes.

The carbon anodes are a special grade available from the supplier of this proprietary bath. Other carbon anodes may degrade rapidly liberating organic binders that could cause bath contamination. The standard carbon anode size is 6-1/4" x 1-1/4" x 18" long tapped on one end with two 3/8" - 16 holes for hooks.

Titanium or monel hooks are suitable. The length of the hook should keep the top 1" or the anode above the solution. Hooks should be plastisol covered or else taped except at the contact point.

Periodic brushing of the carbon anode surface is recommended to dislodge loose carbon and scum which could form an insulating barrier. Carbon anode life is acceptable before replacement is required.

Cadmium anodes may be left in the bath during idle periods since they will not dissolve until a current is applied. Cadmium anode stubs may be used up by placing in a plastisol covered or perforated polypropylene basket hanging on the anode bar. Contact to the bar from the stubs is made by means of a long cadmium stub clamped to the bar and extending into the center of the stubs.

Racks:

Conventional plating racks and barrels are used. Conducting members should be large enough to carry the current without overheating. Stainless steel tips are preferred since phosphor bronze tips could lead to immersion copper deposit on the part in the contact area which may result in a deposit exhibiting blisters in this area.

Power Source:

A 6 up to a 12 volt rectifier is recommended for rack plating, and 15 to 18 volts for barrel plating. The ripple should not exceed 5%.

Ventilation:

Exhaust ventilation is not normally required. The bath is virtually odorless. A foam blanket is usually formed during plating which minimizes any out-spray of solution when hydrogen bubbles break at the surface.

Agitation:

Air agitation is not recommended because of excessive foam that would be generated. Cathode rod movement of 1 to 2 meters per minute is recommended for rack plating.

Waste Treatment:

The cadmium metal may be precipitated from the rinse water by raising the pH to 10.5 or higher with lime or caustic soda. The precipitated metal can be removed by filtration or by allowing it to settle and then decanting off the clear filtrate. Cadmium levels of approximately 0.2 ppm can be attained and if necessary, zero discharge can be achieved using other waste treatment processes.

Bath Control:

Cadmium concentration is determined by EDTA method of analysis. Iron must be removed from the sample, or erroneously high results will be obtained. The acid content is determined by volumetric analysis titrating the sample with 1.0 N sodium hydroxide to a Bromphenol blue endpoint. In the sulfate fluoborate, the exact concentration of sulfuric to fluoboric acid should be determined every few weeks. This is done gravimetrically by precipitating the sulfate as barium sulfate. Using appropriate calculations, the ratio is obtained.

Impurities In Solution:

Iron is introduced into the bath from the ferrous parts being plated. Iron concentrations have not posed any problems even in production installations having iron levels as high as 2000 ppm. In most installations, the iron levels are considerably lower. It appears that the iron content levels off at some constant depending on whether the operation is barrel or rack, the part type being plated, and the housekeeping as to removal of parts and chips from the tank bottom. Iron levels up to 10 g/l do not appear to effect chromating of parts.

Trivalent chromium levels up to 300 ppm are not detrimental to the deposit as determined by Hull cell evaluations, nor is hexavalent chromium detrimental up to a level of 500 ppm. Parts plated from baths having these levels of chromium contamination have been satisfactorily clear chromated.

Tin contamination at 25 ppm can cause skip plating in low current density areas. Copper at 25 ppm can result in a brownish cast on deposits in the 2 to 4 A/dm^2 range and darkening after clear chromating. Lead at 100 ppm causes a white hazy deposit in the 1 to 4 A/dm^2 range, but is not apparently detrimental to clear chromating. Titanium causes a light haze to develop in extreme low current density areas. Silicon up to 900 ppm is not detrimental.

It appears that most metal contaminants are plated out at low current densities and, unless introduced at high levels, do not normally interfere with the deposit.

Conclusion:

The success of the potassium chloride zinc plating process prompted the development of the acid sulfate cadmium bath. Both are free of cyanide, ammonium ions and chelators. The high cost of cyanide waste treatment has been eliminated.

The acid sulfate cadmium bath plates a bright, leveled, ductile deposit. The throwing power is adequate for most part types. Substrates normally plated in the alkaline bath can be plated in the acid sulfate bath. Some carbonitrided surfaces which may be difficult to plate in the sulfate bath are readily plated in the sulfate fluoborate bath. The choice for a job shop that plates a multitude of substrates is the sulfate fluoborate bath.

The future of cadmium as a commercially plated metal is still speculative. Where alternate finishes can be found, they will be substituted. For some applications there appears to be no substitute. Cadmium discharge into the environment from the plating industry can be controled by proper waste treatment.

12-27-78

REFERENCES

1. J. Hajdu and J. A. Zehnder, "Plating" 58 458 (1971).
2. H. S. Schneider, "Plating and Surface Finishing" 64 (6), 52 (1977).
3. No Author, "Products Finishing" 41 (11), 70 (1977).
4. E. R. Jorczyk, "Zinc Plating From The Potassium Bath" A.E.S. Zinc Symposium, Syracuse, New York (1977).
5. K. P. Bellinger, "Plating" 56 (10), 1135 (1969).
6. J. G. Poor, G. B. Rynne, U. S. Patent 3,730,855.
7. "KENBRITE" Process, Product of 3M Company, St. Paul, Minnesota.
8. G. F. Hsu and M. M. Beckwith, U. S. Patent 3,729,394.
9. G. F. Hsu and J. J. Fong, U. S. Patent 4,070,256.
10. J. J. Fong and G. F. Hsu, U. S. Patent 3,577,327.
11. "KENCAD" Process, Product of 3M Company, St. Paul, Minnesota.
12. J. J. Fong, U. S. Patent 3,998,707.
13. J. J. Fong and G. F. Hsu, U. S. Patent 4,045,305.
14. "CADVERT" Process, Product of 3M Company, St. Paul, Minnesota.

B-4

General Interest Session B

Mechanical Edge & Surface Finishing— Some Developments of Relevance To the Electroplating Industry

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MECHANICAL EDGE AND SURFACE FINISHING

Some Suggestions of Relevance to the Electroplating Industry

Paper submitted to American Electroplaters' Society Inc. for 1979 AES Conference in Atlanta.

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Abstract

The cost of mechanical finishing and deburring of most metal components normally exceeds five percent of the total manufacturing cost, yet it is these operations that are still the most neglected in the whole metal working industry. During the past five years, there have been many developments to permit most components to be finished more economically and consistently. There is no longer any excuse for some of the inefficient methods that are still in fairly common use.

Every company can benefit by a fresh look at its mechanical finishing operations, and the electroplating industry has a responsibility to insure that scientific development matches the development of the plating process which so often follows mechanical finishing operations.

Introduction

It is generally accepted that for most organizations within the metal working industry the first key to success comes with improved productivity. There appears little doubt that the first challenge to American industry as it enters the '80's is to improve productivity throughout the manufacturing cycle. It is ridiculous to plan on meeting international competition by curbing imports, lowering standards of living, or working hearder. The only significant opportunity is to work smarter.

From all reports, it appears that the electroplating industry is certainly meeting the challenge. Techniques are being improved, new processes are being developed, and automated applications of coatings is becoming standard. In fact improvements in all types of functional and decorative coatings have been quite dynamic during the past five years, and progress with the technologies of metal and plastic forming has been even more dynamic. It takes little imagination to foresee even faster progress over the next five years.

It is extraordinary that such a high proportion of companies doing advanced research and development, and investing large sums of money in more productive equipment for forming and coating operations, seem to have completely forgotten that there are only a very few parts that can have their final finish applied immediately after the basic forming operations. Mechanical edge and surface preparation are certainly the most neglected operations within the whole manufacturing cycle and there is no logical reason for this neglect. It is as if the scientists and technologists involved in applying surface coating assume that those responsible for forming the part will produce the part with a surface ready for coating, while the machining, castong, stamping, and other

forming technologists assume that the word "finishing" covers all operations after the part leaves their machines. Only very recently have some of the technical societies, such as the SME, the Abrasive engineering Society, the ASM, and the AES become aware of this major problem and have started to take some interest in the mechanical edge and surface finishing operations. It is by the efforts of these societies that industry is becoming aware of the opportunities to make substantial improvements in product quality and productivity. Both the forming technologist and the coating technologist must take direct and positive interest in the mechanical preparation of components but, more important, it is essential that a technology of mechanical edge and surface finish be developed. During the past five years, enough work has been done to define many of the problems and some of the answers. There are probably greater opportunities to improve productivity in this area than any other. It is the object of this paper to remind the engineer that a great deal of information exists and to mention some of the recent developments that can improve productivity in many manufacturing organizations. In particular it is hoped that this paper will offer encouragement to both the metal forming engineer and the surface coating engineer to communicate more effectively and to become more positively involved in development of mechanical edge and surface finishing technology.

The Mechanical Finishing Department

In most companies there will be a deburring department, a polishing department, or a surface preparation department; sometimes considered the responsibility of the finishing or electroplating superintendent, sometimes the responsibility of the machine shop. The functions which this department normally fulfill are:-

1) inspecting parts entering department;
2) deburring;
3) edge radiusing;
4) descaling;
5) improving surface finish;
6) surface brightening;
7) changing surface stress;
8) degreasing;
9) carrying out rework and rectification;
10) inhibiting rust and corrosion; and
11) inspecting parts leaving department.

Of course, radiusing of edges and achieving surface finishes can be the task of the machine shop while descaling, surface brightening, degreasing, and rust inhibition can be the task of the plating shop. It is though worth considering all these functions when planning the activities which may be encompassed within the Mechanical Finishing Department.

It is suggested that specific responsibilities of the department within each company should be very clearly defined. Of even greater importance the quality of components permitted in the department and the quality of component being passed on to the plating shop must be defined.

Far too often the deburring department is used as the general rectification shop, being expected to put right the sporadic defects of the raw material and of previous forming and handling operations. Undoubtedly, the surface preparation department does have to handle the normal variation of quality expected from the machine shop as tooling wears. Most modern mechanical finishing equipmentis designed and built to handle such variations and achieve more uniform results than forming equipment can achieve. However, it is almost never economical and sometimes not practical to install mechanical finishing equipment capable of handling components coming from a machine shop where no consideration to edge and surface quality is given. Before any company starts to select new equipment for their surface preparation department it is vital that the quality of component coming to that department be firmly established and maintained.

The Costs of Mechanical Finishing

As mentioned earlier, the cost of deburring and mechanical finishing most components will exceed five percent of the total manufacturing cost, and in some cases the proportion can be very much higher. For example, cost of finishing some standard bathroom faucets can be 25% of total cost, cost of finishing a wrench may be even 50%, and cost of deburring a high precision gear as much as 75%. Recent estimates of the cost of deburring within the U.S. metal working industry all exceed two and a half billion dollars and the lowest estimate of the total cost of burrs to all U.S. industry that the writer has heard recently is six billion dollars. Cost of all the other operations performed by the mechanical finishing department is certainly even high that the cost of deburring.

It would of course be quite wrong to conclude that the average company's deburring and mechanical finishing costs are either too little or too much. If increasing mechanical finishing cost could be more than offset by reduction of inspection and Q.C. costs, then industry is being derelict in not spending the extra money. One result of the mechanical finishing operations having been neglected for so long is that there is no general understanding of the total costs of producing and controlling edge and surface finish conditions. This type of information is needed both to create proper incentive to industry to take positive action, and also to show the areas of greatest opportunity, both for the individual company and for industry as a whole. The SME has recently started carrying out a market research exercise to investigate the total costs of burrs in some sections of the metal working industry. It is the writer's opinion that a similar survey initiated by the AES to establish some of the costs of pre-plate surface finishing would be extremely beneficial. Such an exercise would be neither very expensive nor difficult to arrange. By carrying out some simple research, companies would learn that those organizations investing most money in their mechanical edge and surface finish departments have lower overall Q.C. costs, lower scrap, lower total finishing costs, and perhaps lower total costs than those companies with less advanced finishing methods.

When a manufacturer can compare his own mechanical finishing costs with costs of machining, Q.C., heat treatment, and plating within his own industry and perhaps how his costs compare with production of other types of product, then he will have far better appreciation and be better able to direct investment of capital to make the needed improvements in productivity.

A Need for New Equipment

More than half of the metal forming equipment in use in the U.S.A. today is over fifteen years old. The average age of all finishing equipment is probably somewhat older and certainly the average age of deburring and mechanical finishing equipment is even older. It is quite apparent that the countries where productivity is increasing the fastest are those where the highest proportion of the gross national product is being reinvested in new and better facilities. It is almost equally apparent that the companies within any industry where productivity is increasing fastest are those returning the highest proportion of earnings to new equipment and improved methods. While less obvious, it seems logical that of the various departments in a company involved in the the production cycle, those where greatest investment is made will normally be the ones where improvements in productivity will be most marked.

The total investment of U.S. industry in machines and equipment is presently in excess of six billion dollars per annum. Of this only about three hundred million dollars, or five percent of total, is being spent on all forms of finishing equipment - deburring machinery, surface preparation equipment, and all forms of surface coating. It would appear that only about one percent of industry investment is being used for the deburring and mechanical finishing department, a department where more than five percent of the total manufacturing cost is being spent. While this does not prove that productivity can be improved in all, or even most, surface preparation departments it certainly justifies serious thought and probably a total review of all processes being carried out in that department and the equipment presently available.

It is the writer's experience that an overall appraisal of total requirements within the finishing department is very rare indeed but that when such an appraisal is made it is invariably beneficial.

Of course, overall reviews should not be carried out with the sole objective of improving productivity; consideration should always be given to present and future capacity requirements for existing and new products. It is probable that improved quality and quality control will also be of direct relevance to any equipment review.

The costs of a mechanical finishing department and the cost of all surface preparation work for each product must be estimated and should include all Q.C., rework, scrap, and guarantee work. When this information is available and all requirements for the mechanical finishing department have been decided upon, then it should be possible to start producing a preliminary estimate of the capital that can be justified for this department, at least for the short term. It then becoms necessary to review the means by which improvements can be made.

Manual Finishing Methods

By far the most standard means of deburring parts, radiusing their edges, and improving their surfaces is by manually filing, scraping, brushing, polishing, or buffing. These are the most versatile techniques and require the least investment in equipment. There are many advantages

to the manual finishing methods; not only is it possible to handle a very wide variety of shapes, sizes, and types of product but it is also possible to modify techniques to handle a variety of edge and surface conditions entering the department. It is not too important, perhaps if size of burr on the parts entering the department varies because tooling is not changed frequently enough or the machine settings on two different units producing the same part are somewhat different. Operators can be trained to inspect their own components, and they can spend extra time on the surfaces and edges of most significance. No re-tooling is necessary when the product changes; when production requirements change there is no long lead time while waiting for new equipment and there is no need to leave machines standing idle when requirements reduce.

Certainly, the craftsmen of the deburring and finishing department are still essential and will be for some years to come. However, most of the arguments for maintaining the status quo could have applied to a justification for keeping the craftsmen of metal forming. In modern industry they are hopelessly inadequate arguments, and a major objective must be to replace these manual operations with faster, less expensive, and more consistent methods which will offer the required standards of quality and versatility. As soon as management determines that manual finishing, being unreliable, archaic, and expensive, must be avoided or replaced then there will be much faster progress. Engineers will be obliged to design components taking the requirements of the finishing department into account. The engineer who designs a product without any consideration for how it will be made, has value in only a very small number of positions in a very few companies. The same should apply to the engineer who has no appreciation for the finishing requirements of the products he is designing.

The producers of equipment and materials for better surface and edge preparation need greater incentive to develop improved methods. Until their potential customers are prepared to look for improvements in the mechanical finsihing department, there is no market for new processes and new equipment, stifling much progress. Of prime importance: it does require a concerted effort to start developing our craft of mechanical finishing into a technology. A great deal of research and development work is needed and this will not be forthcoming until there is a much greater commitment by industry. It is the efforts of the professional societies, such as the Electroplaters' Society, which will act as the necessary spur by showing the benefits that can accrue from scientific development in the field of burrs and surface finish.

The place of the craftsman who manually files and buffs is with the highly specialized products not in the automative, aero-space, appliance, or hardware industries.

Mechanical Finishing Methods

The lack of technology or science precludes the selection of the most suitable means of finishing any component or group of components by examining published data.

Ultimately, selection of the best process will have to be made by some trial and error testing of those processes which appear to meet overall requirements. This need not be a mammoth task for any company prepared to collect the necessary background information and to keep abreast with modern developments. While there are a wide variety of different processes and there are several manufacturers of equipment for most of the processes, there are several means by which the search for the most suitable methods can be narrowed down to manageable proportions. The basic means of deburring, edge radiusing, and surface improvement or conditioning are as follows.

1) Mass finishing. This may indlude barrel tumbling, vibratory finishing, spindle finishing, and centrifugal barrel finishing.

2) Automated buffing, brushing and polishing.

3) Chemical deburring and finishing, including electro-chemical and electro-polishing.

4) Blasting with abrasive, shot or water.

5) Abrasive flow deburring and finishing.

6) Thermal-energy deburring

There are of course many occasions when two or more of the processes will be required to achieve the desired results on some components. Within each of the groups there are many variations and there are some processes combining some features of more than one group: for example, chemically or electro-chemically accelerated mass finishing methods.

There is now a great deal of information available describing the various basic processes and the various modifications of those processes. There is a fund of articles and technical papers describing the capabilities and the limitations of most mechanical finishing methods and there are now some books available covering this subject. While there is still not much quantitative, comparative information, the company which can specify its total finishing requirements should have little trouble in selecting the groups of process most likely to be of benefit. The two groups in most general use for pre-plate finishing are unquestionably mass finishing and automatic buff, brush, and polishing, and it seems likely that development of processes within these groups will insure they remain the most important to electroplating industry for a long time to come. (The electroplater of course knows about the chemical and electro-chemical surface preparation techniques; and it is normally the responsibility of the electroplating department, rather than the mechanical finishing department, to specify and handle these processes. The reader might therefore note some slight bias in the previous comments). This means that the company concerned only with choice of equipment for preparing parts for electroplating need only make a cursory inspection of each group of processes to ascertain that its requirements are typical for the industry; check on any new process developments; and then concentrate upon specific processes and suppliers of equipment in the relevant groups.

In spite of the lack of science and technology real progress is being made and there is real enthusiasm to disseminate information better and to

develop clearer understanding of the capabilities and limitations of different processes and how they compare with one another. This results in most suppliers being able to carry out trial and error testing and then supply specific information to allow the manufacturer to estimate quite precisely the total costs of the process in production, the overall quality that can be expected, and the degree of versatility of the equipment. Most suppliers are enthusiastic to develop and to find fresh answers to both new and old problems. It behooves the component manufacturer to take full advantage of this.

Mass Finishing

It is not the purpose of this paper to act as a guide to selection of the most suitable equipment for any particular application, but it is worth outlining some recent developments.

The reader will be familiar with conventional tumbling barrels, standard means of deburring and surface finishing a variety of parts for several hundreds of years. Most readers will also be aware of vibratory equipment which offers greater versatility and speed than tumbling equipment. Development of vibratory equipment, both the tub-shaped and round bowl, has been truly dynamic during the past ten years and highly sophisticated equipment is now available for an immense range of products in small and large quantities with varying degrees of automation. Combined with the substantial development of the consumable materials used in this equipment, both the abrasive media and compounds, deburring and surface finishing by vibratory machinery is the most standard process in most of the metal working industry. Capabilities and limitations of the process are well documented and there are a dozen manufacturers of equipement in the U.S.A. ready to experiment to develop the technique for any new product.

Centrifugal barrel finishing is a rather newer and less well known process, offering still improved versatility and capability to handle very fragile parts, high precision parts, and components needing extremely fine finishes. The principle of the centrigugal barrel is shown in fig. 1. Equipment is comprised of a number of drums mounted on the periphery of a turret. The turret is rotated at a high speed in one direction while the drums, loaded with components, abrasive media, and most generally water and compound, are rotated at a slower speed in the direction opposite to that of the turret. In operation the turret rotation creates a high centrifugal force of up to fifty times gravitational weight. This force compacts the load into a tight mass. Rotation of the drums causes parts and media to slide against each other, removing burrs and refining the components' surfaces.

This abrading action under high centrifugal force results in very short process cycles. A product very lightly rubbed by an abrasive is not affected significantly, but the same abrasive will change the surface condition when rubbed with pressure increased fifty-fold. Obviously, speeding up the finishing process reduces cost and improves work flow. The real value of centrifugal barrel finishing extends beyond just accelerating process cycles. Counter-rotation of the drums causes a completely smooth slide of media against components with no possibility of one part falling

or banging against another. Because of this action, completely consistent and reproducible results will be achieved. High tolerances can be maintained in even the most fragile parts.

The other mass finishing processes that have been available for some years are spin finishing techniques where components mounted on fixtures and manipulated in a mass of media in a container which is being rotated at high speed. Recipro-finishing is a similar process, presently for somewhat special purpose applications, but which has been used for finishing of long work pieces, such as bumpers and automobile cam shafts.

Very recent developments are the orbital mass finishing process and the combination of vibratory and orbital mass finishing. This latter unit is a round bowl-type vibrator with a base which spins independently from the vibratory bowl. This action results in high speed deburring capabilities but to date applications have not been documented.

The chemically accelerated mass finishing, in particular chemically accelerated centrifugal barrel machinery offers positive benefits for a number of special applications. Chemically accelerating does in part overcome one of the major limitations of the mass finishing process in that it allows deep recesses to be processed. Chemically accelerated centrifugal barrels are used for complex-shaped ferrous parts where extreme uniformity of edge radii and very high quality surface finishes are required.

The mass finishing processes normally offer the most economical means of deburring and improving surfaces, particularly of fairly small components. All the techniques offer capability to obtain total uniformity of action and completely reproducible results. If components have no deep recesses to be deburred and finished and if action over all surfaces and edges accessible to abrasive media is desirable, then it is the mass finishing processes which should be considered when looking for new equipment.

Automatic Buff, Brush and Polish Techniques

Buffing of components for achieving bright, decorative finishes is another very old, established process. Like mass finishing, development during the past decade has been substantial and automatic brushing and polishing is certainly the most general means of achieving pre-plate finishes, particularly for decorative purposes, where high production is required.

Probably the most important development of automatic buffing equipment is the "mush" buffing technique, where components to be buffed traverse across the face of broad wheels operating at low rpm. Costly shaping of buff wheels to conform to the shape of components is eliminated, far greater uniformity of finish can be achieved, and it becomes possible to finish different shapes and sizes of components simultaneously. This of courseenables automation of a finishing line where a variety of products are to be handled.

Development of the consumable materials - buffs and compound, abrasive belts and wheels - has been substantial of recent years and is well documented. Improved consumable materials reduce finishing costs,

offer a broader choice of type of finish to be achieved and, most important, enable the buffing and polishing processes to be truly consistent in the results achieved.

Other important developments have made equipment very much more versatile and readily modified to suit changes of material, design of component, and changes of through-put needs. Improved automatic application of abrasive compounds and precision control of the pressure of buff wheels against components still further increases the capability of equipment to be totally uniform in result. Such developments enable automatic buff and brush equipment to be used for functional purposes where precise surface finishes and edge radii are required as well as the more traditionaly applications of surface preparation prior to decorative electroplating.

Conclusions

The technology of mechanical edge and surface finishing does lag behind the technologies of both metal forming and surface coating but there are real efforts being made to rectify the situation and every manufacturer has considerable opportunity to improve existing methods. Modern deburring, edge and surface finishing techniques offer opportunities to automatically process parts that previously had to be finished by hand and also these methods generally offer highly consistent results giving opportunity for economies in inspection and Q.C.

The two critical steps that component manufacturers must make are:-

1) Consider edge and surface finishing requirements at the design stage for any products. This will not only assist with choice of the best equipment but will also give opportunities to handle some of the operations that might otherwise need to be handled by more expensive machine tools, may reduce inspection and Q.C., and on occasions may give opportunity to obtain a more attractive edge and surface condition to enhance the value of the final product.

2) Actively encourage the research and development necessary for edge and surface finishing to become a true technology. This will only happen when manufacturing organizations and the relevant technical associations feel a responsibility and become positively involved.

References

1) "Deburring - Capabilities & Limitations" SME 1976. Edited by LaRoux K. Gillespie.

2) "Advances in Deburring" SME 1978. Edited by LaRoux K. Gillespie.

3) "Mass Finishing" Metal Finishing Guidebook 1979. J. B. Hignett

4) "Entgraten". F. Schafer 1975

5) "Deburring" SME Technical Paper MR77-471. J. B. Hignett

6) "Deburring: Practical Production Techniques" SME Technical Paper MR76-137. John B. Kittridge.

7) "Automatic Buffing, Brushing and Polishing" SME Technical Paper MR76-543. Thomas C. Andrew.

8) Proceedings of AES 2nd Decorative Plating Symposium, February 8-9, 1978.

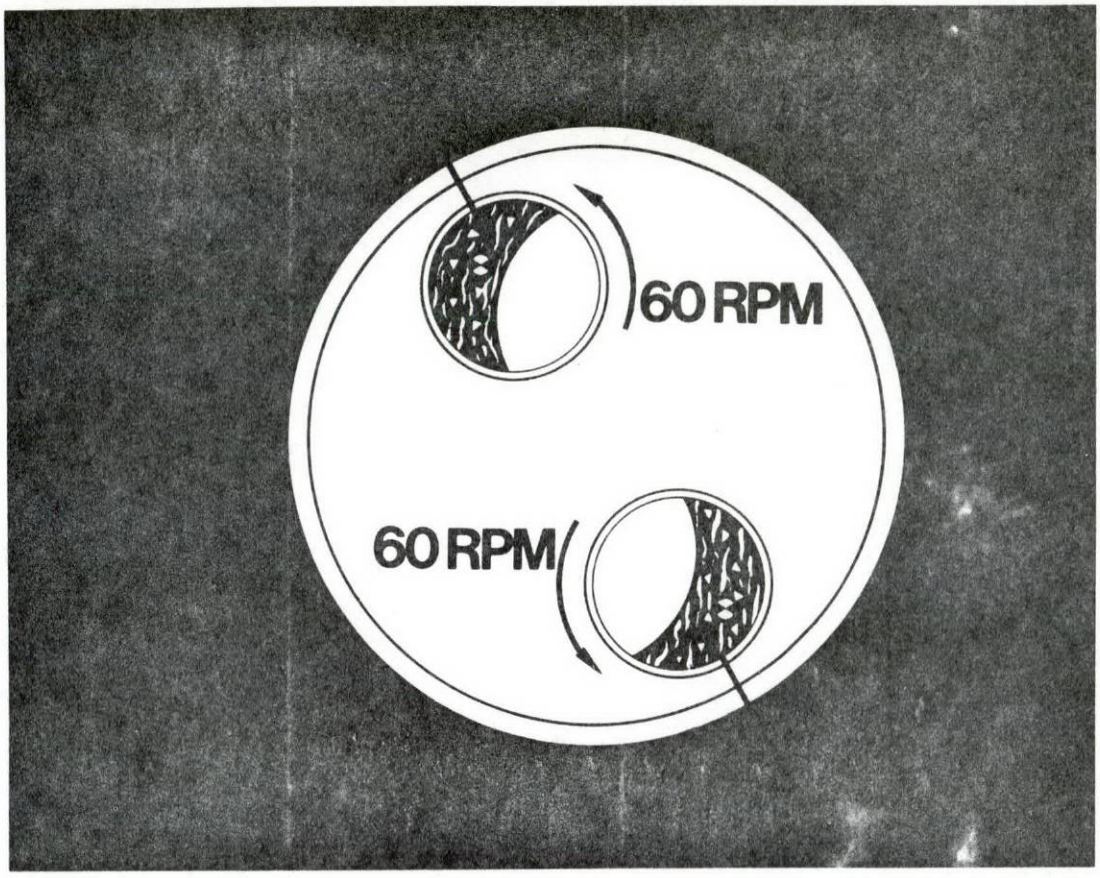

Figure 1--the principle of the centrifugal barrel

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Organic Finishing/ General Interest Session C

Substrate/Phosphate Interactions In Corrosion Performance Behavior Of Painted Surfaces

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Paper not available at time of printing of proceedings.

C-2

Organic Finishing/ General Interest Session C

Technology Forcing— The Changing Industrial Coatings Business

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TECHNOLOGY FORCING - THE CHANGING INDUSTRIAL COATINGS BUSINESS

By

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Federal and state regulations designed to clean up our air have presented the industrial coatings industry with problems and opportunities. In many ways this can be called technology forcing and we in the industry see no respite from the EPA regulations to force out those coatings that contain a tremendous amount of organic solvent. Companies in our industry have learned to live with exempt solvent regulations based on the original Rule 66 from California. While the amount of work done in industrial coatings laboratories to reformulate with acceptable solvents was considerable, it did not require a great deal of sophisticated research and development. Over the past 10 years the coatings that were used were supplied in different solvents but at approximately the same solids contents.

Today the ball game has changed considerably because the EPA has determined that all solvents are photochemically reactive and therefore the amount of solvents emitted from each gallon of coatings must be restricted. This forces each company in the industry to reconsider its research and development efforts and to evaluate its position in its markets to decide where to put the R&D dollar. To some, especially those companies with a good R&D base, this presents an excellent opportunity to obtain more business. To other companies (and the chemical coatings industry is made up of many medium and small companies) the EPA rules represent a threat which could force them to spend a great deal more money on research and development than they have in the past or else go out of business.

Any company, no matter what its size, must decide where it fits in the new technology arena, and then limit its activities to those products which they decide could most profitably be developed to maintain old business or to develop new business. To the small company, this represents, as I mentioned before, a most difficult decision. Yet even the larger companies are finding it difficult to concentrate on all technologies at once simply because of the need to do a substantial amount of defensive R&D work designed to maintain the use of all the raw materials that we currently use in our products. This, of course, is being done essentially to meet the Toxic Substances Control Act and the efforts by several government agencies to effect a control standard on many of our raw materials that in many cases is extremely difficult to achieve.

Many of my colleagues in the industry as well as many in the chemical industry have stated that we will have to make do with the basic materials that we now have available, since it will require a tremendous amount of money and effort to qualify a new raw material as a non-toxic substance. While this does not mean that research and development will come to a halt

all together, it does mean that new monomers designed for the new polymers to develop low solvent coatings will simply not be available. The coatings industry depends not only on their own R&D efforts but also on the efforts of suppliers such as Union Carbide, Rohm & Haas, Dupont, Reichold Chemical, etc. There is much forward research being conducted by those suppliers to come up with some new and exciting concepts. It is my intention today to review some of these new concepts and to describe to you how the coatings industry will change drastically within the next five to ten years.

Before doing this, I would like to review the impact of the new EPA guidelines, to outline the challenges I see in the industry, to talk about the types of coatings that you can expect to see in the future, and then to make a few predictions. One of the most difficult aspects of this headlong rush into new coatings technology is to make rolling adjustments as the targets change. Unfortunately, even as I deliver this talk, these targets are changing in each state, and no one yet knows what will be the final outcome of each state's deliberations to present a new law that will be acceptable to the Federal EPA. The coatings industry through its trade association, is attempting to keep abreast of the latest developments on a federal and state level. It is not an easy task, but we feel that the only effective way to do this is to work closely with the EPA and state regulatory agencies.

In the past two years there have been several sets of guidelines issued for specific industries by EPA. The first several volumes covered coatings for the automotive, can, coil, fabric, and paper coating industries. Coatings for appliances and metal furniture were next studied by the EPA and we will soon see guidelines for several other industries. Until very recently the modus operandi was to issue volatile organic emission (VOC) limitations for specific coatings used by each industry. In other words, each particular coating used on an automobile such as a primer and a topcoat or a coil or can coating was given a specific value.

Some industries which use organic coatings have not yet been covered by any specific guidelines. We anticipate that these industries will be covered by some type of overall regulation which will again set the amount of VOC that can be emitted from each coating. Some of the recent guidelines represent a deviation from this approach. The one for finishing flat wood paneling provides a limitation for the total system. We feel that this concept is an excellent one because it provides the coatings companies with the time to develop the low solvent coatings that are difficult to develop for particular segments of the system. In other words, if we have a three-coat finishing system for one particular application, we may be able to beat the regulation by developing a low solvent coating for one or two of those coatings and maintaining the same low solid organic solvent coating that we have been using for years for the third one. It is most difficult to change coatings for some applications to the lower solvent types.

It is quite obvious that the EPA in their infinite wisdom has issued these guidelines for specific industries in an attempt to develop a uniform

law throughout the country. As EPA guidelines are issued, each state had until June 1, 1979 to develop their own state implementation plan. It is doubtful that the EPA will allow limitations that are higher than those they have set in the guidelines. Therefore, the only changes that can be made would be to make the guidelines even more restrictive, and now the State of California through the California Air Research Board (CARB) has attempted to do so. The main concern of our industry today is that the regulations developed in California will then be adopted across the country as the norm as was the case with Rule 66 ten years ago.

Throughout all of this, the coatings industry must be aware of not only the ecology factors, but also of the energy requirements to cure our coatings and the economics involved. Because of these three factors, the requirement is basically very simple: A low solvent coating that can be cured at a lower temperature than today's conventional coatings and be applied at the same or lower cost. While we may not be able to fill this tall order immediately, I suspect that in the future, as I will try to show today, it will be done. I must emphasize, however, that it cannot be done unless each company using organic coatings takes all of these factors into consideration in deciding what type of coating they will use in the future. All companies must do a broad study in using all of the information that can be obtained from suppliers on the types of coatings that are available. To expect decision without considering the three big E's (Ecology, Energy, Economics) and all their ramifications is tantamount to committing economic suicide. No one today has a crystal ball accurate enough to provide you with the panacea that you may be searching for.

Now that I have given you the background of all of this activity in the organic coatings industry, let us consider the challenge of the new technologies. While solvents are now considered as the molecules in the black hats, they have over the past years provided us with coatings based on high molecular weight polymers as well as a degree of flexibility in solving sticky application problems. While the organic solvent does not wind up as the constituent of the film on the surface, it does play the role of carrier to allow coatings to be applied at the proper film thickness to give the desired film properties at a reasonable cost.

We are faced with an ever increasing cost of the solvents, as well as a possible decrease in the supply of selected ones. We have noted over the past years that many of our solvent suppliers have withdrawn some of these materials from the market simply because they are too expensive to produce or else they want to direct their activities to products that can be sold in a larger amount and will provide a greater return on investment. While it is generally believed that solvent-based coatings will be around for several years, this activity by our suppliers who make the solvents is helping to accelerate the development of low solvent technology.

Another factor is part of the challenge. Though the total effort to establish regulations to minimize the emission of volatile organic compounds to the atmosphere from coatings is tremendous, there are uncertain time frames for the establishment of these regulations, as well as the enforcement of them. This, of course, causes industry to re-evaluate its position constantly. The emphasis on certain types of low solvent coatings ebbs and flows with each development coming from EPA or one of the states. Not so uncertain, however, is the fact that the coatings industry in the future will be relying heavily on the polymer chemist more than we have in the past. The coatings industry is truly a chemical industry and the understanding of exactly what does occur when a coating is applied and cured is essential. Another consideration that must be weighed even with some of the low solvent coatings is the continual emphasis on the reduction of visible smoke and possible regulations in some states on the reduction of odors from plants using industrial coatings.

While it may seem that I have painted a most bleak picture of what must be accomplished, I do believe that the major choices for low solvent coatings are well known. Waterborne coatings, high solids coatings, coatings cured by radiation and powder coatings have been proposed as possible ways to reduce the VOC. Obviously, another choice is to to incinerate all of the VOC being emitted, but, in many cases, this is extremely expensive especially when the application and flash-off areas are considered. Of course, it is not only expensive, but in many sectors of the country natural gas is still in short supply. Therefore, it would be sheer folly to solve the emission problem by trying to incinerate all of the emissions from the application areas because the cost of energy in doing so is extremely high. Many companies have chosen to do this over the past ten years, but most of them are hoping for the development of low solvent coatings to accelerate so that they can turn off their incinerators and reduce their natural gas bill.

The improvement in waterborne finishes over the past few years has been substantial. Coatings based on water-soluble resins, dispersions and emulsions have been used and are continuing to be used by companies throughout industry. It is estimated today that approximately 10% of all of the industrial coatings that are being produced are based on waterborne materials. Outstanding examples are the use of electro-deposition coatings for automotive primers, waterbase coatings for the interior of beer and beverage cans, waterborne primers and topcoats for automobile bodies, and a wide variety of waterborne products used by those companies that apply coatings by spray application to various metal parts.

If such an array of waterborne materials is available, then why are not more coaters switching to these materials at the present time? The answer to this question can be found in the intermittent problems of water sensitivity, blistering and application problems. Water sensitivity problems are far more severe in water-soluble materials, simply because we are not certain that all of the neutralizer needed to make the resin water soluble is eliminated during the application and curing process. Emulsions and dispersions are somewhat better, but even those products contain additives that are water sensitive and sometimes do not escape the film. Although water sensitivity is not important in some applications, in general, most organic coatings that are applied to any surface should have a good degree of water resistance.

Blistering seems to be a common problem wherever multiple coats are applied. Entrapment of water is a common place event, and if the system is not properly designed, then the water cannot escape unless it forms blisters in the film. Consider the case of the automotive manufacturer on the West Coast who converted to a complete waterborne system for car bodies. Instead of applying two coats of a topcoat, he is now forced to apply the same overall film thickness in four coats and bake the coating between coats two and three. This, of course, means that while he is most probably going to comply with the California regulation, he is using substantially much more energy to achieve the same reuslts as he achieved before with solvent-base coatings. This is what I mean by taking into consideration all of the factors when deciding which type of coating to use.

In the first years of use, the waterborne coatings did not have equivalent film properties to their solvent-base counterparts. In particular, the humidity and salt spray resistance, exterior durability, the overall film appearance were far inferior to the solvent-base coatings. Today, that situation has improved considerably, and while the automotive company using the waterborne finishing system needs to use more energy to achieve the same results, at least the properties are equivalent and the films on the automobiles are as good as those that were applied from solvent.

Application problems include foaming of the coating, cratering of the coating as it is applied to poorly cleaned surfaces, and the lack of penetration of one coat by the subsequent one which could cause tremendous adhesion problems. As the user becomes more familiar with a waterborne coating being used in his plant, he generally overcomes most of these problems by paying strict attention to details and doing a good job of training his workers. We have seen, however, some cases where companies have switched to waterbase coatings only to find that these problems were too difficult to overcome. Finally, they switched back to solvent-base coatings. Unfortunately, these same companies will have to change again since they know they will be forced by regulation to use a low-solvent coating in the future.

Several factors must be considered in looking at waterborne coatings, and while these factors are not important for certain applications, they certainly are for others. First of all, one of the advantages of making the change from solvent-borne to waterborne is the fact that there are no major changes needed in application equipment or curing ovens. Possibly, there will be a need for a longer flash-off zone or the line speed may have to be decreased. Almost all of the application techniques used for solvent-base coatings can be used for the waterborne materials. Earlier in the development of waterborne coatings, many people thought that the corrosion of equipment in ovens would be a problem. This has not occurred, although there is more stainless steel equipment being used with water-base materials to prevent flash rusting, specifically with emulsions.

Variations in humidity in the application zone could cause a real problem. The automotive industry in using waterborne coatings has found that it is necessary to control the humidity, thus requiring even more energy. It is safe to say that in any areas where high humidity exists, quite often companies switching to waterborne coatings may have to effect some kind of humidity control in order to insure complete drying of the films. Real care must be taken in storing coatings based on water, especially with regard to the freeze-thaw ability of emulsions and the possible hydrolysis of water-soluble coatings. This hydrolysis leads to a breakdown after a certain period of time making the coating unusable. Waterborne coatings most likely will have to be packaged in lined containers, thus increasing the overall cost.

The next point that I will make will apply to almost any low solvent coating that a company is considering using. There is a tremendous need for a commitment on the part of the user to make the system work. In my opinion with some exceptions because the coatings are not yet available, most anyone can make a waterborne system work on many of the products that now require solvent-base coatings. The commitment calls for close cooperation between coatings supplier and user. It also calls for a willingness to overcome a great deal of frustration--much like the guy who bought a new boommerang and had a terrible time throwing the old one away. This process calls for complete laboratory evaluation of the coatings before proceeding to the coating line to determine what to expect with waterborne coatings as compared with the solvent-base materials they are now using. Failure to do this will certainly bring disastrous results and a negative attitude on the part of the applicator towards waterborne coatings.

The next technology area that is rapidly developing is that of high solids coatings. There is a continuing controversy about what constitutes high solids, although by strict definition a high solids coating should contain at least 80% solids by volume. This number was derived from the old Rule 66 regulation from California and has become the basis of today's high solids definition. As we look at some of the EPA guidelines, we

find that the solids content in many cases need not be any greater than 70% volume. Unfortunately, as I stated before, California is making their rules even more restrictive and while there are still a number of industrial areas undefined within the CARB literature, an 80% solids industrial coating would mean even the most strenuous requirements of the California categories can easily comply with the published limits of the federal EPA. At the same time, those who are using the medium high solids coating of 60 to 65% volume solids cannot become too complacent as history has proven that government control does not normally become more lax, but will become even more restrictive with time.

High solids coatings require very careful polymer design. As we increase the solids of our coatings, we come ever closer to producing what is known as a liquid plastic which is then essentially the same type of material that is currently being used in the plastics industry today. The polymers for high solids coatings are called "oligomers" which are polymers of very low molecular weight. Unfortunately, with organic coatings, lowering the molecular weight tends to detract from the good film properties of the coating. This can be overcome by improved polymer design, and it could also be overcome by using polymers of medium molecular weight and using heat to reduce the viscosity of the coating as it is applied.

Although the main purpose in using a high solids coating is to comply with air pollution regulations, we should not overlook the economic motivations. There are three primary advantages for a high solid system. The first one is that the user no longer has to pay for reducing solvent. The conventional solvent containing industrial coating is usually about 60% solvent in the container. To this an additional 30 to 50% solvent is added just prior to application on the line. The solvent is heated and vaporized in the atmosphere with no real benefit other than as an aid in applying a film of pigmented resins that money was spent to obtain. By replacing that 60% of solvent volume with 40% of additional solids and only 20% solvent the user doubles the square feet of surface he can coat with an equal volume of paint. In short, why pay for something that is not really needed?

The second major advantage in economic area involves storage, shipping and handling. Because high solids coatings do provide essentially double the amount of useable material in the container, the user only has to store only half the inventory previously dealt with. After all, the user is only concerned with the solids of the coating to determine the application cost. Although the cost per gallon of the high solids coating is higher than a conventional coating, equal or lower application cost can be achieved because of the higher solids.

Another advantage is seen in the finishing ovens. With decreased solvent levels, exhaust rates can be drastically reduced while still complying with the lower explosive limit needs. This, of course, significantly decreases air consumption and the heat requirements, thus the cost of the line operation.

One of the major problems with high solids coating is the control of film thickness upon application. Where heavy films are applied normally, this can be an advantage. But where films of one to two mils are applied (and this is the normal situation), control of this film thickness across the surface area of the product becomes increasingly difficult with the higher solids products.

The ability to spray these coatings depends a great deal upon the efficiency of the equipment to atomize it. All of the equipment manufacturers, including those who provide electrostatic application equipment, are working on new products to provide better atomization of the high solids coating and, thus, a smooth and useful film. Other equipment modifications may also be needed, such as modification of the conveyor loop size, redesigning the filter arrangement, re-thinking the booth cleaning process, and considering constant paint temperature control.

High solids coatings have tremendous problems of flow, cratering, wetting and sagging. The last problem, sagging, is particularly offensive if you are applying a coating to a flat sheet and then curing it in an oven where the panels are in a vertical or semi-vertical position. Many high solids coatings will stay put on the flat sheet, but when heat is applied and the solvent is driven off, the low molecular weight coating begins to melt and sag before curing.

There is great potential for the high solids coating technology, but these coatings are a long way from commercialization. During the past three or four years some industries have adopted these materials. These include extrusion finishes on aluminum, steel building components, selected automotive steel parts, and a variety of other metal finishing areas. And speaking of metal--I should emphasize the necessity to do a more than adequate job of cleaning the surface. High solids coatings, because they contain less solvent and solvents do promote metal wetting, have tendency to crater and not properly wet the surface.

I suspect that the comment I made concerning the need for commitment on the part of the user is even more important with this type of coating than it is with waterborne materials. One reason why such coatings are not used in greater quantities today is that few users are willing to give the type of commitment needed and to effect the type of control in their operations that will allow high solid coatings to be used with a

minimum amount of problems. Nevertheless, I feel that if the guidelines as adopted by the states promote a gradual increase in solids, then I think the high solids approach in the long run is the very best one.

A third technology that is slowly emerging is the use of radiation to cure a coating essentially which is 100% solids. This area can be broken down into two sectors: those coatings that are cured by ultra-violet light and those coatings that are cured by an electron beam. I must emphasize in the beginning that both of these types of coatings have a long way to go before they will be commercial, even though there are some of these types being used today. In both cases, the conventional oven which is usually quite long can be eliminated and replaced by a curing unit which is much more compact, thus saving a great amount of space in the plant.

Coatings cured by ultra-violet light have been around for some time. Unfortunately, if these coatings are pigmented with the normal pigment of our industry, which is titanium dioxide, they will not cure. Therefore, the technology has been restricted up to now to clear coatings used as finishing varnishes on metal or wood or translucent fillers that are used to fill a particleboard prior to the final finishing operations. While the energy savings with this type of coating has been documented, the high cost per gallon of these coatings (anywhere from $15 to $35 per gallon compared to $7 to $12 per gallon for conventional solvent-borne coatings) is a factor that must not be overlooked.

Coatings cured by electron beam were tried many years ago. In fact, a coil coating line utilizing this coating was built by a group of companies. This line is no longer operational primarily because of the tremendous energy requirements for curing the coating, as well as the lack of coatings which provide the necessary film properties. The electron beam process is currently being successfully used by companies coating plastics. The energy requirement and equipment costs are being reduced considerably, and I think we will see a resurgence of research and development work on this type of coating in the near future. It should be noted that the coatings cured by electron beam do not suffer from the same disadvantage as the ultra-violet cured coatings in that they may contain titanium dioxide, thus providing cured films that hide the surface.

A fourth option for users looking for low solvent coatings is powder coatings. Powder coatings are 100% solids materials that are applied electrostatically normally to metal substrates. Each particle of powder is a discrete particle, including all the ingredients in the coating. When the powder particles hit the surface, they are held by electro-static attraction and then fused into a continuous film under heat.

Powder coatings were essentially invented in Europe and came to this country approximately ten years ago. The slow growth in powder

is due mainly to the fact that it has been very difficult to achieve the low film thicknesses that are normally used in metal finishes. Powder can also be applied in a fluidized bed, but here again the film thickness is high. The powder is normally collected and recirculated, thus the efficiency of the operation is high. The automotive companies took a good look at powders several years ago and painted many cars with it, but abandoned the process because there was no way to effect a quick color change on the line.

There are many metal articles that are now coated with powder to provide films with excellent properties. Powder coatings require normal or somewhat above normal heat for cure, so there is no advantage in energy savings. Because there are little or no emissions from this process it is universally accepted by all regulatory agencies as being the most pollution-free process. Powder coating has experienced a rather slow growth, but progress is being made and several companies have adopted the process. A complete change in application equipment, including special booths and powder collectors, makes the capital investment requirements rather high.

The last process which has found use mainly in the automotive industry is electrodeposition. Here a coating is deposited from a low solids content water bath electrically to a metal surface. Each bath is continuously replenished by adding high solids waterborne concentrate and the process is very efficient. It has been restricted mainly to the application of primers, but there are some uses of electrodeposition for topcoats on steel. Obviously, the investment in electrical equipment, as well as the cost of a tank provided with equipment to continously refilter the material that is washed off before the product goes into the oven again, makes the investment in equipment substantial when considering this process versus several others. A new development where coatings are deposited in similar fashion from a water bath without the use of energy called "chemiphoresis" is a distinct possibility and a process that could be utilized by many companies in the future.

Now that I have talked about all the possible options, what do I feel would be the direction of industrial coatings industries in the next few years? Since waterborne coatings require little extra capital investment and because they are developed to a greater degree than any other process, I feel that they will capture a large share of the market in the next five years. On the other hand, the problems that are inherent with waterborne coatings and favorable economics of high solids make it especially attractive for the high solids material which will gain in favor as time goes by. In fact, I would predict that by the year 1985 that the high solids coatings will capture as much as 30% of the industrial coatings market.

Finally, I must emphasize that anyone considering a change to low solvent coatings (and that change will be absolutely essential if you are going to continue finishing a product with an organic coating in the future) must make a complete study of his operations before deciding which way to go. He must ask three questions: 1) In terms of ecology, will it meet today's and tomorrow's regulations? 2) Economics--will the process cost more in capital investment and what is the application cost of the coating? 3) Will the process require more or less energy and what type of energy will be necessary to cure the coating?

Robert S. Bailey

C-3

Organic Finishing/ General Interest Session C

Development of Finishing Equipment For a Changing Paint Technology

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DEVELOPMENT OF FINISHING EQUIPMENT TO MEET CHANGING PAINT TECHNOLOGY

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ABSTRACT

Industrial finishing has been significantly impacted during the past decade by the environmental movement. Stringent regulations have been enacted by many states and localities to meet "Ambient Air Quality Standards" specified by the Environmental Protection Agency. Compliance with environmental legislation has become a primary criterion employed by an industrial finisher when selecting a coating. Material suppliers continue to explore new coatings technology by engaging in extensive research and development activities to determine the practicality and merits of high-solids, water-borne coatings and plural component catalyzed coatings. These "environmentally acceptable" coatings pose an application problem because of their inherently higher viscosities and sensitivities. Because research and development activities by material suppliers far exceed those of equipment manufacturers, it is not envisioned that finishing equipment technology will evolve as rapidly as coatings technology. It is difficult, indeed, to envision the next generation of finishing equipment. Rather, it is thought that existing application methods will be modified to accommodate these new "heavier" and "susceptible" coatings.

Prior to the '70s industrial coatings were evaluated primarily on two criteria. The user judged a coating on its performance, defined as the ability to provide the desired appearance and/or requisite degree of protection from harmful elements. Additionally, the economics were measured based on a formula to calculate the cost per square foot of coverage at a specified film thickness. Often the latter was the most significant determinant.

Today, however, the user must assess a coating against a recently introduced standard which has become paramount: Is it environmentally acceptable?

Approaches to solving the environmental problem abound. Certain exempt solvents are being considered as an interim measure. Material suppliers are working feverishly to perfect environmentally acceptable coatings -- water-bornes, high-solids, powders and radiation-cure coatings. In many seminars and technical publications each of these coatings has been judged along several attributes: economics, performance characteristics, energy requirements and emissions. Material suppliers are not in an enviable position; formerly, they had to satisfy only the user. Now they must serve two masters -- government and users.

Most of the attention, however, has focused on coatings technology; "Change the coating; solve the problem". Relatively little attention has been devoted to the application of coatings.

METHODS OF APPLICATION

We must recognize that of the changing coatings, most will continue to be applied by existing application methods:

Conventional air spray - automatic and manual
Heated conventional air spray - automatic and manual
Airless spray - generally manual
Heated airless - generally manual
Electrostatic - automatic and manual
Electrocoating - anodic or cathodic

There is little likelihood of revolutionary change in the method of applying a thin paint surface coating on part, assembly, building, container or vehicle; however, methods of moving, atomizing, measuring and controlling heavier and consequently more viscous materials will change. The degree of such change will vary with products, production levels, finish quality and multi-color applications, but the physical and chemical qualities of new formulations will primarily dictate equipment performance.

Paint handling, surface pretreatment and application techniques for high solids, water reducibles and catalyzed coatings will require modification, adjustments and special care; the extent of which is to be described herein as it would specifically apply to industrial finishing.

From the equipment viewpoint, one can categorize the coating formulation options on the basis of their pumpability, sprayability, application sensitivity and handling complexity as they apply to high solids, water reducibiles and catalyzed coatings in that order.

HIGH SOLIDS COATINGS

Conventional paint handling equipment, (air operated reciprocating pumps, hydraulically driven reciprocating pumps and electrically driven turbine pumps) are capable of providing the motive force for moving high solids materials. Conventional air spray and airless spray application equipment may be taxed to provide proper atomization, but the use of heat for viscosity reduction will serve the dual purpose of improving atomization and assuring paint consistency, essential to stablizing the paint film hanging and curing qualities.

Obviously airless spray application holds the edge in the atomization of heavier materials but the use of heat for maintenance of uniform viscosities is as essential to the product's hanging qualities and curing as to its fluid application. Viscosities of conventional solvent systems (35% - 40% solids), generally range from 50 to 100 centipoise at ambient temperature, while a typical 75% volume solids polyester paint with a viscosity of 400 centipoise viscosity at 75°F may vary from 700 centipoise at 40°F to 100 centipoise at 140°F. Thus, the viscosity of high solids, in the range of three to four times that of conventional paints, is the primary physical property affecting atomization, coating build, hanging and proper curing and viscosity adjustment by heat will undoubtedly be needed for most coating materials. Electrostatic bell centrifugal application may supply the necessary motive force for atomization at lower fluid pressures without heat but this application method will not necessarily serve all coating requirements.

Savings in solvent costs (direct and indirect) and increased production rates make the choice of high solids attractive; however, through paint loss in application, the loss of solids equates to that of conventional loss dictating care in the selection of application methods and procedures. There are no other chemical characteristics of high solids coatings that would affect the normal use of conventional air or airless spray equipment. To date, characteristics of abrasion or corrosiveness have not prescribed changes in equipment design or in materials of construction.

WATER REDUCIBLE COATINGS

Latex water base coatings of high solids content are commonly applied by airless application methods in the architectrual coatings field and an increasing number of industrial finish coatings are being applied by conventional air spray and electrostatic air spray/airless equipment. Not unlike high solids solvent formulations, viscosity levels of water coatings are double or triple that of conventional solvent coatings. They can be handled by standard airless application methods but require increased fluid pressure levels for air spray supply and application. Capital investment economics suggests the use of corrosion resistant equipment (usually stainless steel) but it is not essential to acceptable

fluid handling and spray application.

Constraints to acceptable application lie primarily in the formulation's hanging ability, ambient humidity conditions and curing requirements. The only characteristics affecting equipment availability or choice are:

- Higher viscosities - requiring higher than conventional air spray application pressures.
- Susceptibility to foaming, affecting paint consistency and sprayability, requiring care in paint preparation and recirculation methods.
- Corrosion effects over time and,
- Equipment cleanup due to drying of the liquid paint and its irreversible cure.

TWO-PART CATALYZED COATING

Resistance to change of age-old-practiced-paint application methods is the greatest restraint to the acceptance of new exothermic paint coatings. Once regarded as sophisticated specialty formulations requiring specialized chemical knowledge and laboratory type equipment and techniques, such coatings are fast becoming an acceptable answer to both environmental and energy demands.

Application methods and equipment have evolved to practical use and are only limited by users resistance to the envisioned operational care of more complicated paint products and equipment. With respect to the needs of protective finishing in other industries, such plural component coatings and equipment have already established a proven record of reliability, functionality and success; aircraft painting, shipbuilding and repair, refinery maintenance, bridge highway station maintenance and other heavy manufacturing as heavy construction equipment, storage tanks, shipping containers, etc. Slowly such equipment is being recognized as practical for industrial finishing use and equipment manufacturers are fine tuning their designs for performance under high production continuous operations.

Practical application ranges from premixing, often envisioned as messy but the only assured method of application, to the more acceptable and proven method of pumping, metering, mixing and applying by conventional airless and air spray methods.

For large-scale protective applications, portable airless systems are used with little more complexity than conventional methods. This additional complexity is in the care for and handling of two liquids and added care in the operation, cleanup and maintenance of the equipment, which is not unlike the pumps, hoses, and guns of conventional equipment.

AIRCRAFT PAINTING

Application of 1:1 ratio urethane coating (U.S. Paint and lacquer)- viscosity 40 c.p.s. (22 secs. #2 Zahn) Single coat applied to level of 3 mils material is 50% solids -- $50 for 1:1 2 Pak System; i.e., $50.00/2 gal. = $25/gal. To Northwest Airlines Aircraft under their standard maintenance repaint program.

SHIP PAINTING

Common application of 2:1 ratio solvent free epoxy coats up to 19 mils -- High viscosity material.

Certainly such materials and equipment will require additional care and perhaps a higher level of operator capability, but recalling the old cliche, "there is no such thing as a free lunch", progress will have its costs. New developments in paint technology of magnitude to meet both the high demands of environmental protection and energy reduction will require understanding and appreciation of the necessary upgrading of methods, personnel and care in finishing operations.

Another development for the metering, mixing and application of two component paints is an in-plant system designed to proportion paint directly from a permanent in-plant circulating supply system of individual supply pumps or pressure pots.

Designed primarily for decorative air spray finishing, it can be applied by either conventional hand or automatic air spray or it can be used to feed electrostatic guns; manual, automatic and rotary bell. Other variations of the air-operated airless spray variable ratio proportioning systems described previously in a portable configuration are also being installed for in-plant use. This equipment offers the benefits of higher volumes and higher viscosity application by the airless method, quite applicable to the protective finishing requirements of the railroad market.

SUMMARY

Equipment for the application of new paint materials as we know them today and as we may expect to find them in the future is available for practical application. More difficult to handle perhaps, but we cannot expect to leap-frog from conventional solvent materials and accepted practices to heavier, more concentrated chemical coatings without some increase in the degree of application complexity.

Current paint equipment continues to be upgraded for practical application of higher and higher solids material of the solvent variety. Alternatives are available for the practical application of water-borne varieties; and, for those conscious of the benefits of more sophisticated chemical coatings and understanding of the more dedicated care and attention necessary, there now exists a wide range of plural component equipment choices, all applicable to efficient industrial product finishing.

C-4

Organic Finishing/ General Interest Session C

Chemical Characterization of a Mixed (Orthosphosphoric/Polyphosphoric) Acid Aluminum Etchant

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CHEMICAL CHARACTERIZATION OF A MIXED (ORTHOPHOSPHORIC/POLYPHOSPHORIC) ACID ALUMINUM ETCHANT

By Htain Win and Terry J. Morin

Sensitivity of an orthophosphoric acid, a polyphosphoric acid, and an iron (III) chloride etchant to variations in process conditions was examined to determine the potential production application of the etchant system in the photolithographic fabrication of pure aluminum circuits. The effects of changes in temperature, orthophosphoric acid concentration, polyphosphoric acid concentration, iron (III) chloride concentration, and dissolved aluminum concentration on etched circuit quality and etch rate were examined. The etchant system allows reasonable variation in preparation and circuit processing without drastically affecting the etched circuit quality. Control of the etchant can be maintained over a broad range of temperatures and compositions.

In print and etch production of precision patterns in thick metal films, a fundamental understanding of the chemical etchant is required to achieve process optimization and process control.

In the printed circuit industry, chemical etching has long been the accepted method for producing precision patterns in metal films. Etching, in conjunction with present photolithographic technique, affords submicron line resolution.[1] Despite the trend to additive "lift-off" techniques for the production of circuit patterns as the pattern dimension order of magnitude approaches the grain size, chemical etching remains an important method of pattern production.

For etching of pure aluminum circuits, there are many etchant formulations available. For example, more than 80 etchant formulations are reported in the literature for the etching of pure aluminum roll foil circuits.[2] In a preliminary investigation, 80 such formulations were evaluated on the basis of a reasonable etch rate, uniformly good pattern definition, and positive photoresist compatibility. A later work reports on a spray etchant that gave edge definition variation of ± 1.27 μm.[3] This formulation was acceptable but further development was required to find a formulation that would give more predictable results, reduce dependence on operator skill and experience, and increase the use life of the etchant.

Since May 1977, an immersion etchant[4] having a composition of 75 percent (v/v) orthophosphoric acid, 25 percent polyphosphoric acid (v/v) and 20 g/L iron (III) chloride has been used at Bendix to etch pure aluminum circuits. This etchant gives good edge definition and is stable over a relatively long period. No circuit etched in this formulation has been rejected on the basis of etch quality.

The intent of this investigation was to characterize the sensitivity of aluminum etch rate and pattern definition to variations in orthophosphoric acid concentration, polyphosphoric acid concentration, temperature, iron (III) chloride concentration, and dissolved aluminum concentration and to correlate the resulting etch quality to these process variables.

With such an understanding of the etchant, appropriate process controls can be prepared to establish production readiness of the etchant.

EXPERIMENTAL METHOD

In all cases, 250 mL of freshly prepared mixed acids were placed in a 750 mL beaker. The solution was brought to the desired temperature, then the desired weight of iron (III) chloride was dissolved in the mixed acids. After dissolution of iron (III)

chloride, the etch bath temperature was stabilized at the desired temperature, and an aluminum on Kapton (Du Pont) sample mounted in a specially made polypropylene holder was immersed in the mechanically agitated bath. The sample was positioned with the plane of the sample normal to the etchant flow (Figure 1).

The etch rates were determined from the etch time and sample aluminum thickness. The etch end point was determined visually. Aluminum thickness was determined from beta backscatter measurements[5] made on the material from which the samples were punched. Samples were prepared from 127 μm thick Kapton on which 11 μm of 99.999 percent aluminum had been deposited on physical vapor deposition (PVD).

Each PVD aluminum on Kapton sample was punched to a 1.346 cm diameter. In all cases except where noted, the samples were prepared from Kapton coated with PVD aluminum on which photoresist pattern had been developed. The pattern consisted of a 860 μm wide line positioned in the approximate center of the 1.42 cm^2 sample area.

In the determination of the effect of various anionic and cationic environments, the various salts were dissolved in 25 mL of freshly prepared 75 percent orthophosphoric, 25 percent polyphosphoric acid etchant at 60°C. Dissolved salt concentrations were approximately 0.05M.

The definition and reduction from the photoresist pattern line width was used to describe etch quality. To quantify line width reduction, the photoresist pattern width before etching and the circuit line pattern width after etching were measured with a closed circuit television system (CCTV) at 75X. Light micrographs (50X) were taken of the samples before and after etching. Scanning electron micrographs (700X) were taken of samples having good pattern definition or line width reduction with a scanning electron microscope (SEM). Samples for SEM work were coated with a gold-palladium film.

A constant temperature bath was used to maintain etch bath temperature to $\pm 0.5^{\circ}C$. Heavy paraffin oil was used as a bath fluid. The 250 mL volume of etchant was agitated mechanically at a constant speed (250 rpm) with a 5 cm diameter impeller.

Etchant solutions were prepared from polyphosphoric acid [$H_2PO_4(PO_3\ H)_nPO_3H_2$, 83 to 86 percent P_2O_5], orthophosphoric acid (H_3PO_4) of reagent grade, and reagent grade iron (III) chloride ($FeCl_3 \cdot 6\ H_2O$).

For atomic absorption spectrophotometry of the etchant solutions, 1000 ppm aluminum sulfate and iron (III) chloride standard solutions were diluted to 2 to 50 ppm range with purified water.

All experiments were performed in a laminar flow clean room environment operating at 21°C, 35 percent relative humidity and with a room air particle count not exceeding 350 particles per liter (ppL) of a size 0.5 μm and larger, or 2.3 ppL of a size 5.0 μm and larger.

RESULTS

An excellent characteristic of the etchant formulation (ortho-phosphoric acid, polyphosphoric acid, iron (III) chloride) is its stability and the reproducibility of test results. In earlier experiments with standard hydrochloric, nitric and phosphoric acid etchants, such reproducibility was rare, making analytical characterization difficult.

Effect of Temperature

Although the mechanism of the etching reaction is hitherto unreported, it is desirable to know how the etch rate changes during the etch. In one test, the sample aluminum weight loss was monitored over the duration of the etch period. The rate of etching of aluminum was found to be constant during the etch period, and a linear relationship was exhibited between the sample weight loss and elapsed time (Figure 2).

The temperature dependence of the etch rate is Arrhenius in nature.

The activation energy of the etching is estimated from the plot and is about 8 kcal/mol (Figure 3). It is interesting to note that reported activation energies for the dissolution of aluminum under alkaline conditions range from 7.5 to 11 kcal/mol.[6,7]

Effect of Iron (III) Chloride

Though the presence of iron (III) chloride is not necessary for the bath to etch, the etch rate and etch quality are sensitive to iron (III) chloride concentration.

At 60 and 70°C there is a range of between 10 and 20 g/L in which increasing iron (III) chloride concentration is associated with increasing etch rate, as exhibited in Figures 4 and 5. The data indicate (Figures 4 through 6) that the etch rate is not sensitive to iron (III) chloride concentrations lower than 10 g/L. This indication may require further substantiation. At 50°C this range of insensitivity covers iron (III) chloride concentration of 10 to 40 g/L for all but the highest orthophosphoric acid concentrations. At higher temperatures and with iron (III) chloride concentration of between 20 and 40 g/L, the etch rate becomes relatively insensitive to iron (III) chloride concentration.

Iron (III) chloride has a significant effect on etch quality (Figures 7 through 9). Generally, iron (III) chloride concentrations greater than 20 g/L gave poor edges and line width reductions greater than 50 μm. Of the conditions studied, 10 g/L iron (III) chloride gave both good edge definition and line width reduction from the resist image of 10 to 25 μm.

Effect of Orthophosphoric Acid Concentration

Within the range studied, the relationship between etch rate and the concentration of orthophosphoric acid is one of direct proportionality (Figures 10 through 12). While the indicated relationship between orthophosphoric acid concentration and aluminum etch rate at constant temperature is clear, the relationship between orthophosphoric acid and line width reduction is not as conclusive (Figures 7 through 9). At higher temperatures (Figure 9), the data seem to suggest that the general effect of increasing orthophosphoric acid concentration is to decrease the line width reduction.

Orthophosphoric acid concentration of between 75 and 95 percent gives line width reduction from the resist image of 10 to 25 μm and an edge profile free of footing (Figure 13).

Effect of Bath Age

The effect of bath age on etch rate was evaluated by comparing the etch rate of pure aluminum in etchant samples that have been aged 30 days

(1) with iron (III) chloride added before aging,

(2) with iron (III) chloride added after aging, but before the sample was etched,

with that of pure aluminum etched in a freshly prepared etchant. The etch rate of pure aluminum in an etchant sample of the aged mixed acid in which iron (III) chloride had been added before etching did not differ significantly from the etch rate of pure aluminum in a freshly prepared bath. However, the etch rate of pure aluminum in a sample of aged mixed acid, to which iron (III) chloride had been added before aging, was 20 percent lower than the etch rate of pure aluminum in a freshly prepared bath.

Effect of Dissolved Aluminum Concentration

To test the effect of dissolved aluminum concentration on etch rate, several samples of PVD aluminum on Kapton were successively

etched in one 250 mL bath, giving a final aluminum concentration of 0.0231 g/L. No significant change in etch rate from sample to sample was observed with all values within 3 percent of the mean value (Table 1). Based on this data, an initial catalytic effect of aluminum on etch rate is not indicated.

In another test, samples of PVD aluminum on Kapton were successsively etched in one 250 mL bath. Pure aluminum wire of the same purity was dissolved in the bath to vary the dissolved aluminum concentration of the bath from 1 to 5 g/L. About a 4 percent decrease in etch rate was observed for every 1 g/L increase in dissolved aluminum concentration (Figure 14). It is also noted that dissolved aluminum accumulation in the bath does not significantly affect the quality of pattern definition within the product concentrations investigated.

From other tests dissolved aluminum corresponding to 6 g/L remains in homogeneous phase in the etchant. However, dissolved aluminum corresponding to 6 to 8 g/L produces a heterogeneous phase solution (precipitate formation). Dissolved aluminum concentrations of 8 g/L and above could not be obtained.

It was concluded that aluminum dissolved in the etchant does not appear to have an initial catalytic effect on etch rate. However, between 1 and 5 g/L dissolved aluminum concentration in the etchant there is a steady decrease in etch rate. Within the

range investigated, the accumulated etch products do not have a significant effect on the quality of pattern definition.

Effect of Salts

The effect of iron (III) salts and transitional metal salts closely related to iron on etch rate and edge definition are listed (Table 2). Iron (III) sulfate and iron (III) phosphate give edge definition and etch rate comparable or superior to iron (III) chloride.

Methods to Determine Aluminum and Total Iron Concentration in Etchant

An analytical method for aluminum and total iron determination was developed to monitor variations in bath composition. The analytical method uses the etchant directly without prior chemical separation for the analysis. In a typical analysis, a 0.200 mL (200 λ) portion of an etch solution is diluted to a 100 mL volume with purified water. The resulting solution is analyzed for the two elements in an atomic absorption spectrophotometer using a hollow cathode lamp and a nitrous oxide/acetylene flame.

The accuracy of the method for the determination of aluminum was established by calibrating the absorbance of a series of synthesized etchant solutions consisting of varying concentrations of

dissolved aluminum. Each synthesized solution represents a different ratio of dissolved aluminum to phosphate background. These synthesized solutions were compared to standard aluminum sulfate solutions in the range 2 to 50 ppm aluminum ion concentration and complete agreement in absorbance was found. For similar calibration in the case of total iron, there is a $\pm$3 percent agreement between synthesized solutions and iron (III) chloride standards. The absorbance of the aluminum free etchant is identical to that of deionized water. The detection limit of the method is 2 ppm.

An atomic absorption spectrophotometric method can be used as a rapid and simple quantitative analytical method for the determination of dissolved aluminum and total iron of the bath.

SUMMARY

It has been established that an etchant formulation of 75 to 95 percent (v/v) orthophosphoric acid, 25 to 5 percent (v/v) polyphosphoric acid, 10 g/L iron (III) chloride at 60 to 70°C is a potential production etchant for photolithographic fabrication of pure aluminum circuits.

The sensitivity of aluminum etch rate and circuit pattern definition to variations in the orthophosphoric acid concentration,

polyphosphoric acid concentration, iron (III) chloride concentration, dissolved aluminum concentration, and temperature was characterized. Because the etchant system allows reasonable variation in etchant preparation and circuit processing without drastically affecting line width reduction and pattern definition, adequate process control can be maintained with a conventional temperature controller and a monitor of dissolved aluminum concentration. A rapid and reliable atomic absorption spectrophotometric method to monitor dissolved aluminum concentration was developed.

ILLUSTRATIONS

Figure	
1	Experimental Apparatus (P102229)
2	Weight Loss Versus Elapsed Time for Etching of Pure Aluminum
3	Natural Logarithm of Etch Rate Versus Inverse Absolute Temperature for Etching of Pure Aluminum in 75 Percent Orthophosphoric Acid, 25 Percent Polyphosphoric Acid, and 20 g/L Iron (III) Chloride
4	Etch Rate Versus Iron (III) Chloride Concentration for Pure Aluminum Etched in 50, 65, 75, 85, 95 Percent (v/v) Orthophosphoric Acid at 60°C
5	Etch Rate Versus Iron (III) Chloride Concentration for Pure Aluminum Etched in 50, 65, 75, 85, 95 Percent (v/v) Orthophosphoric Acid at 70°C
6	Etch Rate Versus Iron (III) Chloride Concentration for Pure Aluminum Etched in 50, 65, 75, 85, 95 Percent (v/v) Orthophosphoric Acid at 50°C
7	Line Width Reduction Versus Orthophosphoric Acid Concentration for Pure Aluminum Etched at 50°C
8	Line Width Reduction Versus Orthophosphoric Acid Concentration for Pure Aluminum Etched at 60°C
9	Line Width Reduction Versus Orthophosphoric Acid Concentration for Pure Aluminum Etched at 70°C
10	Etch Rate Versus Orthophosphoric Acid Concentration for Pure Aluminum Etched at 50°C
11	Etch Rate Versus Orthophosphoric Acid Concentration for Pure Aluminum Etched at 60°C

12 Etch Rate Versus Orthophosphoric Acid Concentration for Pure Aluminum Etched at 70°C

13 Sample Edge Profile at 700X (Polaroid)

14 Etch Rate Versus Dissolved Aluminum for Etching of Pure Aluminum in 75 Percent Orthophosphoric Acid, 25 Percent Polyphosphoric Acid, and 20 g/L Iron (III) Chloride at 60°C

TABLE

Number

1 Relationship Between Dissolved Aluminum and Rate of Aluminum Dissolution at Low Aluminum Concentrations

2 Effect of Salt on Etch Rate and Edge Definition

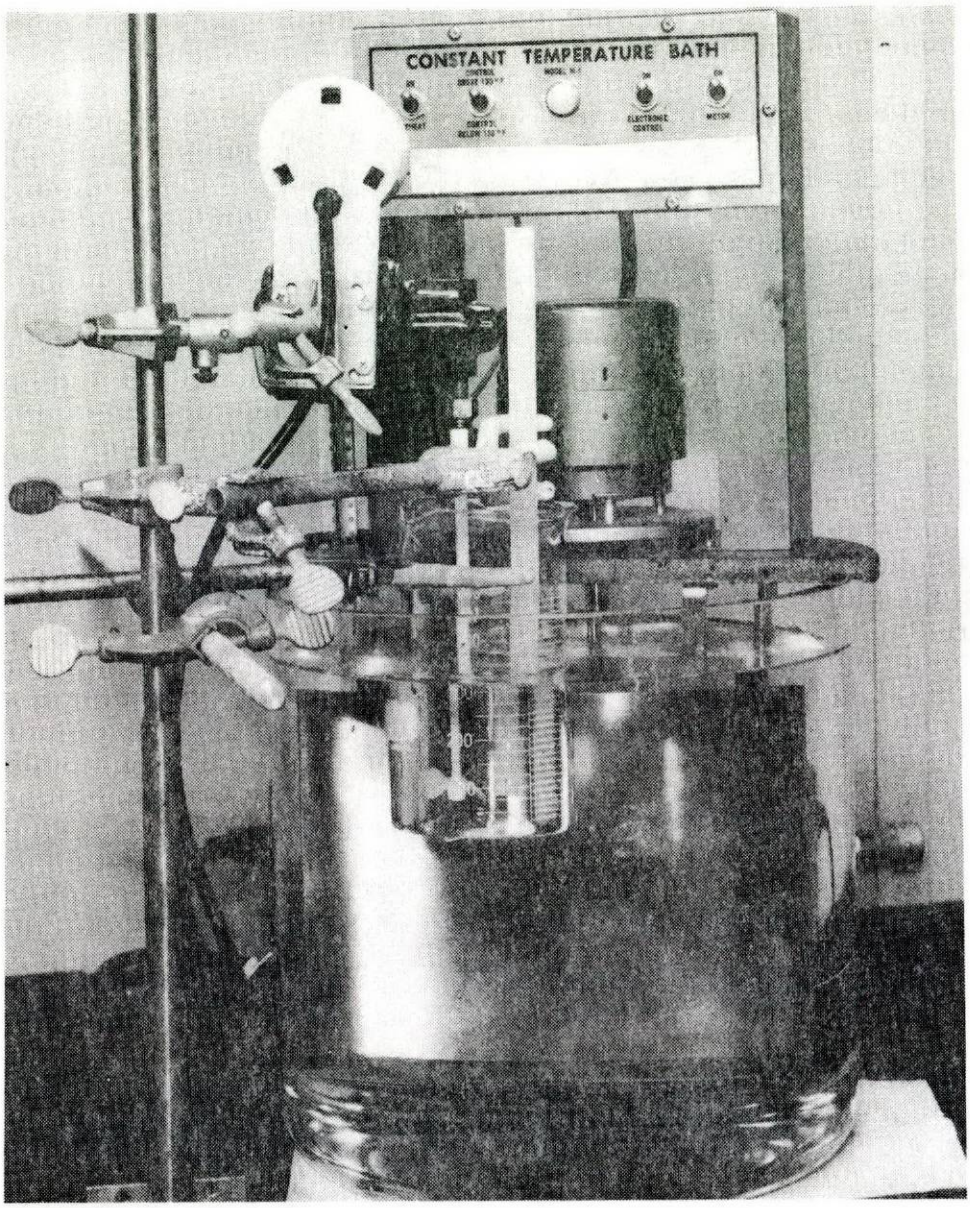

Figure 1. Experimental Apparatus

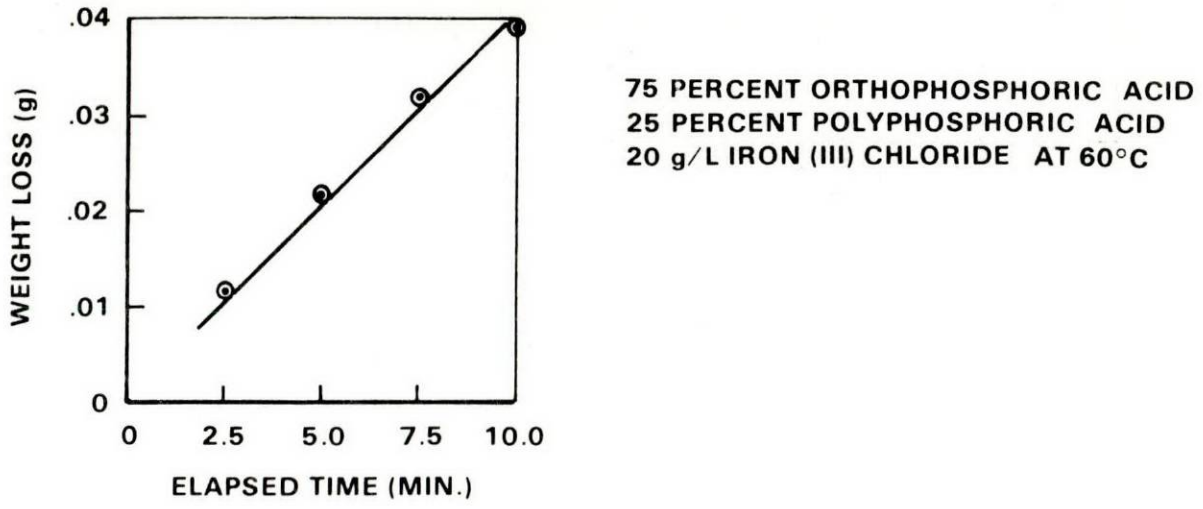

Figure 2. Weight Loss Versus Elapsed Time for Etching of Pure Aluminum

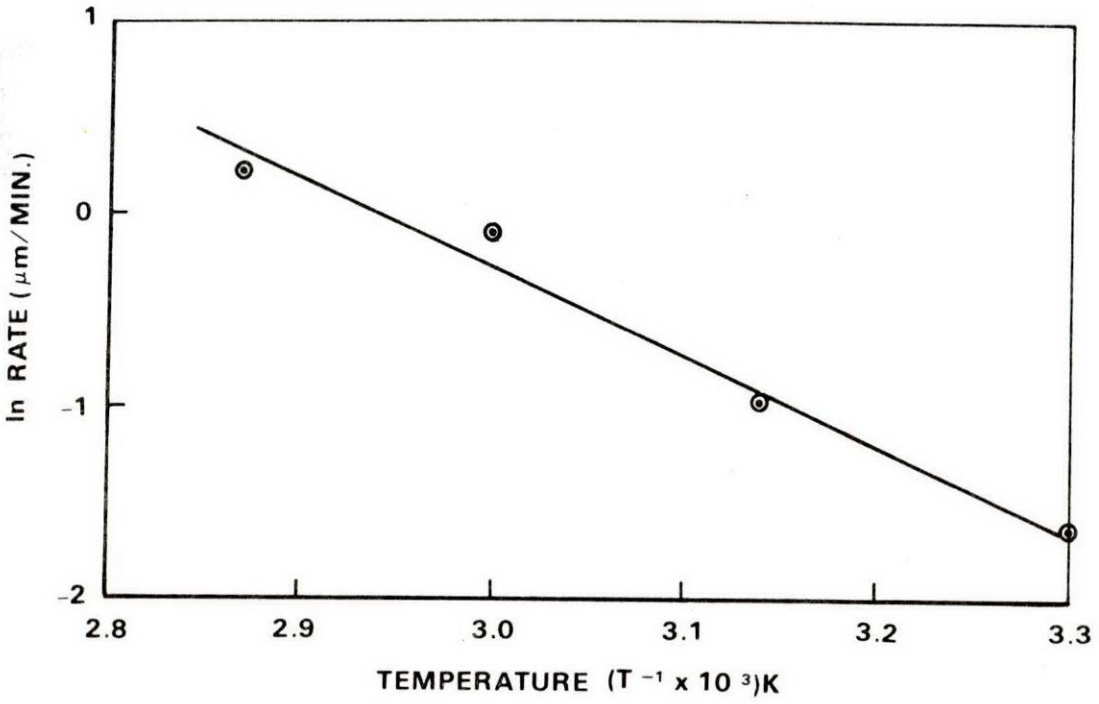

Figure 3. Natural Logarithm of Etch Rate Versus Inverse Absolute Temperature for Etching of Pure Aluminum in 75 Percent Orthophosphoric Acid, 25 Percent Polyphosphoric Acid, and 20 g/L Iron (III) Chloride

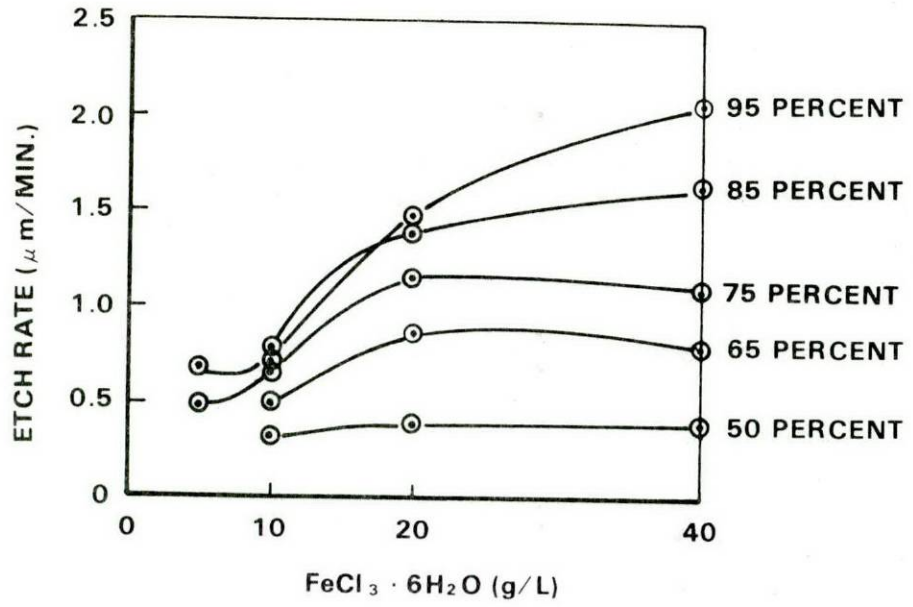

Figure 4. Etch Rate Versus Iron (III) Chloride Concentration for Pure Aluminum Etched in 50, 65, 75, 85, 95 Percent (v/v) Orthophosphoric Acid at 60°C

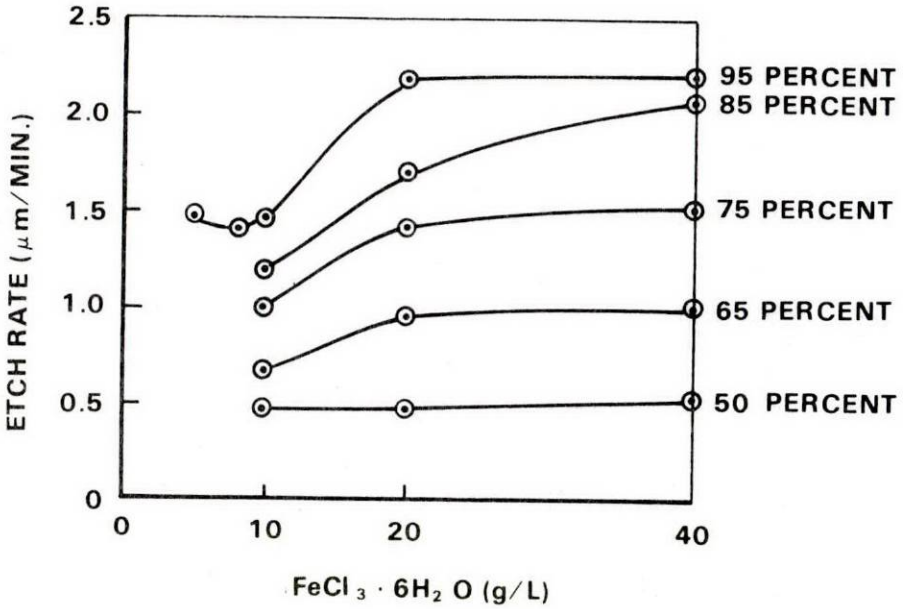

Figure 5. Etch Rate Versus Iron (III) Chloride Concentration for Pure Aluminum Etched in 50, 65, 75, 85, 95 Percent (v/v) Orthophosphoric Acid at 70°C

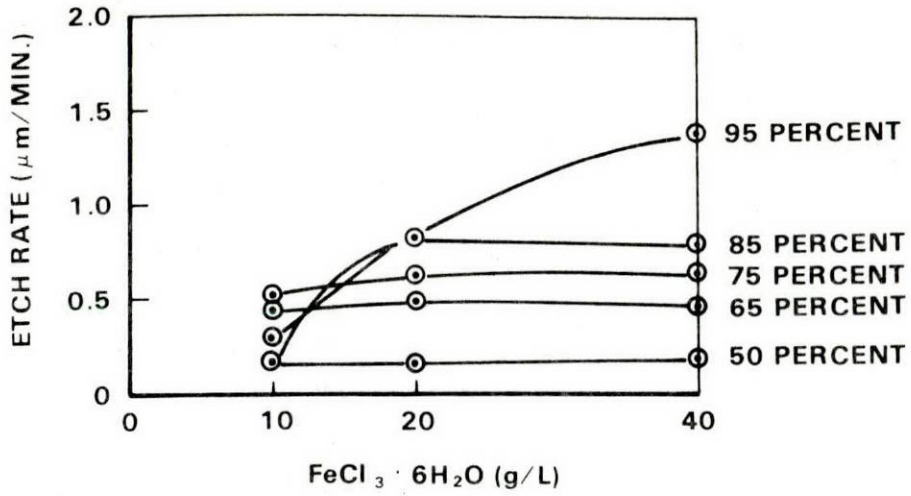

Figure 6. Etch Rate Versus Iron (III) Chloride Concentration for Pure Aluminum Etched in 50, 65, 75, 85, 95 Percent (v/v) Orthophosphoric Acid at 50°C

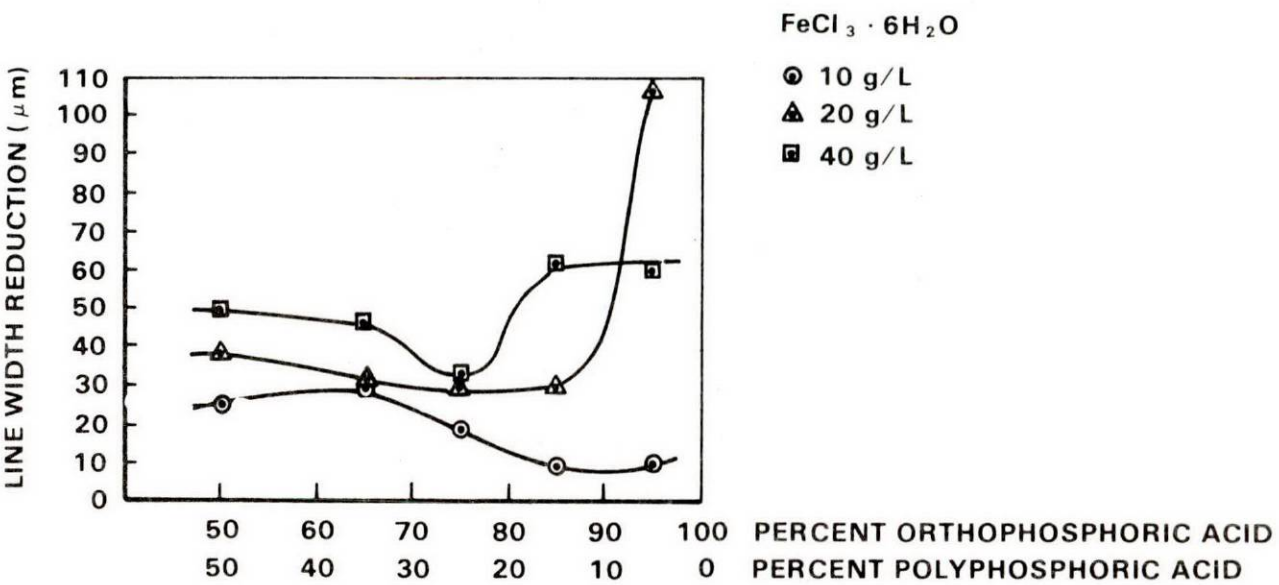

Figure 7. Line Width Reduction Versus Orthophosphoric Acid Concentration for Pure Aluminum Etched at 50°C

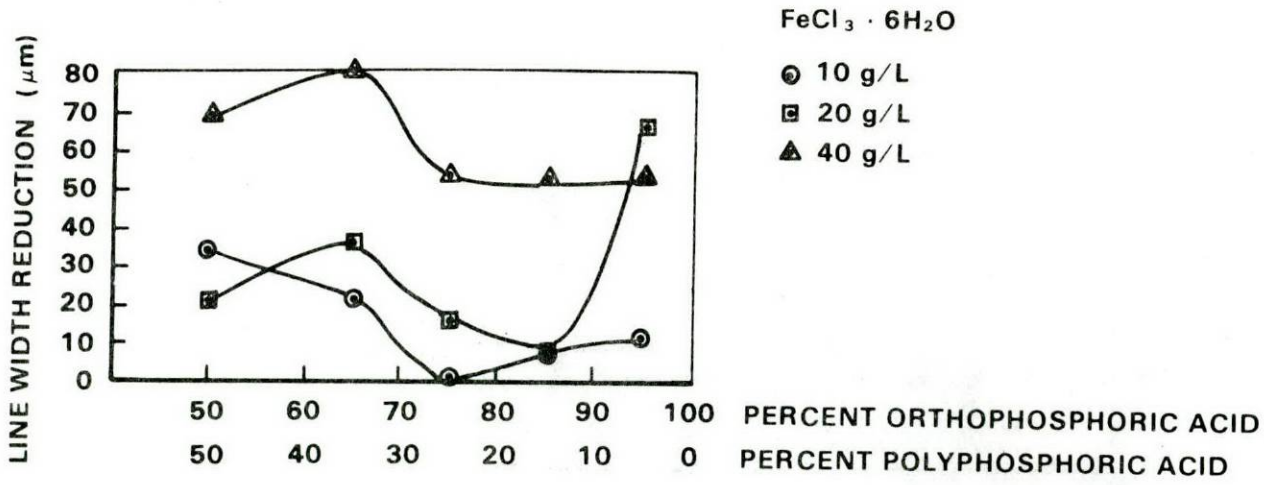

Figure 8. Line Width Reduction Versus Orthophosphoric Acid Concentration for Pure Aluminum Etched at 60°C

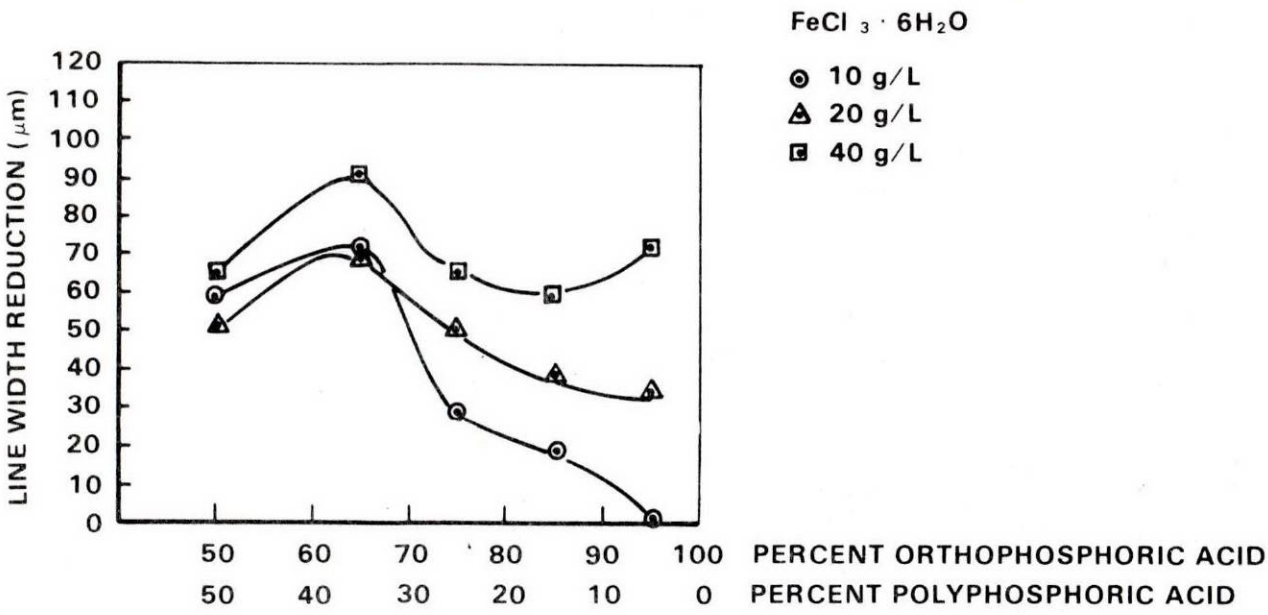

Figure 9. Line Width Reduction Versus Orthophosphoric Acid Concentration for Pure Aluminum Etched at 70°C

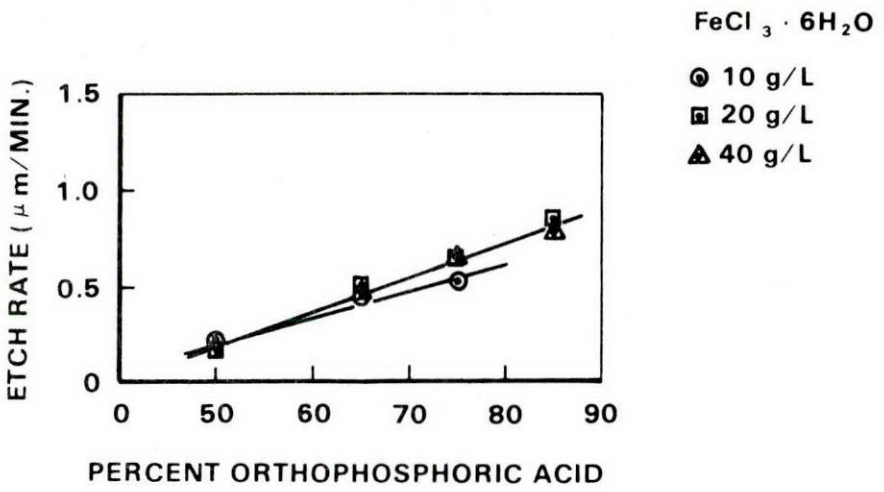

Figure 10. Etch Rate Versus Orthophosphoric Acid Concentration for Pure Aluminum Etched at 50°C

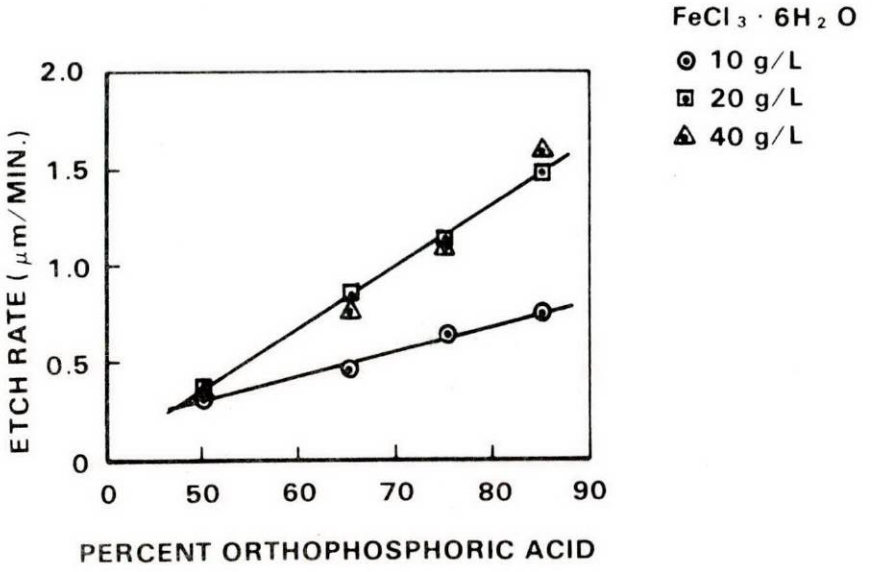

Figure 11. Etch Rate Versus Orthophosphoric Acid Concentration for Pure Aluminum Etched at 60°C

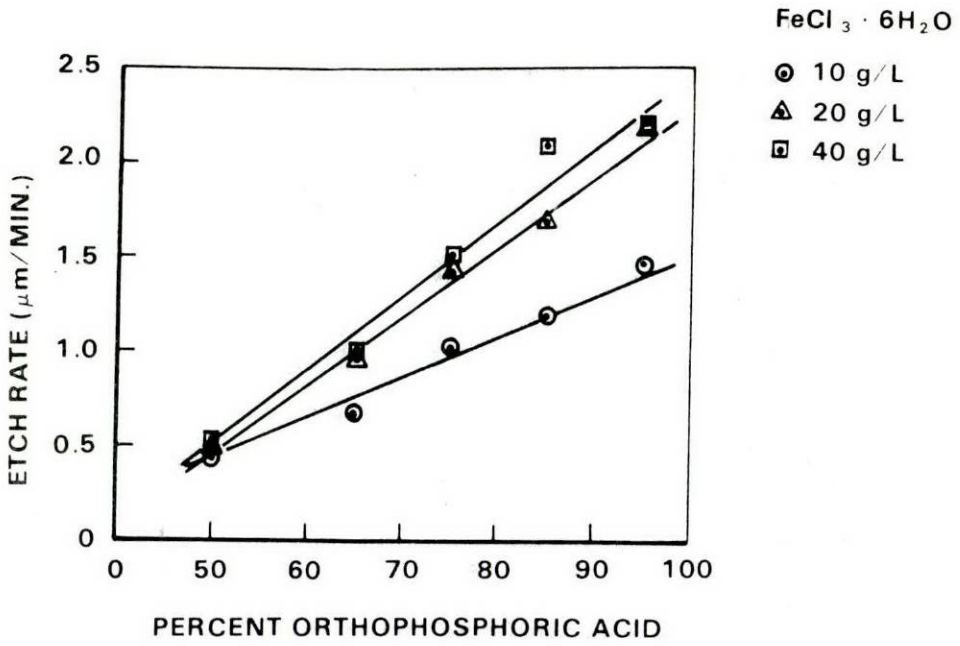

Figure 12. Etch Rate Versus Orthophosphoric Acid Concentration for Pure Aluminum Etched at 70°C

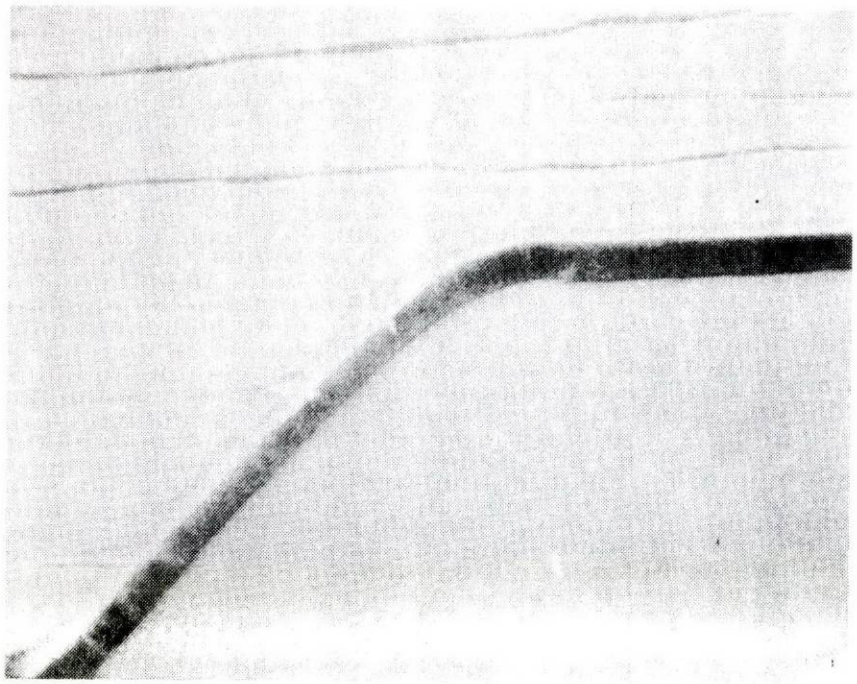

Figure 13. Sample Edge Profile at 700X (Polaroid)

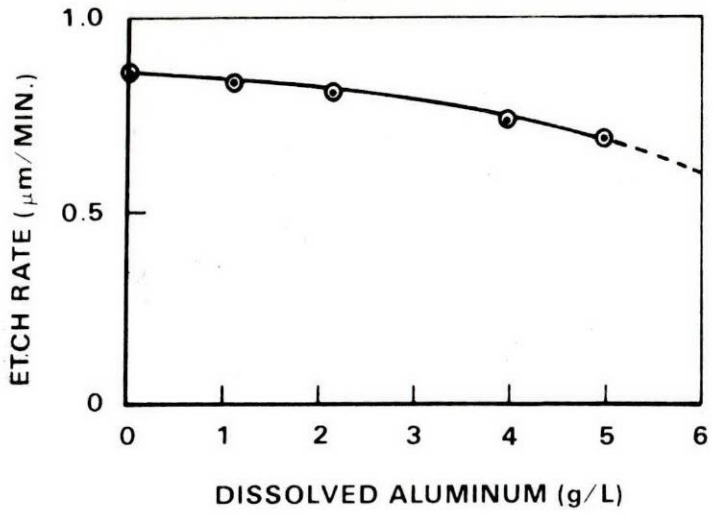

Figure 14. Etch Rate Versus Dissolved Aluminum for Etching of Pure Aluminum in 75 Percent Orthophosphoric Acid, 25 Percent Polyphosphoric Acid, and 20 g/L Iron (III) Chloride at 60°C

Table 1. Relationship Between Dissolved Aluminum and Rate of Aluminum Dissolution at Low Aluminum Concentrations

Dissolved Aluminum (g/L)	Etch Rate* (μm/min)
0.0000	1.42
0.0039	1.36
0.0077	1.33
0.0116	1.34
0.0154	1.42
0.0192	1.38
0.0231	1.36

*In 95 percent (v/v) orthophosphoric acid, 5 percent (v/v) polyphosphoric acid, 10 g/L iron (III) chloride at 70°C.

Table 2. Effect of Salt on Etch Rate and Edge Definition.

Salt	Formula	Solubility	Relative Etch Rate	Edge Definition
Iron (III) chloride	$FeCl_3 \cdot 6H_2O$	Soluble	1.00	Good
Iron (III) fluoride	$FeF_3 \cdot 3H_2O$	Some Solub.	1.61	Rough edges
Iron (III) bromide	$FeBr_3$	Soluble	0.70	Fair
Iron (III) sulfate	$Fe_2(SO_4)_3 \cdot xH_2O$	Soluble	0.67	Good
Iron (III) nitrate	$Fe(NO_3) \cdot 9H_2O$	Soluble	0.81	Footing
Iron (III) phosphate	$FePO_4 \cdot 18H_2O$	Soluble	0.91	Good +
Cobalt (II) chloride	$CoCl_2 \cdot 6H_2O$	Some Solub.	1.05	Poor
Cobalt (II) sulfate	$CoSO_4 \cdot 7H_2O$	Some Solub.	0.73	Fair
Manganese (II) chloride	$MnCl_2 \cdot 4H_2O$	Slight Solub.	0.72	Fair
Nickel (II) chloride	$NiCl_2$	Slight Solub.	0.84	Poor
No salt added			0.74	Rough

Approximate salt concentration 0.05M
Etchant 75 percent ortho, 25 percent poly at 60°C

REFERENCES

[1]Y. Wada and K. Uehara, *Japanese Journal of Applied Physics*, 13, 2014 (1974).

[2]W. H. Knopf, Aluminum Etchant Studies (Topical). Bendix Kansas City: BDX-613-1105 (Rev.), September, 1974 (Available from NTIS).

[3]W. H. Knopf, Improved Precision Aluminum Etchant (Topical). Bendix Kansas City: BDX-613-1281 (Rev.), August, 1975 (Available from NTIS).

[4]H. J. Wiesner, *Circuits Manufacturing*, 18, 20 (1978).

[5]W. B. Abel, Beta Backscatter Measurements of Aluminum Coatings on Mylar Substrates (Topical). Bendix Kansas City: BDX-613-1028 (Rev.), September, 1974 (Available from NTIS).

[6]G. Gerlagh and P. Baeyens, *Trans. Inst. Metal Finishing*, 53, 133 (1975).

[7]B. Chatterjee and R. W. Thomas, *Trans. Inst. Metal Finishing*, 54, 17 (1976).

D-1

Electronics I
Session D

High Speed Plating Solutions For Selective Plating Application

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HIGH SPEED PLATING SOLUTIONS FOR SELECTIVE PLATING

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ABSTRACT

The equipment used in selective plating operations consists of highly specialized machines specifically engineered for each application. In general, they are designed to plate at high speeds, continuously and selectively onto the metal as it unwinds from a reel at one end of the machine and rewinds completed onto a reel at the other end.

Just as the machines are specially designed for each application, the plating solutions also must be tailor-made in order to obtain a deposit that has the required metallurgical characteristics.

This presentation is confined to a discussion of the solutions that are used in these highly sophisticated machines to plate pure gold, hard gold, low Karat gold, silver, palladium, tin, tin-lead, nickel and cobalt.

PLATING SOLUTIONS FOR SELECTIVE PLATING APPLICATION

Introduction

Selective plating operations require highly specialized machines that are specifically engineered for each application. In general these machines are designed to perform all the required plating and finishing operations on the metal as it unwinds from a reel at one end of the machine and rewinds, all completed onto a reel at the other end. Selective plating is achieved by partial immersion in the plating bath, or through the use of an insulating mask of some type.

Masking is generally accomplished in these machines by using blocks of plastic, such as teflon, polypropylene, or equivalent; or some form of rubber or its equivalent. The mask is fabricated to guide the solution to the area that requires an electro-deposit while preventing any deposition from taking place on the masked area. If the mask and the equipment are properly designed, good definition can be achieved with the deposit confined only to the selected areas.

In order to maintain a high production rate, all of the various steps in the plating sequence must be as short as possible. One of the most important parameters in the electroplating operation for achieving high speeds is solution agitation. Agitation is achieved by pumping the solution as rapidly as feasible in order to have the maximum solution movement against the part being plated.

Three types of reel to reel plating machines are most often encountered for selective plating and they are engineered to produce controlled depth, stripe, and spot plating. In controlled depth plating, the deposit must take place near an edge of the strip which is partially immersed in the plating solution. In this application, agitation cannot be overly vigorous since a fine line of demarkation would then not be achieved at the interface above which no plating is desired. Current densities in controlled depth plating are in the range of 25-100 ASF.

In order to plate a thin stripe of deposit on a wider strip of metal in reel to reel equipment, the solution is generally pumped as vigorously as possible and is confined by the masking device only to the stripe area that requires plating. In this type of an operation, the current densities generally can vary from 100 to 500 ASF.

The highest plating speeds can be achieved in reel to reel equipment that is designed to deposit small spots of metal onto the strip being plated. In this case, the solution is pumped as vigorously as possible through an orifice to form a jet stream which impinges onto the metal being plated and is confined by the masks so as to produce only the small spot of plated metal that is required. In this application, the current densities can vary from 500 up to 2500 ASF.

Just as the machines are specially designed for each application, the plating solutions also must be tailor-made to operate as required in each particular type of machine to obtain a deposit that has the required metallurgical characteristics. The success or failure of any selective plating operation depends not only upon the equipment but also upon the ability of the plating solution to operate properly in that equipment to produce the desired results.

This presentation will deal mainly with the various plating solutions that are used in these highly sophisticated plating machines.

PLATING SOLUTIONS

A. Soft Pure Gold Deposits-Semiconductor Work

High purity, soft gold deposits are needed to perform the alloying, bonding and sealing operations used in semiconductor manufacturing. The deposits must be able to withstand temperatures of about 450-500° C for about 2-5 minutes without discoloration.

In the alloying operation, the gold deposit is in contact with silicon or germanium wafers or gold solders in a reducing atmosphere at elevated temperatures during which the gold deposit alloys with the silicon,germanium, or gold solder, thereby forming a reliable attachment with the basis metal.

In the bonding operation, a thin wire of either aluminum or gold is firmly attached to the gold deposit. Aluminum wire is bonded to the gold deposit with ultrasonic energy and gold wire is bonded with heat and pressure called "thermal compression bonding". Sealing is similar to alloying during which the gold deposit must alloy to itself or to gold solder. These are functional requirements of the gold deposit.

In most cases these gold deposits are plated on Kovar, nickel, or nickel plated copper lead frames using reel to reel spot plating equipment. The solutions and operating parameters used in the equipment are adjusted to achieve gold deposits that pass these functional requirements. Differences in bonding and die attaching equipment used by semiconductor manufacturers to perform the functional tests may also require some differences in the gold deposit characteristics but this cannot be definitely known until the functional tests are performed.

It has been our experience that the cosmetic appearance of the deposit has a significant effect on its metallurgical properties even though both the yellow, lustrous, dense deposit and a dull brown coarse deposit can satisfactorily pass the required heat test of 450-500°C for 2-5 minutes. The bonding characteristics of these two types of deposits are significantly different. Owing to the coarse finish of the dull, brown deposits, alloying or die attach generally takes place spontaneously and rapidly, not requiring pressure or "scrub" action.

The yellower, lustrous pure golds on the contrary do not generally alloy as rapidly and consequently, do not lend themselves to high speed automated die attaching techniques as readily as the so-called coarse brown deposits. Wire bonding characteristics of the two pure gold deposits are also quite different, whereby both yellow and brown gold deposits can form successful bonds with gold or aluminum wire although their resultant bond strengths can vary. Generally, the coarse brown deposits bond better using ultrasonic techniques and the yellow deposits form stronger thermal compression bonds.

The major advantage of the yellow deposits other than the cosmetic appearance is its uniform high density, which more closely approaches that of pure wrought gold. Consequently, deposit thickness measurements can easily be accomplished by utilizing time proven beta backscatter techniques. Using these techniques, better control of the deposit thickness, inventory and pricing can be accomplished. On the other hand, brown gold deposit thickness measurements are virtually impossible to achieve with reliability using beta ray backscatter or cross-sectioning techniques. The only method practical to determine deposit thickness is weigh-strip-weigh which is not a reliable method of thickness determination since the density of the brown deposits is less than theoretical and is variable. It is necessary that the engineer be aware of the type of deposit that is best for his die attaching and bonding equipment. He must also be aware of the solutions necessary to plate these deposits in his specific equipment. It has been our experience that no one single gold plating formulation can produce gold deposits that meet all the requirements. We have divided the solutions available into three categories depending on current density range:

a) Those that operate in the 1000-2000 asf range
b) The 300-1000 asf range, and
c) The 10-300 asf range

a) 1000-2000 ASF Range

In this range the available gold solutions have high gold metal concentrations. In most cases, the available baths produce coarse brown deposits and plating takes place at nearly 100% cathode efficiency. The higher the gold metal concentration the higher the permissible current density in any given machine to produce deposits that pass the functional tests. One micron can readily be achieved in one second in modern spot plating equipment.

When plating at these high speeds the plating bath is subject to rapid changes and must be formulated accordingly. Problems or potential problems are as follows:

1. Free cyanide build up. Since the gold complex used in these formulations is potassium gold cyanide, potassium cyanide is left in solution after gold is plated out. Free cyanide therefore tends to build up and unless the bath is properly formulated to handle this build up trouble will eventually develop.

2. High anode current density. The anodes used in these applications are platinum, platinum coated titanium or tantalum, and anode current densities are generally considerably higher than cathode current densities. Because of the insoluble anodes and unusually high anode current densities, strong oxidizing conditions are maintained in the solution which preclude or limit the use of any material that can easily be oxidized.

3. High operating temperature. These solutions generally operate at temperatures of 70-80°C in order to achieve the high speed characteristics needed to plate at these current densities. The solution ingredients must be stable and capable of high temperature operation without forming harmful breakdown products.

4. Metallic impurities. The most common metallic impurities encountered in the gold plating solutions used in reel to reel machines are iron, nickel and cobalt when the basis metal is kovar or other alloys of iron and nickel. When plating onto copper, the additional impurity of copper must also be taken into account. If these metals were codeposited with gold, then the deposit would lose its high purity and tend to fail the functional tests. In some types of rack plating formulations such as alkaline baths containing excess free cyanide, these metallic impurities would tend to codeposit more rapidly at high than at low current densities. Such a bath would not be desirable since even small quantities of metal contaminants would have a deleterious effect. A far better plating bath would be one whose solution chemistry can result in the opposite effect where large amounts of metallic impurities would tend to codeposit with gold only at low current densities and would not codeposit at the high current densities of about 900 asf or over. This can be accomplished through proper choice of solution chemistry and operating parameters.

b) 300-1000 ASF Range

In addition to the previously mentioned problems of cyanide buildup, high anode current density, etc., formulations operated in the 300-1000 asf current density range must be modified somewhat to take into account metallic contamination which must be prevented from codepositing with the gold. This can be accomplished in two ways: (1) Formulate solutions that are far less aggressive to the basis metal being plated. The buildup of metallic impurities from this source is therefore substantially reduced or eliminated. These solutions operate at reduced gold concentrations such as 6-10 grams per liter, and do not contain chelating agents. This type of solution plates deposits that are the yellow, lustrous and dense category. Significant advantages of these baths are the relatively low gold metal concentration and ability to accurately measure the deposit thickness using the standard methods. Disadvantages are higher voltage requirements, lower cathode efficiencies and limited bath life span. (2) Add chelating agents that are capable of chelating the contaminants in the existing solution formulation.

The chelating agent must be stable under conditions of electrolysis and chelation should be of sufficient magnitude in the plating bath to substantially decrease codeposition of contaminants. These baths generally operate at higher gold concentrations of 16-24 grams per liter, higher temperature and higher cathode efficiencies than the chelate free systems. Deposits are the coarse brown type.

c) 10-300 ASF Range

Pure gold deposits designed to operate at these current densities are generally installed in controlled depth plating equipment that does not have the extremes of solution agitation existing in jet plating machines. These formulations are similar to those used in rack plating. Their plating speed is increased by raising operating temperatures somewhat, raising gold concentrations or by adding addition agents that improve cathode efficiency and high current density range. The choice of gold plating bath is broader for this current density range since the extremes of anode current density and temperature are not necessarily present.

HARD GOLD DEPOSITS

Cobalt or Nickel Hardened Golds

When good wearability is required on parts such as electrical contacts and connectors, hard golds have been specified. The hardnesses vary from approximately 150-200 Knoop and for many years these gold plating deposits have been alloyed with about 0.1-0.2% cobalt or nickel. For the most part, these deposits are hardened with cobalt, and plating baths for depositing these alloys have been steadily improved over the years to plate at higher speeds and with higher cathode efficiences than those heretofore achieved. The high plating speeds required in reel to reel selective plating equipment, can be obtained with the following variations of a well designed rack plating formula.

a. Raise the gold content to about 2 tr.oz./gal. or higher.

b. Raise the cobalt (or nickel) content of the solutions sufficiently to yield the same 0.1-0.2% cobalt (or nickel) in the deposit to offset the increased gold content.

c. Use chelating agents or combinations of these for cobalt (or nickel) which are stable even with high anode current densities.

d. Raise operating temperature

e. Agitate rapidly using jet streams with vigorous pumping.

The final adjustment of the solution and plating parameters must be made in the actual production equipment to compensate for the degree of agitation achieved in the equipment. Metallic impurities in these baths are not as detrimental as they are in pure gold plating; however, the deposit must be monitored and the maximum impurity level permitted in most cases is 0.1% (cobalt or nickel added as hardening agents are not considered to be impurities).

Many successful reel to reel plating installations are in existence and it is possible to plate cobalt hardened gold at extremely high speeds (up to 600 asf) and still obtain deposits which will pass all of the hardness, porosity and purity tests that are specified for these deposits.

Some inherent problems do exist in these hard gold plating baths, particularly those that produce cobalt hardened deposits. These problems become most evident in plating baths that are worked very hard and where the average total current per unit volume is about 1 Ampere/gallon or higher. Since gold metal is added to the solution in the form of potassium gold cyanide, the cyanide ion is left behind after gold is plated out of this complex. What happens to this cyanide ion? Some of it is oxidized at the anode, a greater portion combines with the hydrogen ion of the acid bath and is liberated in the form of HCN which must be picked up by the exhaust system over the bath, and some of it combines with the cobalt in the plating bath to produce a divalent cobalt cyanide complex. This divalent cobalt cyanide complex is very readily oxidized at the anode to produce the trivalent cobalt cyanide complex which effectively removes cobalt from its active state leaving cobalt that no longer codeposits with gold to produce the bright hard deposits that is required. The total effect in these baths that are worked very hard is that the rate of cyanide that is liberated is so high, that it cannot leave the bath fast enough in the form of HCN and therefore builds up in the bath and combines with cobalt. The divalent cobalt complex or chelate that is originally in the bath is changed by free cyanide which effectively depletes the gold plating bath of the desired amount of the alloying element in its most active state. The equations can be summarized as follows:

$$Au(CN)_2^- + e \quad -- \quad Au^o + 2CN^-$$

$$CN^- + H^+ \quad -- \quad HCN$$

$$Co^{++} + 5\,(CN) -- \quad Co^{II}(CN)_5^{3-}$$

$$Co^{II}(CN)_5^{3-} + CN^- - e \; -- \quad Co^{III}(CN)_6^{3-}$$

Some of these equations are reversible. In particular, the divalent cobalt cyanide complex can revert to the divalent cobalt chelate which was originally added to the plating solution and

this can take place when the bath is idle as cyanide is liberated in the form of HCN. During these idle periods, there is no potassium gold cyanide added and the cyanide impurity does not build up. In these rapidly worked plating baths, the amount of active cobalt available for producing bright and hard deposits varies throughout the day, and from day to day, which accounts for the variable hardness that is often achieved. Plating installations that have high solution volumes with low total current, such as 0.1 - 0.25 Amperes/gallon, do not suffer significantly from these effects since the cyanide is liberated at a fairly slow rate in relation to the solution volume and it therefore has a much better chance of escaping from the bath before reacting with cobalt. In some types of these cobalt gold baths where the chelating agents are not too strong, a further complication can take place. The cobalt may precipitate in a complex form combined with cyanide and gold and form an insoluble material which has the physical appearance of "Pepto Bismol".

Cyanide can be made to escape faster from these baths through the use of higher temperatures, higher agitation, and lower pH. Together with the use of a low total amperage per gallon, and the use of more effective complexing or chelating agents, these are the methods commonly used to help stabilize existing gold-cobalt plating baths.

Some of these acid, cobalt hardened gold plating baths are based upon carboxylate chelates; whereas others are based on phosphonate chelates. The differences in these plating baths can be of great significance when plating hard gold directly onto copper or high copper alloys.

If there is any possibility for the copper basis metal being plated to become anodic in the presence of the gold plating bath due to bi-polarity, copper would tend to dissolve and build up in the plating bath as an impurity which will codeposit thereby causing the deposit to exceed impurity limit specifications. It was found that there is a large difference in the rate of anodic attack of copper basis metals when exposed to hard gold plating baths. This rate of attack is dependent upon the type of chelating agents that are present.

A plating test was performed in the laboratory to determine this difference. Two plating cells were charged with cobalt-gold plating baths, one based upon carboxylic acids and the second on phosphonic acids. In each case, the anode was copper and the cathode was steel. After electrolysis, both solutions and deposits were analyzed for copper. Tests were run at varying anode current densities. Results indicate that carboxylic acid baths have an attack rate on copper that is twice that of the phosphonic acid bath at current densities of 0.5-5 asf. At current densities of 10-100 asf, the attack rate increases to 4-5 times that of the phosphonic acid bath. Not only is the rate of attack significantly less, the corresponding codeposition rate of copper is also less. For the same copper impurity concentration in the plating bath at a given current density, the codeposition rate of copper is 3-4 times lower with the phosphonic system. Consequently not only is the rate of buildup lower, but the tolerance to copper is also significantly greater when phosphonic based baths are incorporated.

Cadmium Hardened Gold

At the recent Electronics Symposium held this past January, a new cadmium hardened gold was introduced. The plating process for producing these new deposits can also be installed in high speed reel to reel plating equipment. The most serious drawback of cobalt or nickel hardened gold deposits is the gradual increase in contact resistance which occurs when these deposits are exposed to elevated temperatures for extended periods. In electronic equipment which operates at high temperatues, this problem can become very serious and eventually cause a contact failure. When plating gold directly onto copper or copper alloys, the increase in contact resistance referred to is particularly rapid. Comparative tests were made showing the effects of heat and time on copper contacts plated with cobalt gold compared with cadmium gold. A study of the graphs clearly shows the superiority of the cadmium golds with respect to this property. (See figs. 1 - 4).

Unlike the cobalt hardened golds, the cadmium gold solution is not affected by cyanide and the solution will remain stable even under the adverse conditions of high total current per unit volume of solution. The porosity characteristics of the cadmium gold are superior to that of the cobalt hardened gold and the wearability of cadmium gold is equivalent to the cobalt-gold or slightly better.

Pure 24 Karat Hard Golds

The conventional cobalt and nickel hardened golds used in the connector and contacts industries are too brittle to permit forming operations after plating. Many plating specifications specifically prohibit any forming or bending of these deposits. The brittleness is particularly evident in thicker deposits and over 100 microinches, spontaneous stress cracking and even exfoliation can take place. For this reason, as well as economy, gold thicknesses are generally limited to 60 microinches or less when plating hard gold.

Pure 24 Karat hard gold deposits can also be achieved from specially formulated baths. With these deposits, it is possible to obtain high hardness coupled with good dectility and the deposits can readily be formed or otherwise flexed after plating. Plating solutions for producing these pure 24 karat hard golds are also adaptable to high speed reel to reel selective plating machines. They generally operate at about 2 Troy ounces per gallon from essentially neutral baths, and plating speeds can be as high as 500 asf with cathode efficiencies close to 100%. The deposit lends itself very well toward manufacturing contacts that require thick deposits by plating a stripe of pure hard gold onto a strip of metal, after which the strip is cut and formed into contacts with only the gold plating area as the contact surface. The hardness obtained from these deposits is 150-200 Knoop (25 gm load) and when

lubrication has been applied, it has wearability equivalent to cobalt golds. These deposits are generally mated with other parts that are plated with cobalt hardened gold since there would be a tendency to gall if the unlubricated deposit were mated against itself.

18 Karat Gold

18 Karat gold-copper-cadmium alloys have been in use for contact applications and offer a saving in gold because of lower karat and density. This deposit has also been plated from high speed reel to reel jet plating equipment and has had good commercial acceptance. Since the high current density and high solution agitation used in jet plating would tend to affect the alloy composition, changes in the solution composition normally used for rack plating are needed to plate the proper alloy. This is accomplished by adjusting the solution parameters in the actual plating machine and analyzing the deposit after each change in order to arrive at the final parameters that are required. As an example of what can be achieved in production, one micron or 40 microinches has been deposited in 4 seconds while plating at 650 asf.

High Speed Silver

Conventional silver plating solutions used for rack plating generally contain relatively low silver metal, high free cyanide, addition agents for both high and low current density plating, and a wetting agent. These solutions can also be adapted to high speed reel to reel plating equipment by raising the silver content to double or triple the initial value as needed, reducing the free cyanide somewhat to about the same concentration as silver, and eliminating the wetting agent. With baths of this type, it is possible to achieve as high as 500 asf at 100% cathode efficiency.

Silver plating solutions that are capable of achieving current densities of up to 3,000 asf to deposit 150 microinches per second have been specifically designed to operate in modern jet plating equipment. These solutions operate at about 150°F, zero free cyanide and contain about 8 Troy ounces of silver per gallon. The deposits are lustrous, of high purity, and are suitable for semiconductor work as a replacement for gold in some operations.

Using the conventional high free cyanide silver plating solution, a silver strike is required for most basis metals. With the newer high speed zero free cyanide formulations, it is possible to silver plate directly onto copper without using any strike at all. When plating onto kovar or other high nickel alloys, a strike is required for maximum adhesion and for this purpose, a gold strike is often used. A specially formulated silver strike can also be used to achieve equivalent adhesion, and in reel to reel machine, the work proceeds directly from the strike into the plate without intermediate rinsing.

When plating silver selectively onto a copper basis metal, it is very difficult to prevent immersion silver deposits from taking place under the mask where the solution wets the surface or when the strip is dragged through the solution with current shut off. For such an application, a special silver plating solution has been developed which will not immersion plate onto copper. This solution is particularly useful in jet plating operations that plate spot silver onto copper where no silver is permitted anywhere on the surface other than the spot that requires the deposit.

Unlike conventionsl silver solutions in conventional equipment, the silver solutions used in high speed jet plating applications generally operate with insoluble platinum or platinum plated anodes and silver is then replenished by adding a potassium silver cyanide salt as needed. Addition agents are provided that assist in achieving the high speeds and luster that are required.

Tin

Bright tin plating formulations that are successfully used for rack and barrel plating in the electronics industry are based on stannous sulfate, sulfuric acid, and addition agents to achieve brightness and throwing power. The same bright deposits can also be achieved in high speed selective plating machines, but these solutions are mostly based upon stannous fluoborate and fluoboric acid in order to achieve increased current densities. It is also important to incorporate an anti-foaming agent in the bath since the addition agents used to brighten the deposit have high foaming characteristics which would otherwise produce excess foam and interfere with the operation. Current densities can go as high as 80-250 asf in one of these machines depending upon the degree of solution agitation. In most cases, the anodes are pure tin. Polarization of the anodes due to high anode current densities is prevented by maintaining good solution agitation at the anodes and as high a surface area as possible.

Tin Lead

Bright tin lead depositshave been achieved in rack and barrel plating for some years and, like tin plating, these solutions are also adaptable to high speed selective plating machines. Also as with tin, these solutions are based upon fluoborates and they contain high foaming brightening agents as well as an anti-foam. The applications, as with tin, are generally limited to controlled depth and stripe on strip plating, and the current densities that are generally achieved are 250-500 asf depending on agitation rate.

Nickel and Cobalt

Nickel and cobalt plating are both being achieved in reel to reel high speed plating machines. The solutions are generally

based upon sulfamates although fluoborates have also been successful. Deposits from the sulfamate baths are said to have lower internal stress than those from the fluoborate baths, but the fluoborate baths are higher in speed for equal metal concentration. In most applications, the nickel or cobalt is used as a diffusion barrier between gold or silver and copper basis metal. For these applications, no addition agents are permitted that codeposit sulfur with nickel. The plating baths that are used are conventional high speed formulas, but the metal and temperature of operation is increased to achieve the desired current density range.

In modern spot plating machines, a current density range of 2,000-2,500 asf can be achieved from a cobalt sulfamate bath whose cobalt concentration is 250-300 g/l. With nickel, 1,000-1,500 asf can be obtained from a nickel sulfamate bath whose nickel content is 135-150 g/l. Anodes in these machines are usually platinum or platinum plated titanium or tantalum and the metal is replenished from the corresponding sulfamate or fluoborate concentrate. When operating these nickel or cobalt baths with insoluble anodes, the pH control is generally more difficult since the baths which normally operate at a pH of 4-4.5 tend to decrease in pH rapidly due to the discharge of OH ions at the insoluble anode surface which results in liberation of oxygen. Nickel or cobalt carbonates or hydroxides can be added periodically to increase the pH or a slurry can be used of these basic carbonates to form a filter cake through which the solution is circulated until the pH is raised to the required value.

Machines that plate a larger area than a small spot have far less agitation on the cathode surface and 100-400 asf is generally achieved in a high concentration nickel bath that uses soluble nickel anodes.

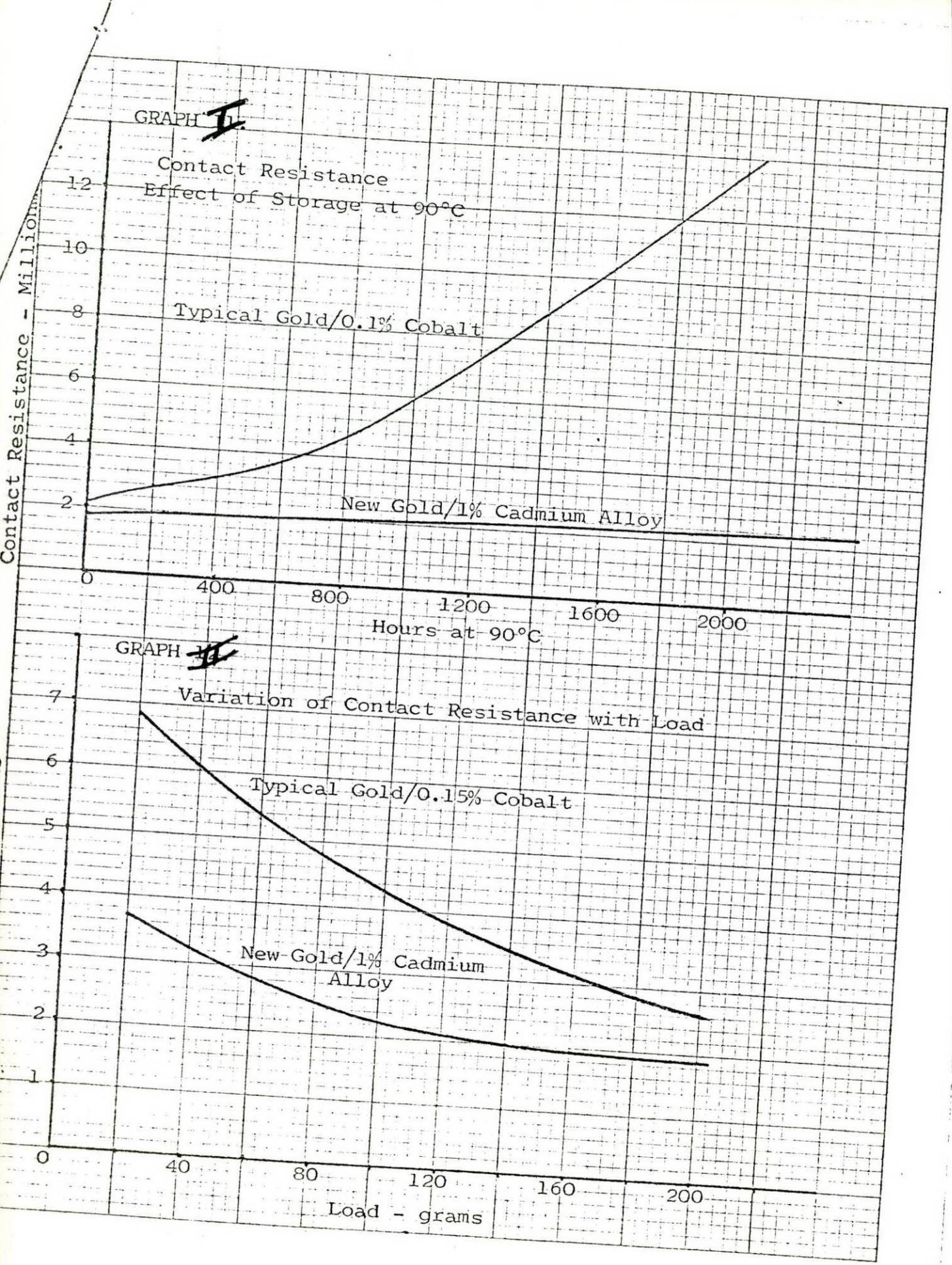
Palladium

Palladium plating baths that deposit relatively ductile, porosity free, reasonably bright deposits are in use today to plate electrical contacts using conventional barrel and rack plating equipment. Solutions of this type are mainly proprietary and contain about 8-10 g/l of palladium metal.

The solution can readily adapted to plating in modern spot plating machines by raising the metal content to about 20-25 g/l. With the proper jet stream, it is possible to deposit 100 microinches of palladium in 45 seconds at 250 asf to achieve sound, lustrous deposits. The anodes are platinum or platinum plated titanium or tantalum.

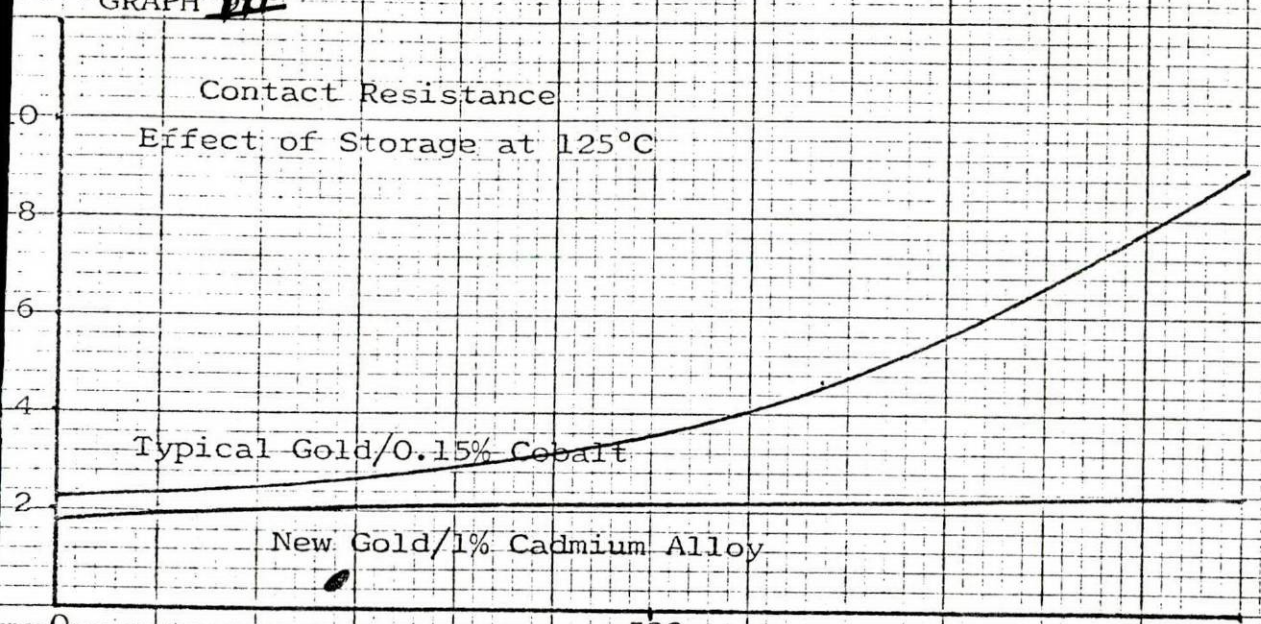
Conclusion

The metals discussed above are those that have achieved the most commercial acceptance in high speed selective plating equipment. Since manufacturers are always interested in production rates and metal savings, the future will see solutions and plating machines capable of even higher plating rates with even greater selectivity than those discussed above.


GRAPH I.
Contact Resistance
Effect of Storage at 90°C
Typical Gold/0.1% Cobalt
New Gold/1% Cadmium Alloy
Contact Resistance - Millionths
12
10
8
6
4
2
0
400
800
1200
1600
2000
Hours at 90°C
GRAPH II
Variation of Contact Resistance with Load
Typical Gold/0.15% Cobalt
New Gold/1% Cadmium Alloy
7
6
5
4
3
2
1
0
40
80
120
160
200
Load - grams

GRAPH III

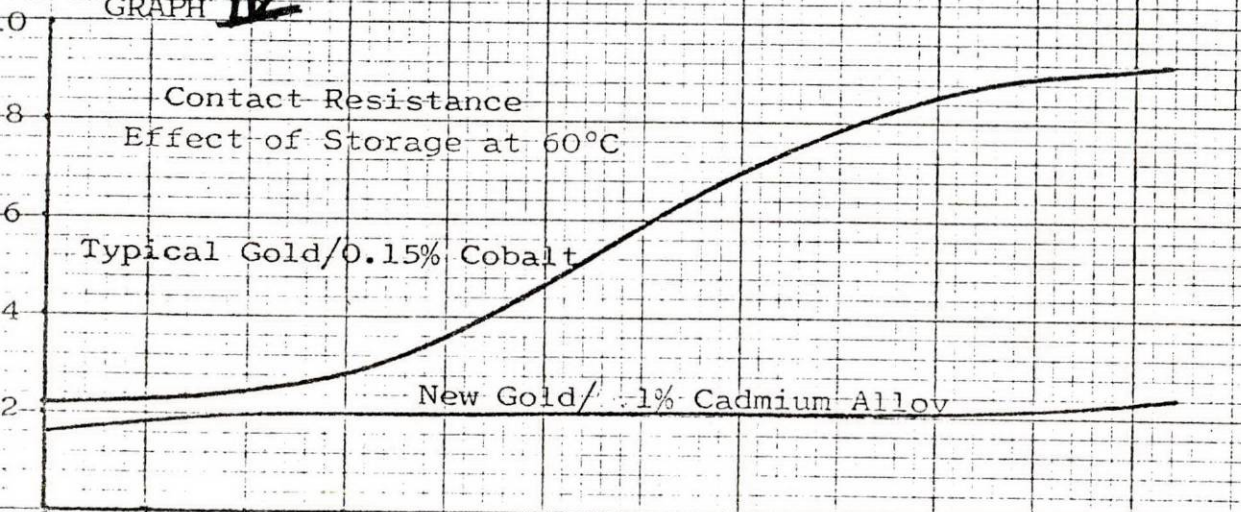
Contact Resistance
Effect of Storage at 125°C



Hours at 125°C

GRAPH IV

Contact Resistance
Effect of Storage at 60°C



Hours at 60°C

D-2

Electronics I
Session D

Contamination of Gold Plating Solutions

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CONTAMINATION OF GOLD PLATING BATHS

Bev Sewell
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Introduction

Contamination is a word all too frequently heard in plating shops through-out the world. The word is used, not unjustifiably, whenever trouble is encountered with a bath that cannot be explained by any other factor. The word "contaminant" as applied to plating baths, may be defined as a chemical, elemental or compound, present in the bath but not by design or as specified in the original formulation. Most contaminants are detrimental to the correct functioning of the bath and are therefore termed disadvantageous. In those few cases where a contaminant is found to have a beneficial effect, bath formulations are modified to include the advantageous contaminant and thus the word contaminant is commonly interpreted as detrimental. Contaminants exist in most plating baths, however, since it can be shown that the composition of specific baths is in a continuous state of change throughout the working life of the bath or until a steady state is reached when drag-out equalises the rate of introduction or formation of contaminant. It can be argued, therefore, that not all contaminants are detrimental since many baths have a long working life. This is true in many instances but largely, the life of the bath reflects the demands made of the plated deposit by the end user and some applications are much more demanding than others.

The variation in properties of deposit obtained from a bath with increasing use can only be explained by change in composition of the bath, that is, by accumulation of contaminants. This statement assumes that all physical variables are under control and that the concentration of the original bath constituents is maintained. All too frequently, physical parameters must be changed in order to maintain the desired deposit characteristics. In most instances, the first suspicion of contamination comes from the end user of the plated deposit which fails to meet functional requirements. The pattern of investigation then emerges, physical examination of deposit, followed by a search of the batch records for abnormalities in bath operation, analysis and maintenance. Deposits are then analysed, followed by detailed analysis of the bath which will reveal a list of likely contaminants.

At the same time, the operator will be listing all materials which may possibly be introduced into the bath during operation and an electrochemist may be asked to predict the likely biproducts of electrolysis.

Provided the investigation is sufficiently exhaustive, the offending contaminant will be revealed and remedial measures taken to eliminate the contaminant in the bath and also the source. Often, the suitability of the particular electrolyte will be questioned.

Sources

It is helpful to list the possible sources of contamination and the selection below can apply not just to gold baths.

1. From preceding pretreatment or undercoat baths. Chemicals are introduced in this way because of inadequate rinsing of component shape or improperly applied masks.

2. Accidental, through operator error, mistakes in additions, spillages, etc. Accidents of this type are often deliberately concealed.

3. Incompatibility of materials of construction of plating equipment with the electrolyte. The increasing sophistication of equipment used in high speed and selective gold plating demands the use of many new materials which should be checked before use by practical plating tests on a sample of the electrolyte after prolonged soaking of the material.

4. From soils introduced on components to be plated due to inadequate cleaning.

5. Dirt, dust and foreign objects falling into baths with no cover.

6. By chemical or electrochemical decomposition of bath constituents, due to operation outside the recommended physical parameters. Temperature and current density are often deliberately increased in high speed plating and the new high speed techniques can cause a high degree of oxygenation of electrolytes. For example, these factors combine to considerably reduce the level of free KCN normally found in low consideration in some gold baths, increase carbonate, oxidise organics, and also influence the valency state of metals present in acid gold baths.

7. Direct dissolution of the substrate or undercoat metal, commonly because components fall into the bath from damaged or inadequate racks or barrels. Also increasingly found in selective plating applications because of inadequately designed or applied masks or in partial immersion plating.

The author does not intend that this paper should make an exhaustive review of all contaminants but would like to draw attention to some commonly encountered contamination phenomena, which can have wide reaching implications.

Acid Gold Baths

Acid gold baths are generally formulated to include one metal in addition to gold, the function of which is to impart hardness to the gold deposit. Metals commonly used in this application are cobalt, nickel and latterly, iron and complexants of various stability constants can also

be added. In the absence of contaminants, the operating parameters of such baths can be clearly defined. Should a bath be contaminated with a second "hardening" metal, however, it will be found necessary to change operating parameters to achieve the desired deposit properties. In general, it can be said that such contamination results in an enhanced brightening effect and the symptoms are reduced ductility and increased tensile stress. The cathode efficiency of the electrolyte is also reduced. A significant increase in the organic content of the gold deposit also results from such contamination. A cobalt hardened acid gold bath used to plate reeds became contaminated with iron (60 p.p.m) and nickel (minor). The plated reeds from this bath showed high contact resistance and open circuit failures on life test. Experimental evidence suggested that such failures were coincident with abnormally high organic (polymer) content of the gold deposits as analysed by gas chromatograph on suitably prepared samples.

It was also shown that samples of the same bath produced significantly higher polymer content in deposits when artificially contaminated by nickel and by cobalt in a different complex.

In the field of sliding contacts, it has been shown that polymer content of gold deposits enhances wear resistance. In certain applications, however, in which contacts flex during mating operations, brittle fracture within the gold layer can occur. Such failures have been encounted in deposits plated at high current density in a cobalt acid gold bath contaminated by nickel. A feature of these deposits was a high polymer content.

Temporary relief can be obtained from contamination of this type by progressively altering bath variables, for example, by increasing temperature or pH or by reducing the proprietory brightener concentration in specific instances. In demanding applications, however, an upper limit for contaminant must be set and appropriate action taken when the limit is reached.

One of the most pressing requirements for research in the gold plating sector is the dependance of wear resistance and ductility on polymer content and the effect of plating variables, bath constituents and contaminants on polymer content across the range of acid gold formulations.

Pure Gold Baths

Gold baths used for plating semiconductor hardware are traditionally termed 'pure' and yet limits of impurities are rarely set by the end user. Most baths in commercial use to-day contain a variety of base metal contaminants in frightening concentrations. Substrate and undercoat metallic elements predominate and give rise to a number of problems at the assembly stages particularly in die and wire bonding.

The high degree of metallic contamination is largely due to the selective plating techniques applied to economise in the amount of gold used. Many types of high speed selective plating equipment allow rapid contamination of gold electrolytes because unplated areas of components are allowed to come into contact with the electrolyte in low potential areas and during inter-cycle idle periods. Substrate and undercoat metals dissolve in the plating batch by simple electrochemical displacement reaction and this reaction is dramatically speeded up by the very high solution velocity used for agitation to increase plating speed. In reel to reel plating machines, the strands of bandoliered components may pass from process to process too quickly for adequate rinsing often because the machine is operating at a speed much higher than for which it was originally designed.

Remedial Measures

A number of plating baths have been formulated recently either as contamination resistant or contamination tolerant and have gained ready acceptance. The contamination resistant variety, however, tend to produce unsatisfactory deposits at lower contaminant concentration and the tolerant variety tend to pick up contaminants more rapidly, so the beneficial effects are partly nulified. The use of these types of baths together with modified power source such as pulsed current, asymetric A.C. or superimposed A.C. will enable the plater to obtain extended bath life, but if no attempt is made to significantly reduce contaminant input, then this costly sophistication is being misused.

In high speed spot plating, equipment must be designed to eliminate wash of unplated areas by the fast flowing electrolyte, particularly during "current off" periods. In equipment where this is not possible and for partial immersion equipment, it is very worthwhile considering incorporation of an over all gold strike flash stage before the selective gold plating operation. Use of pulsed current in the flash operation will allow a very thin coating to be applied with better coverage and hence reduced porosity than conventionally applied thin coatings. Costs of this flash coating can be almost negligible if the coating is then stripped off again after the heavy selective deposit has been applied. This procedure is certainly possible for semiconductor applications. The stripping solution may be a hot, highly agitated 2% solution of KCN, which has no adverse effect on the performance of the preserved gold deposit.

The use of over-all flash considerably extends the life of the main gold bath by reducing build up of contaminants from the component base metals. Gold from flash and stripping baths can be recovered cheaply as described later.

A number of methods exist for removing contaminants from baths, but in the author's experience, none of these methods is suitable for in-process purification, and electrolytes must be removed from the equipment for inconveniently long periods for rectification.

Selective ion exchange is tedious, requires solution modification and considerable apparatus and analysis facilities. Complexant additions can lead to a whole new series of problems. Selective electrolysis is time consuming, requires bath modification and is not wholly effective.

The problem of contamination would be far less serious if gold baths were expendable, provided that the bath life was clearly defined with respect to contaminant limits. In general, it can be said that the only expensive constituent of a gold bath is the precious metal, the other chemicals being relatively inexpensive. If the gold metal from discarded contaminated gold baths can be quickly and inexpensively recovered in a form suitable for immediate re-use in preparing a new bath, then the possibility of scheduled replacement of baths becomes viable. More-over, the regular replacement of a part of the production bath with new clean electrolyte becomes more attractive, thereby achieving a steady state with respect to electrolyte composition and contaminant concentration within the previously ascertained safety limits. A method which offers these advantages to large users of gold is described below.

The gold metal is plated out from the discarded electrolyte onto a stainless steel mesh cathode formed into a cylinder. The apparatus for this first stage recovery is shown in Fig. 1. The discarded electrolyte may advantageously be modified by raising pH sufficiently to support an addition of KCN.

Elevated temperature and vigorous agitation will also assist in a fast metal recovery. Agitation is particularly important in achieving a high recovery rate for relatively pure gold and up to 99% yield is possible in a first stage electrolysis. When the recovery is complete, as adjudged by analysis and also appearance of the recovered gold on the mesh, (may be dark brown but not black) the cylinder is removed, washed and dried, and transferred to the conversion cell. The electrolyte remaining in the recovery apparatus will be treated according to analysis. If it contains less than 1% of the original concentration, say 100 mg/litre it may be considered sufficient to complete the recovery by ion exchange, otherwise a second stage electrolytic reclaim may be used to recover a much more impure gold which will require a double stage purification and conversion.

The conversion cell, which forms the second stage is shown schematically in Fig. 2. The anolyte is KCN solution which should be maintained above 100 g/l free KCN at all times. The catolyte is KOH solution and cathodes are stainless steel mesh. The membrane used in practise is a porous pot similar to that of the Leclanché Cell and a number of pots are used in order to achieve as high as possible membrane area.

The current passed will depend upon the membrane area and the anode over-voltage and the speed of conversion may be increased by elevating the temperature to 50°C and introducing mechanical agitation.

Gold dissolves at the anode and when the anolyte is saturated, crystals of K Au $(CN)_2$ appear. The cell is operated during the day and allowed to cool over-night after which the crystals are removed by withdrawing the tray. The gold potassium cyanide is washed with water at 1°C and oven dried.

The near saturated anolyte solution may be used repeatedly until the impurity level as determined by analysis of product is deemed too high. Many kilograms of gold may be processed through 1 litre of electrolyte before it becomes necessary to provide a fresh anolyte. The old anolyte is then used in an impure gold conversion cell until it becomes grossly contaminated, at which stage it can then be recovered by re-commencing the whole procedure as for a discarded bath.

The process is best operated in a laboratory and with careful supervision and technique will give yields better than 99.9%. It is necessarily an ongoing process but it will be found that gold from a discarded production bath can be converted to gold potassium cyanide for make up of a new bath within 72 hours. Process costs are also favourable when compared with conventional bullion recovery techniques.

Fig. 3 shows the sequences of the recovery system, as operated in conjunction with a partial bath replacement scheme. This latter scheme allows for operation of a gold bath within controlled limits of contaminant concentration such that specific deposit properties can be guaranteed. The fraction of the production bath replaced will be determined by analysis of contaminant concentration but with high volume production on automatic equipment it will be found possible to calculate the fraction and frequency of replacement.

Conclusion

Because of the inherent difficulties in removal of contaminants from plating baths, and the problems associated with eliminated re-curring sources of contamination, it is preferable to adopt a policy of contaminant control. A scheduled scheme of regular partial bath replacement will not only control the level of contaminants from external sources but also any harmful biproducts of electrolysis. The economical reclaim of gold is, however, of paramount importance in any such scheme.

FIG. 1

GOLD RECOVERY CELL

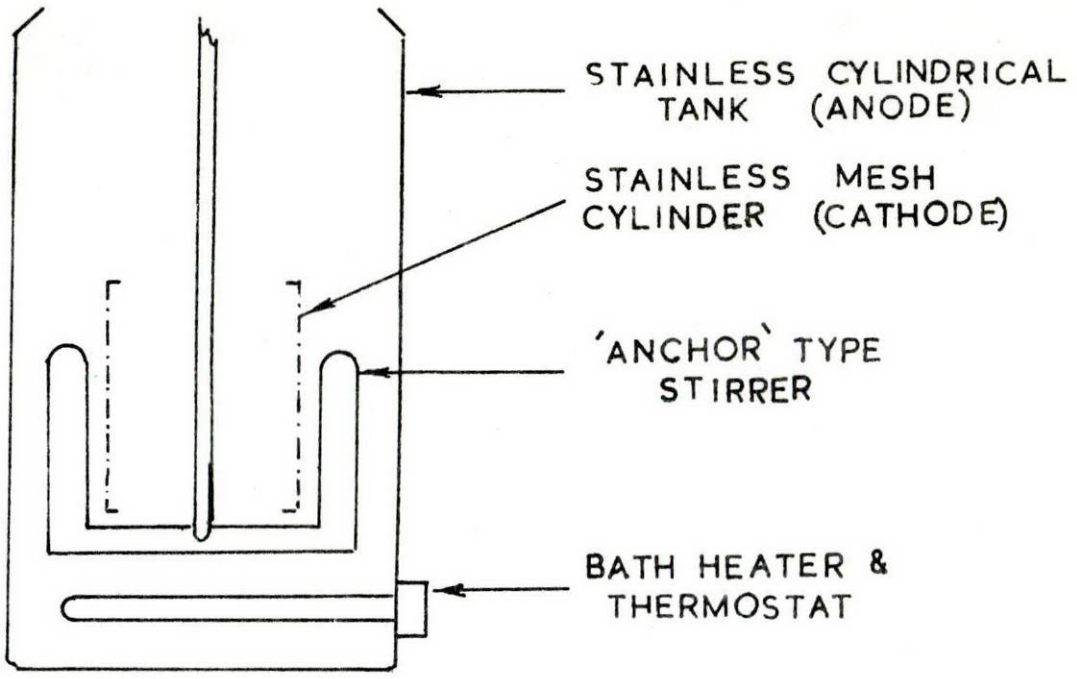


FIG. 2

CONVERSION APPARATUS

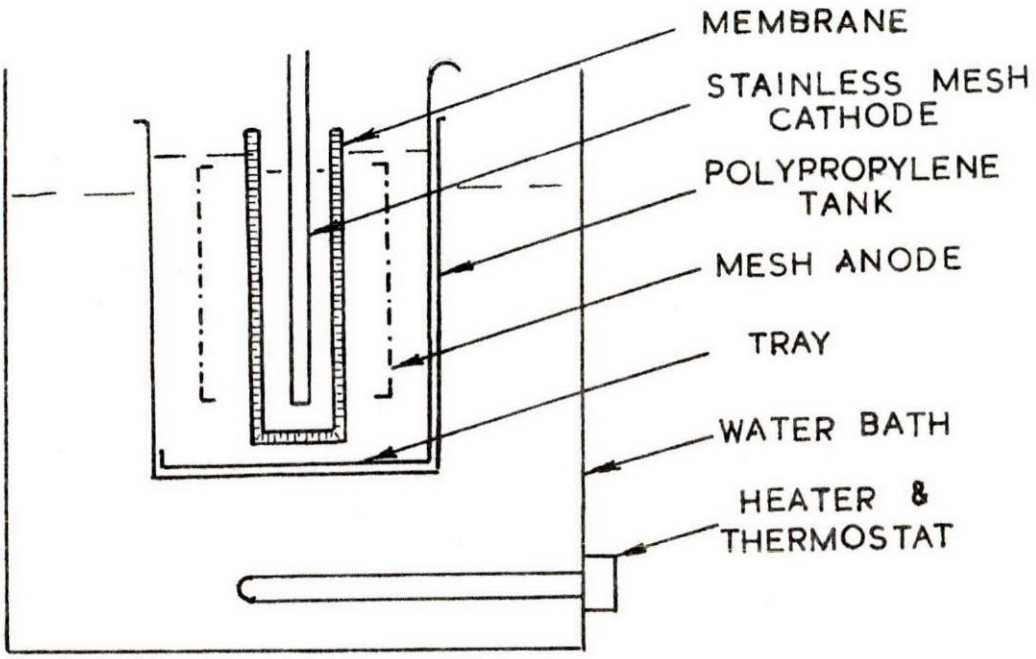
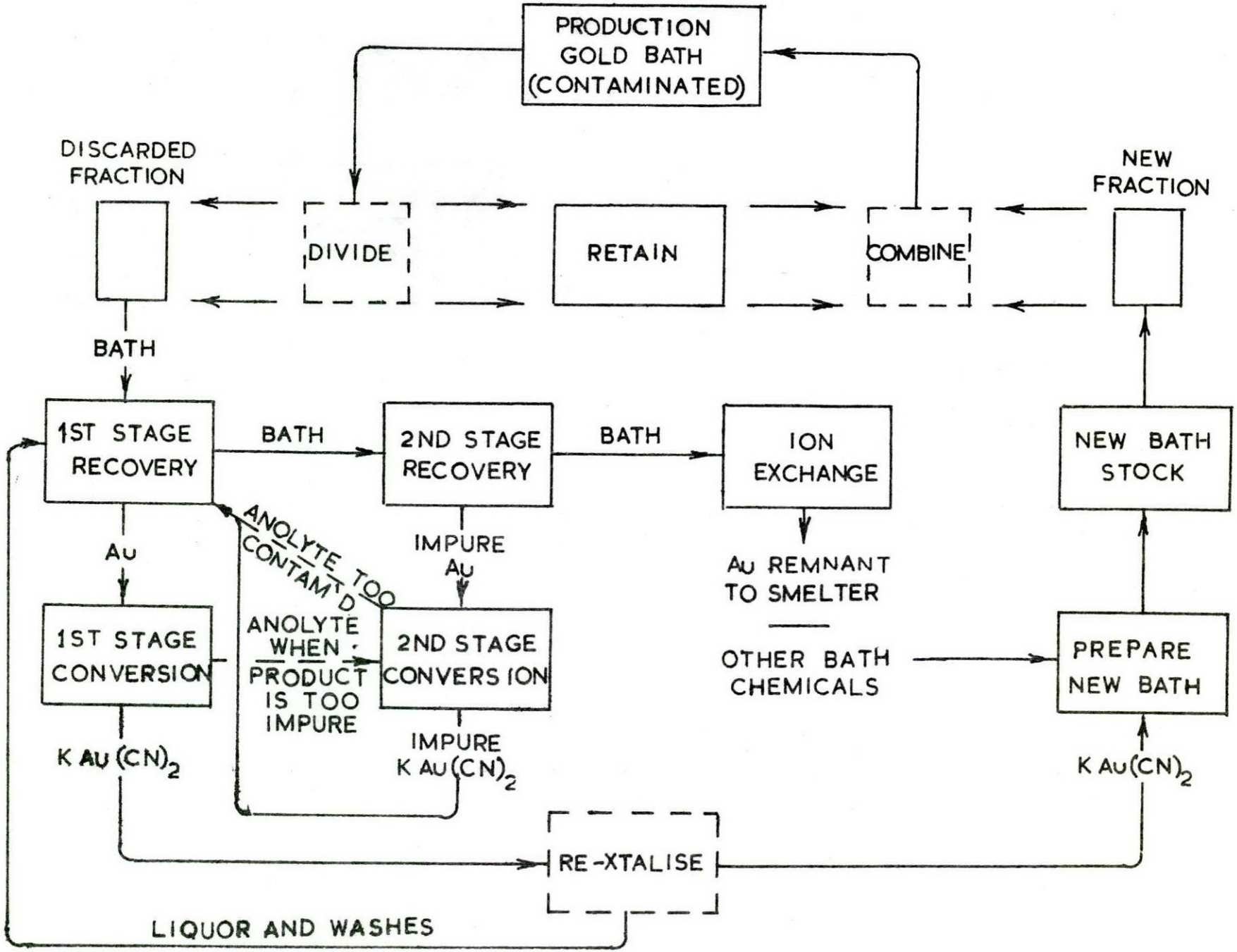


FIG. 3


PRODUCTION GOLD BATH (CONTAMINATED)
DISCARDED FRACTION
DIVIDE
RETAIN
COMBINE
NEW FRACTION
BATH
1ST STAGE RECOVERY
BATH
2ND STAGE RECOVERY
BATH
ION EXCHANGE
NEW BATH STOCK
AU
ANOLYTE TOO CONTAM'D
IMPURE AU
AU REMNANT TO SMELTER
1ST STAGE CONVERSION
ANOLYTE WHEN PRODUCT IS TOO IMPURE
2ND STAGE CONVERSION
OTHER BATH CHEMICALS
PREPARE NEW BATH
K AU (CN)2
IMPURE K AU(CN)2
K AU(CN)2
RE-XTALISE
LIQUOR AND WASHES

D-3

Electronics I
Session D

High Speed Gold Plating From Dilute Electrolyte Part I

D. W. Endicott and G. J. Casey Jr., CEF
Motorola, Inc.
Phoenix, Arizona

HIGH SPEED GOLD PLATING FROM DILUTE ELECTROLYTES

Part I - "Solution Development and Functional Testing"

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Electronic Materials Group
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ABSTRACT

A gold process utilizing 9.0 gm/l of gold, capable of operating at 80 amps/sq. decimeter in high speed plating cells has been developed. Reel to Reel selective plating equipment operating at 1830 cm/min. is utilized at Motorola Inc. to produce 1 micron thicknesses over nickel electroplate on copper lead frames. Subsequent thermal compression die and wire bonding is performed on the lead frames.

SEM microphotographs and Auger analysis of gold surfaces have been correlated with bond failures. Nickel diffusion to the gold surface was found to be the major cause of wire bond failure.

Introduction

Commercial high speed selective gold plating has been utilized extensively in the semiconductor industry since about 1970. In the intervening years equipment and plating formulations have improved to the level that some platers are operating at 200 amperes per square decimeter (A/dm^2) and are able to deposit a micron of gold in less than one second. Strip speeds of 1200 cm/min have been attained.

In order to accomplish these speeds and current densities, typical gold formulations have been utilized which contain 25 - 50 gms/liter of gold metal and specific gravities of 15 - 30° Be. Disadvantages of these formulations include high inventory values and drag out losses of up to 50% of the gold metal, thus increasing plating costs. This project was initiated at Motorola Inc. to develop a high speed gold plating system which would overcome these disadvantages.

To reduce the cost of gold plating the lead frame for the Motorola small signal transistor device commonly called a TO-92, a high speed, selective plating system which deposits gold only in functional areas of the lead frame has been developed. The deposit had to be satisfactory for fast die attach and thermal compression wire bond assembly techniques. An example of the lead frame and assembled device is shown in Figure 1a and Figure 1b.

Past experience with rack plated lead frames has established that for bonding purposes, one micron of gold is necessary and 0.125 microns is necessary on the external package leads for solderability. Any gold plated on the top and bottom carrier rails or the back of the die bond pad is not functional to the device performance and is eliminated in this selective plating system.

Because of production requirements, the system was to produce product from coils of lead frames in an uninterrupted manner at a minimum rate of 900 cm/min. This rate of production through continuous plating equipment makes it highly desirable to deposit gold from a solution of low metal concentration and low specific gravity in order to minimize solution drag-out from the plating cell. To achieve our basic objective in this project the following goals were established.

1. A selective gold deposit which would drop die attach and thermal compression wire bond without modifying die backing or thermal excursions in the assembly process.

2. Equipment which would selective plate in functional areas of the lead frame at speeds in excess of 900 cm/min.

3. A gold process which contained less than 10 grams per liter with a specific gravity less than 10° Be

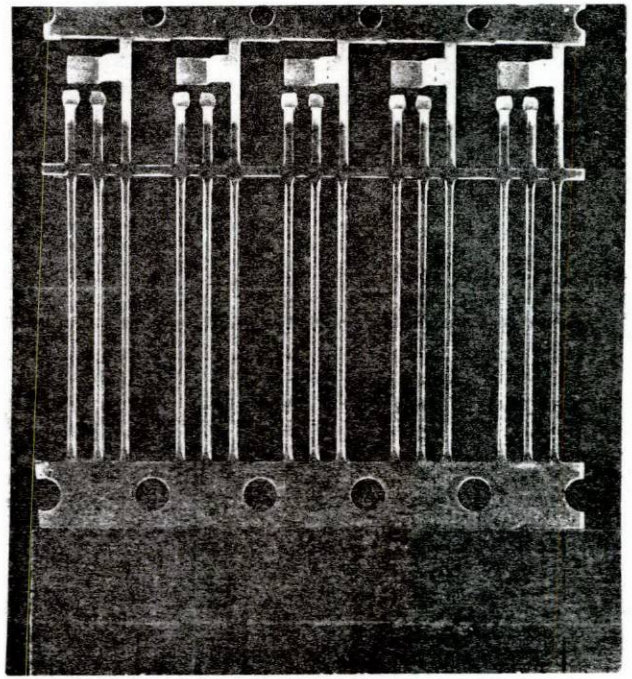

Fig. la Selectively plated
Lead Frame

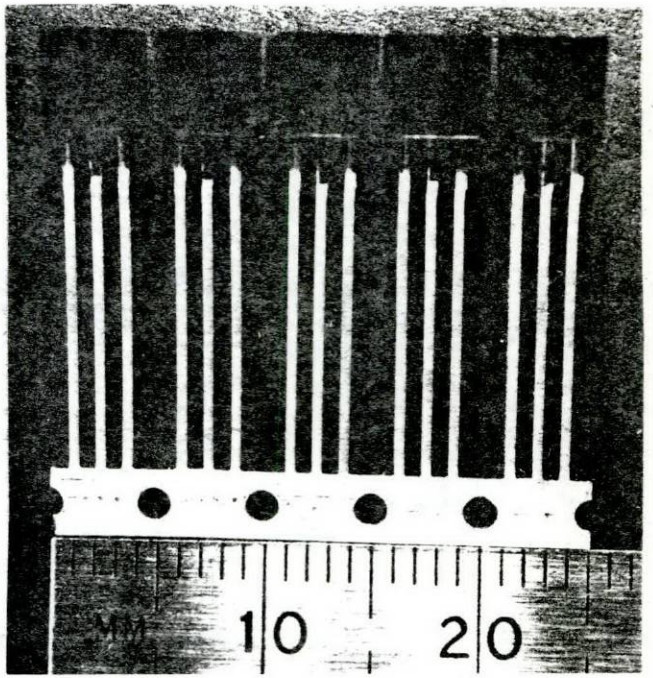

Fig.1b Assembled Transistor

Fig. 1 Small Signal TO-92 Transistor

with an operating current density in excess of 30 A/dm^2.

Experimental Approach

The basis metal plated is Olin 194[a] copper alloy, supplied from various stamping companies on cardboard reels. Each reel contains 101.5 meters of lead frame wound with paper interleaf to prevent damage. The strip is contaminated with a light coat of stamping oil which must be removed in the preplate cleaning process.

A. Equipment Selection

The plating equipment chosen to accomplish the desired selective masking is a commercial machine supplied by American Chemical and Refining.[b] An overall view of the equipment is shown in Figure 2. The lead frame is transported in a continuous manner through the various process cells which are supplied with the appropriate solution from reservoir tanks located beneath those process cells. A spray rinse and an air knife blow-off device are located between each process step to prevent contamination by the previous step. Incorporated in the equipment are plating cells which utilize a moving mask technique to accomplish the selective gold plating as the strip moves continuously from the payout reel to take-up reel. A schematic drawing of a typical selective cell is shown in Figure 3. The first selective gold cell is utilized to deposit 0.125 microns of gold on both sides of the lead frame between the top and bottom carrier rails while the second cell deposits 1.0 micron of gold on bonding surfaces. Effective lengths of these cells are 213 cm.

Continuous uninterrupted operation of the system is accomplished by having dual reel platforms at the payout and take-up stations which rotate 180° when the reels are emptied or filled at each respective station. At the payout station the end of the strip is stopped and a new reel attached by resistance welding to the new reel. During this period of time (15 - 20 seconds) the strip is supplied into the plating system by an accumulator mechanism which travels on a rail, festooning strip into the first cell. The accumulator returns to its original position when the strip is released at the welding fixture.

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a Olin Corporation, New Haven, Conn.
Alloy 194 is typically 97.5% copper, with the remainder iron and phosphorous.

b American Chemical and Refining Co., Waterbury, Conn.

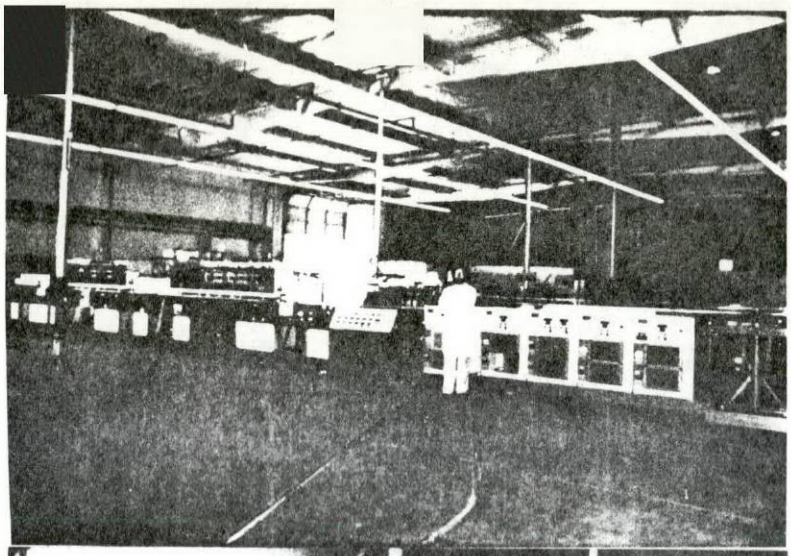

Fig. 2a

Overall Equipment View

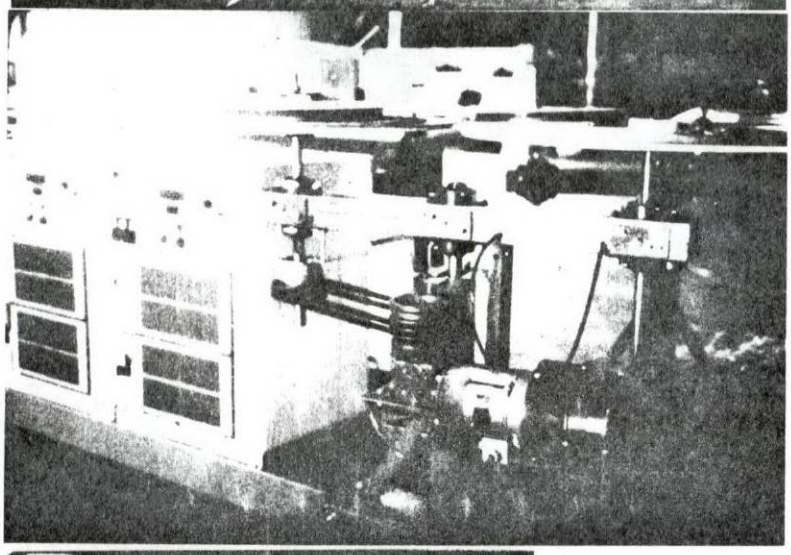

Fig. 2b

Takeup Platforms and Rectifiers

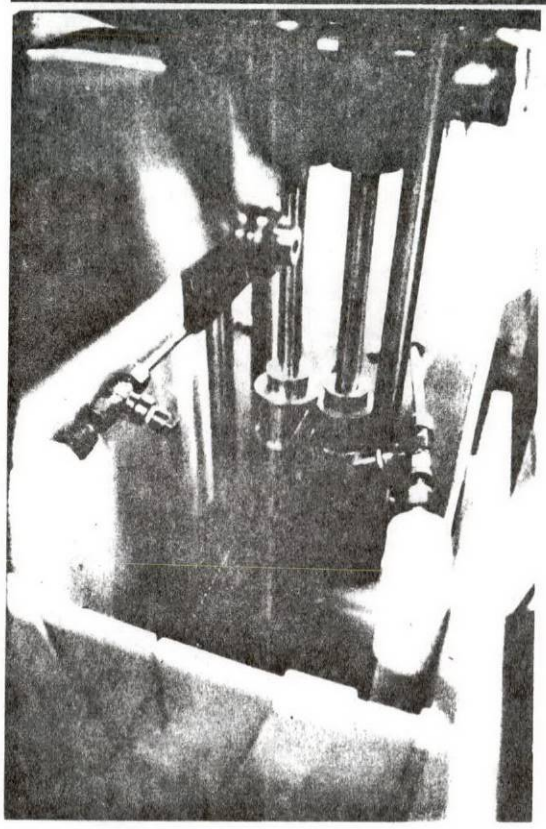

Fig. 2c

Strip Drive and Rinsing Cell

Fig. 2 Continuous Reel to Reel Selective Stripe Equipment

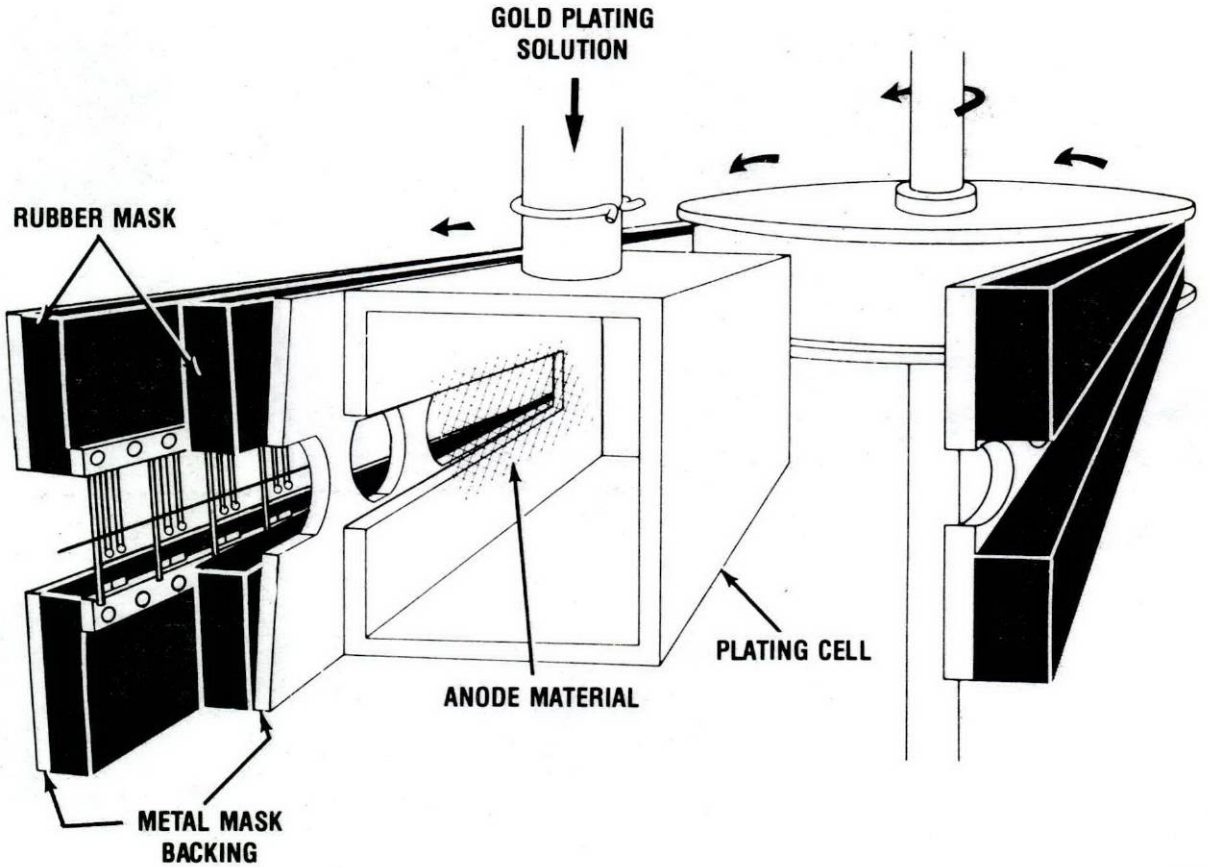

Fig. 3. Selective Cell Schematic for Gold Strike

Synchronization of the strip is maintained throughout the horseshow shaped equipment by drive rollers and plating masks which are driven from the endless stainless steel belt located along the length of the machine above the process cells.

The process steps selected to clean and plate the copper lead frame are described in Table I. Rinse steps are omitted from the table for the sake of brevity.

TABLE I

PROCESS CYCLE FOR SYNCROPLAT EQUIPMENT

Step No.		Description
1	Degrease	- Room temperature 1,1,1, trichlorethane
2	Electroclean	- Proprietary alkaline cleaner at 77°C and 6-8 volts cathodic
3	Bright Dip	- Proprietary nitric acid type solution at 43°C
4	Acid Rinse	- 10% by volume sulfuric acid at room temperature
5	Nickel	- Sulfamate nickel at 60°C
6	Acid Rinse	- 5% mineral acid by volume at 43°C
7	Selective Gold Strike	- 0.125 microns of gold deposited from 4 gma/liter gold solution
8	Selective Gold Plate	- 1.0 micron of gold deposited from 9.0 gms/liter gold solution
9	Hot D.I. Rinse	- 82°C spray
10	Hot Air Dry	- Rectangular drying chamber supplied with industrial blower

Prior to depositing the final selective gold stripe, nickel is deposited from a sulfamate solution over the entire lead frame. This is accomplished in a 366 cm long total immersion cell located after the cleaning cells. Nickel was chosen to prevent the diffusion of copper through the gold during the bonding thermal excursions.

The equipment has the capability of infinitely variable speeds from 0 - 1830 cmβmin. Additional variables at the gold cells which are controlled include solution temperatures and flow rates through the plating cells (see Figure 3). Rectifiers utilized in all metal deposition are constant current controlled with variable rheostats.

B. Solution Development

In developing the gold solution, compatability was maintained between the strike and plate by utilizing the same components at different concentrations. The basic formulation compounds were supplied Lea Ronal, Inc.[c] with general guidelines as to their qualitative effects on the deposit. The solution constitutents are described in Table II.

TABLE II

GOLD STRIKE AND PLATE SOLUTION CONSTITUENTS

Item	Description and Function
A	Highly ionized conductivity salt
B	Inorganic salt for pH buffering
C	Additive effecting deposit density and brightness. Does not co-deposit.
D	Organic chelating agent for nickel and other base metals
PGC	Potassium Gold Cyanide

These designations, i.e., A, B, C, will be used throughout this article instead of the generic chemical names to protect the proprietary nature of the solution. In order to establish the optimum formulation for producing functional deposits, each bath constituent was varied along with temperature and flow rates and the deposit studied with respect to bondability, surface topology, and resistance to diffusion of substrate metals which interefere with die and wire bonding.

The nickel solution utilized throughout the tests is a high purity nickel sulfamate formulation. Typical operating conditions are described in Table III.

TABLE III

NICKEL PLATING FORMULATION

Component	Operating Condition
Nickel	120-140 gms/liter nickel as nickel sulfamate
Boric Acid	40 gms/liter minimum
Nickel Chloride	8-16 gms/liter
Temperature	60 ± 3°C
Copper	<10 ppm

c Lea Ronal Inc., Freeport, N. Y.

The nickel system included low current density electrolytic purification for removal of copper, and weekly recirculatory treatment with granular activated carbon to control organic contamination.

C. Testing Procedures

During the die attachment, both the die bond area on the lead frame and the wire bond posts experience thermal excursions to 460°C for several seconds. A typical dynamic thermal cycle is shown in Figure 4. The wire bonding is accomplished with 0.00318 cm diameter gold wire which is thermal compression bonded on the die and lead frame post at 325°C. Figure 5 shows both the die and wire bonds in place on the lead frame.

In order to test the integrity of the die and wire bonds, destructive testing is performed on the die and both wires. Figure 6 is a close-up of the eutectic melt which surrounds the die. The die is mechanically probed at one edge with a blunt tool which shears the die from the pad (Figure 7). The pad area is then examined for a complete wetting of the gold deposit and/or separation of the eutectic melt from the nickel underplate. This failure mode is commonly called "die pop" by the semiconductor industry. Examples are shown in Figures 8 and 9.

Bonding is considered acceptable if the silicon fractures as in Figure 6 upon probing and a minimum of 75% of the area under the die was covered with silicon.

Testing for wire bond integrity is normally done by using a pull test apparatus which hooks into the center of the wire loop and pulls upward until failure occurs. The force necessary to cause failure is recorded along with the mode of failure. A desirable failure point is to have the wire break (Figure 10) while a reject is to have the bonded portion of the wire lift from the lead frame post (Figure 11). An additional failure mode can occur when the wire breaks at the heel of the bond (Figure 12). This failure mode is usually caused by adjustment problems in the bonding pressure and the wire is thinned out in the heel area and becomes the weakest point in the wire. This failure mode is not dealt with in this paper.

All wire bonding was performed with a Motorola designed thermocompression bonder equipped with 0.00381 cm needle and 0.00318 cm gold wire. Needle weight was held at 45 ± 5 grams and the block temperature controlled at 325 ± 5°C. Wire bonds were made so as to control the bond width from 1.4-2.5 times the diameter of the gold wire.

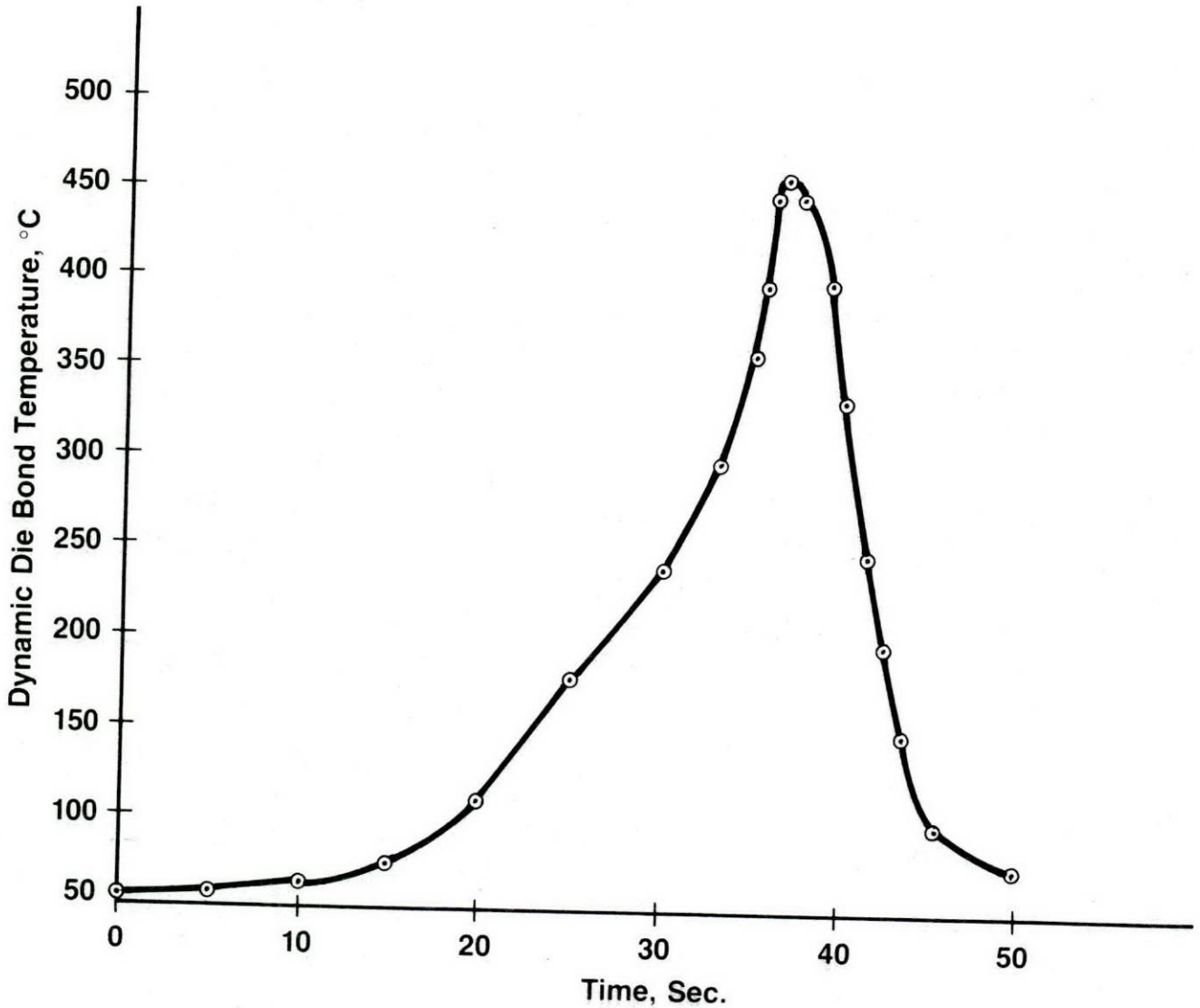

Fig. 4. Die Bond Temperature Excursion

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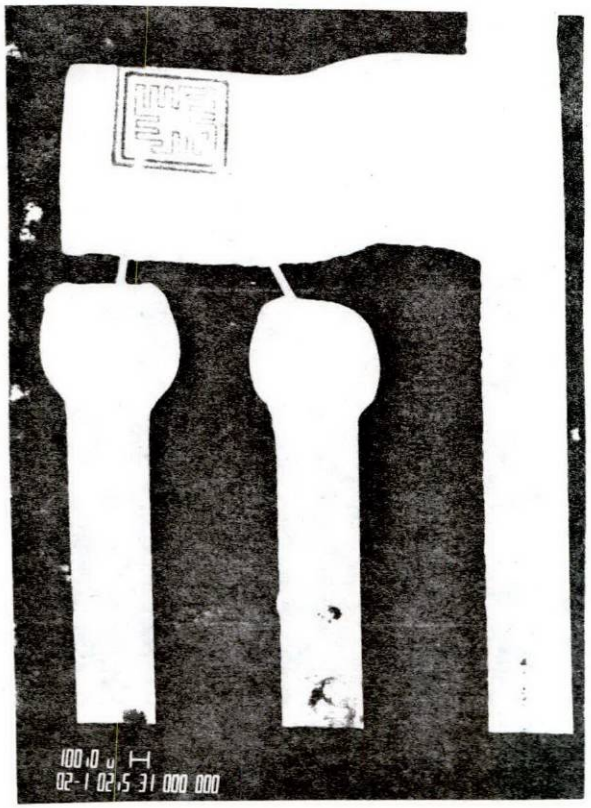

Fig.5 Lead Frame with Silicon die and gold wires in place

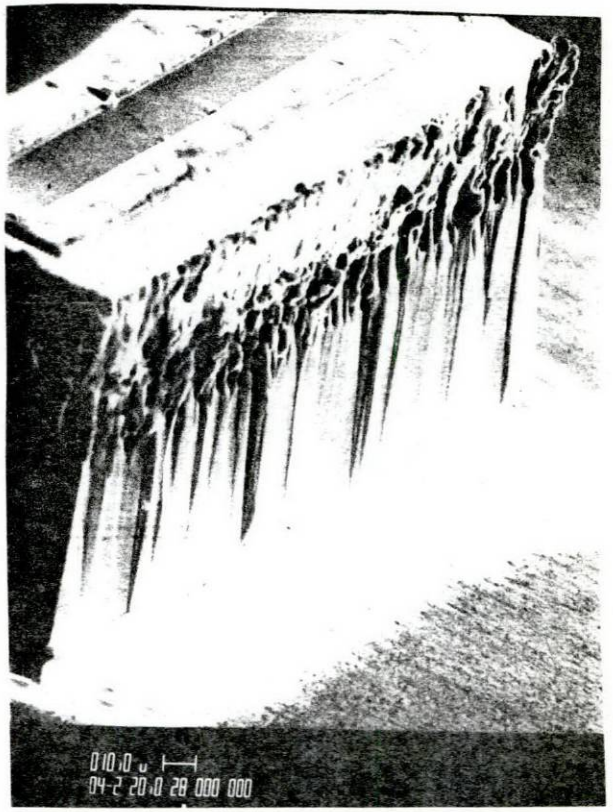

Fig. 6 Edge of die showing silicon gold eutectic

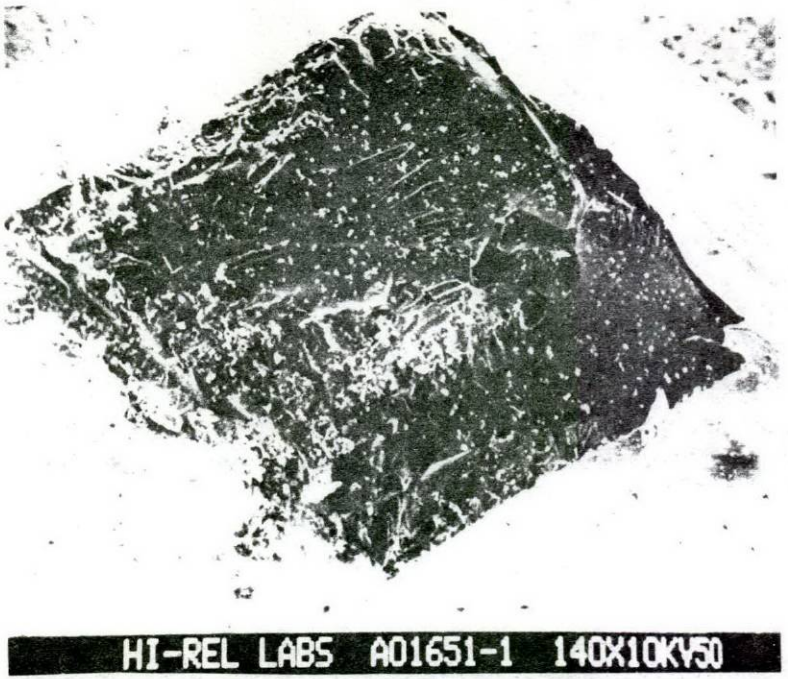

Fig.7 Acceptable die bond after shear test

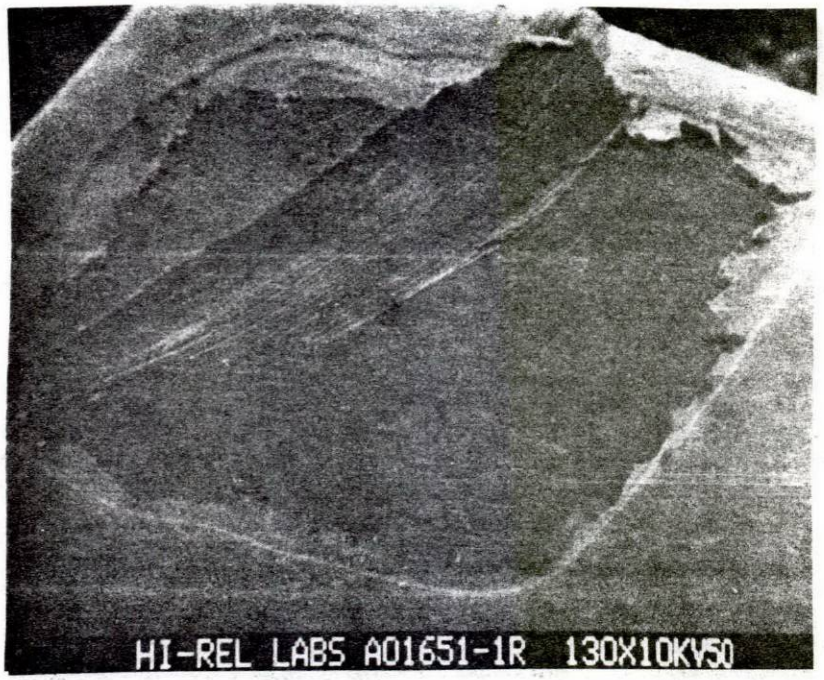

Fig.8 Die separation at nickel interface. "die pop" (smear caused by shearing tool)

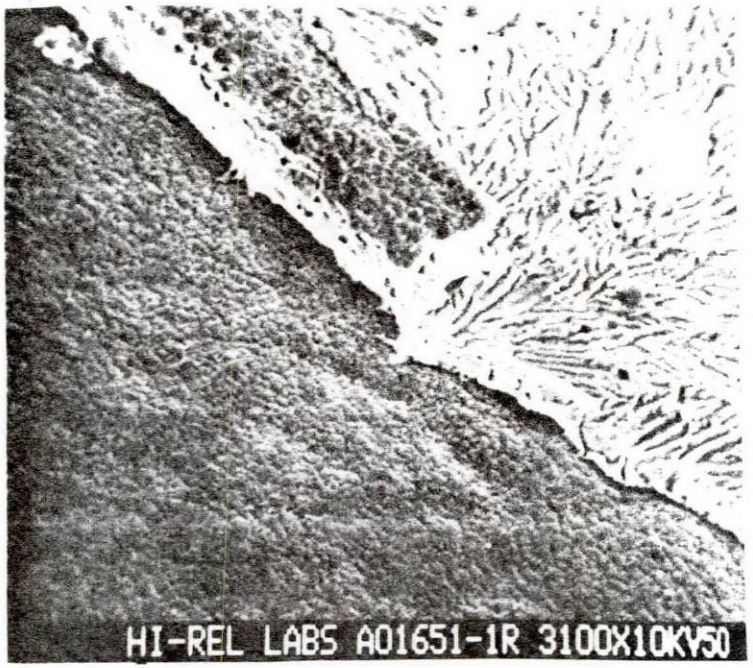

Fig.9 Nickel substrate after die separation



Fig.10 Center wire break from normal pull test



Fig.11 Complete wire lift from gold surface

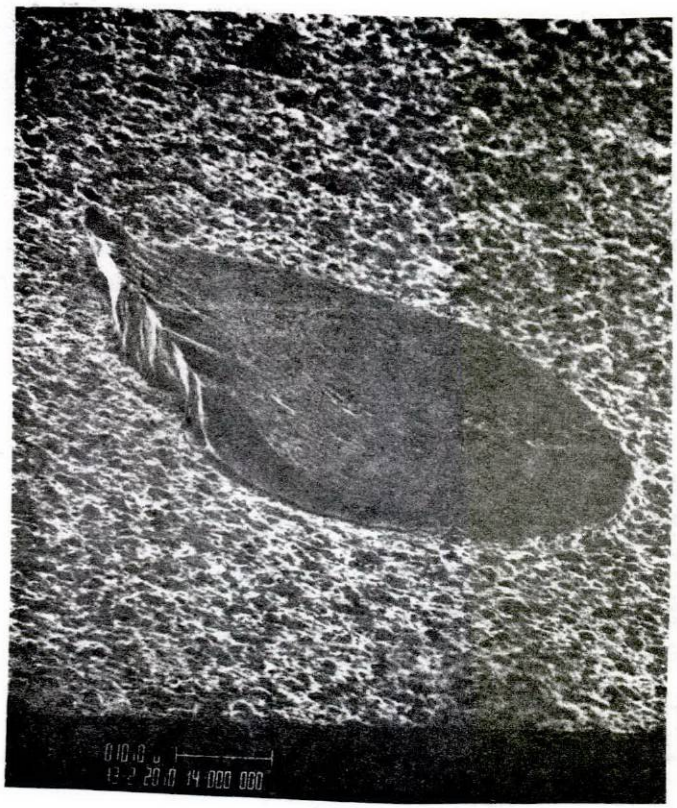

Fig. 12 Wire break at heel of bond

Wire bond tests performed and reported on in this paper were done by the "peel test." The wire is bonded to the lead frame post and pulled or "peeled" back against the direction of bond. (See Figure 13.) A reject consisted of a lifted bond while an acceptable bond caused the wire to break. Correlation studies have been performed but not reported here that clearly demonstrate the "peel test" is more severe than the standard pull test as described above and in Mil. Std. 883B Method 2011.2 par. 3.1.3.

D. Experimental Results

Causes of Die Pop

Copper in the silicon-gold eutectic has been identified as one cause for "die pop." Analysis of the nickel plate under the die shown in Figure 8 showed the presence of 2% by weight of copper in the nickel.[1]

The copper can diffuse through pinholes in the nickel deposit. The cause of such holes was suggested by Wells[2] to be contamination of the nickel solution by copper ions in excess of 30 ppm. Examination of our nickel solution by chemical A.A. analysis revealed 34 ppm of copper. Magnification of the deposit clearly showed the presence of pinholes. See Figure 14. Electrolytic purification at 0.10 A/dm^2 removed the copper to <3 ppm and S.E.M. examination of the nickel surface on subsequent occasions failed to detect any holes. No "die pop" failures have occurred since this correction was made which could be attributed to copper in the eutectic.

In addition to copper, as plated contamination on the surface of the nickel electroplate has been identified as a cause of "die pop." For that reason our nickel sulfamate is formulated without wetting agents or brightners which might co-deposit in trace amounts or leave a film on the nickel surface before the gold is deposited.

Nickel solutions are carbon treated before using and an eight hour recirculatory treatment with 5 gms/liter of granulated carbon is performed each five working days to remove undesirable organics. Inadvertant introduction of organics from the raw copper strip has occurred during production operations due to a pump failure in the cleaning section of the machine and caused "die pop." Subsequent cleaning of the equipment eliminated the organic contamination and the associated "die pop" problem.

A third cause of "die pop" has been identified as oxides on the nickel plated surface which are not serious enough to cause delamination between the nickel and gold but are detrimental to the eutectic die bond melt when subjected

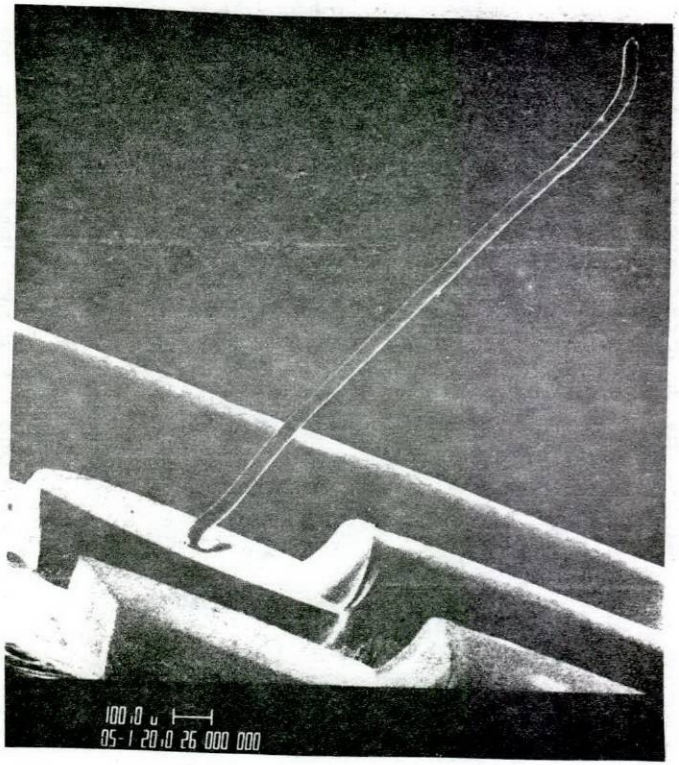

Fig. 13 Center wire break from "peel test"



Fig. 14 Pinholes in nickel deposit

to heat. In order to prevent the possibility of oxide formation before gold striking in the continuous machine, the nickel is rinsed in the acid associated with the gold electrolyte, then followed by a deionized water rinse before gold is deposited on the nickel. No production problems have occurred in this project which have resulted in identifiable "die pop" problems attributable to this cause. In general, "die pop" has not been a major problem since the early stages of development. The significant problem that had to be resolved was wire bond failures.

Causes of Wire Bond Failure

It has been documented in the literature that inorganic and organic films on the surface of gold deposits interfere with the strength of thermocompression wire bonding.[3,4] In the present work Auger spectroscopy was utilized to determine the contamination present after the die bond temperature excursion. This technique has been utilized by MacDonald[5], Johnson et al[6], Panousis et al[7], Holloway et al[8], and Gonzales[9] to determine surface contamination on electrodeposits.

The significant contaminant in this study was found to be diffused nickel during the die bonding process which oxidized on the surface of the gold plate. It was necessary to determine if this nickel was being co-deposited or diffusing to the surface from the nickel plated barrier. Our conclusions will be addressed in Part II of this study.

Gold Formulation Studies

Table IV contains the matrix study used to determine the gold plate composition. Gold concentrations were kept at 10 ± 1.5 gms/liter. The deposits were made over electrolytic nickel and a gold strike which was formulated as shown in Table V.

TABLE IV

FORMULATION STUDY OF GOLD PLATE

Current Density 30 A/dm^2

Solution Constituents A gm/liter	B gm/liter	C gm/liter	Solution Temperature °C	Percent Lifted Wire Bonds After Die Bond	
15	60	0	71	2	Effect of Solution
15	60	0	60	7	Temperature
30	60	0	60	89	Effect of Increased
30	60	0	60	93	Conductivity Material
30	60	0	71	82	at Various Solution
30	60	0	49	86	Temperatures
30	60	15	71	7	Effect of Additive C at
15	60	15	71	0	Different Conductivity Levels

In order to keep the rectifier voltage within limits of the equipment (less than 30 volts), 15 gm/liter of conductivity salts (A) were considered the minimum practical concentration. As can be seen from Table IV increased amounts caused large increases in wire bond failures. The buffering material (B) was found to visually brighten the deposit as the concentration increased. A concentration of 60 gm/liter was chosen because this is near the saturation level of the solution and higher amounts were therefore impractical. Additions of the (C) material coupled with the low concentration of (A) and a high operating temperature of 71°C produced the only deposits with 0 bonding failures. Temperatures above 71°C were not considered because of the materials of construction of the selective cell.

The deposit which produced zero bonding failures also appeared visually to be the brightest of any conditions tested. Flow rates through the selective cell were then evaluated. Optimum deposit luster was obtained at 23 - 30 liters/min while higher or lower ratios darkened the deposit.

The strike solution which is used to deposit gold on the leads of the device for solderability purposes (see Figure 1a), was formulated to give the brightest desposit at 5 - 7 A/dm^2. In order to achieve this, the electrolyte component concentrations were reduced by 50%. These are shown in Table V.

TABLE V

GOLD STRIKE FORMULATION

3.3 - 4.1 gm/liter

Solution	Component	Concentration
A		7.5 gm/liter
B		30 gm/liter
C		1 gm/liter
D		0.75 gm/liter
PGC		0.38 gm/liter

Drag Out Gold

The objective in lowering the drag out from the gold solutions is obvious. Any gold leaving the solution via drag out must be reclaimed. Drag out losses from reel to reel machines which operate with a specific gravity of 19° Be and a gold concentration of 40 gms/liter typically are equal to the gold that is selectively plated.

Table VI illustrates the success of removing the low specific gravity gold solution from the strip by a carefully designed air knife within the plating cell. Note that the final air knife design further reduced drag out even when the speed of the strip through the machine was increased by 50%.

TABLE VI

Date	Drage Out Loss gm/gms Plated	Strip Speed cm/Min	Comment
7/77	0.034	1220	Initial air knife design
11/77	0.024	1220	Intermediate air knife design
8/78	0.013	1830	Final air knife design

Thickness Distribution of Gold

The minimum acceptable thickness of gold on the die bond pads measured by Beta Backscatter techniques is 0.875 microns. Figure 14a is a thickness distribution curve obtained from random measurement of 300 bonding pads. A population of 660,000 units was used. The mean thickness obtained was 1.08 ± 0.22 microns. This compares favorably with gold spot plated and rack plated lead frames as shown in Figure 14b.

Microscopy Examination of Deposits

Figure 15 is a microphotograph taken at a 30° angle from the vertical to show the topology of the nickel deposit from the sulfamate solution. The small nodules seen are thought to be caused by microscopic sized particles of sulphur compounds from the sulfurized anodes used. Although heavy bagging of the anodes was done, it is obvious that nucleation particles of this size could escape and be responsible for some roughness. No detrimental effects could be attributed to roughness of this magnitude.

Figures 16 and 17 are typical surface topology obtained from deposits plated from the gold strike and plate solutions over sulfamate nickel. Photographs normal to specimen are shown in Figure 18 which are typical of the topology variations with current density. The most consistent bonding performances were obtained from gold deposits plated at 60-80 A/dm^2. (See Figure 19.)

Effect of Organic Chelating on Wire Bondability

Nickel contamination in the gold solutions has not been significant. Spray rinsing and air knife blow off

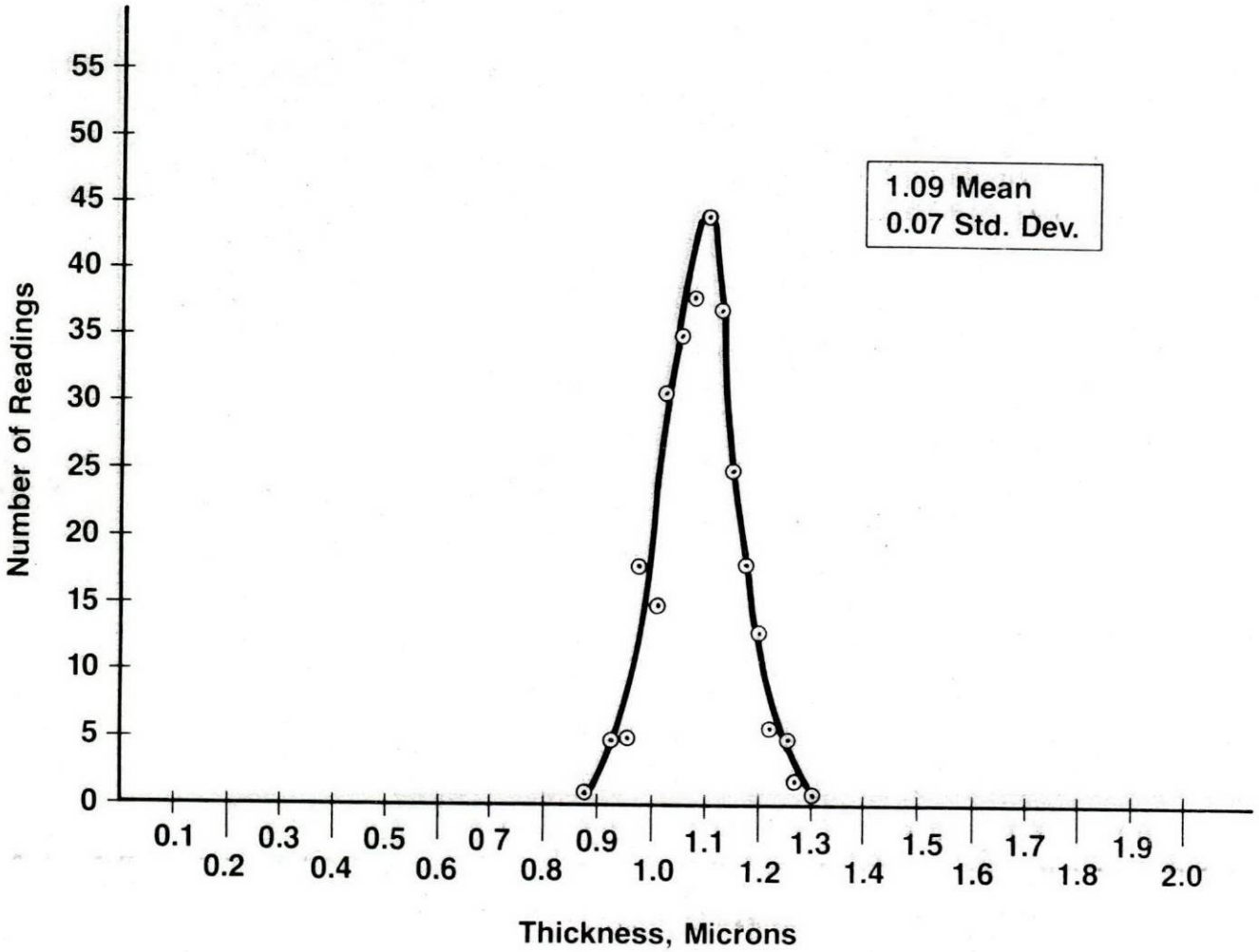

Fig. 14a. Gold Thickness Distribution from Continuous Selective Process

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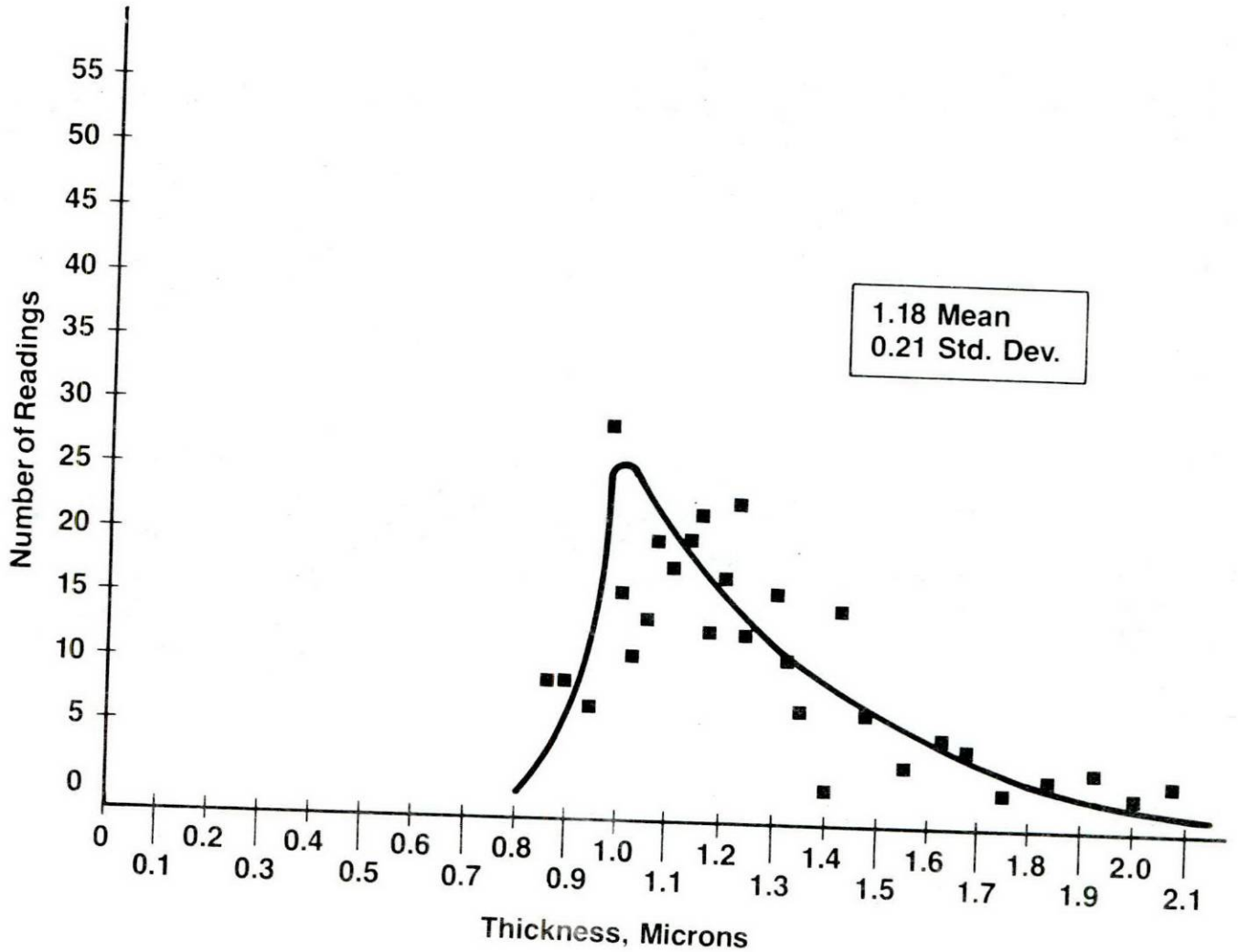

Fig. 14b. Gold Thickness Distribution from Selective Rack Process

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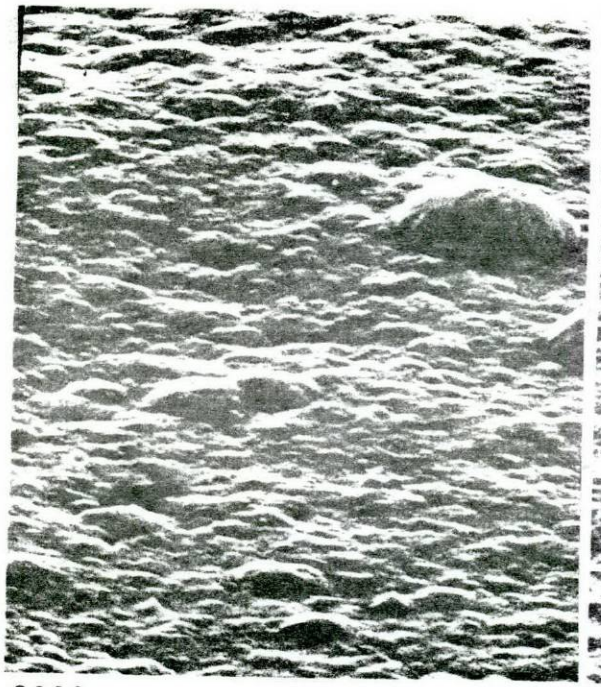

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Fig. 15 Sulfumate nickel at 41 A/dm^2

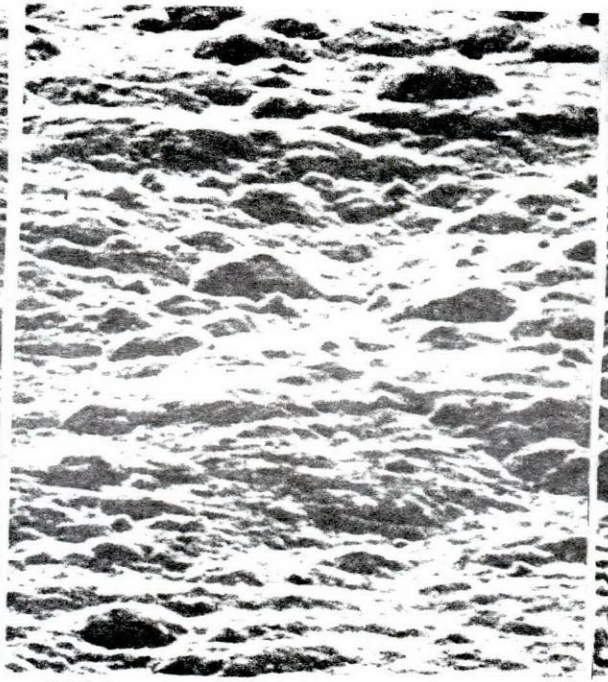

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Fig. 16 Gold strike at 7 A/dm^2

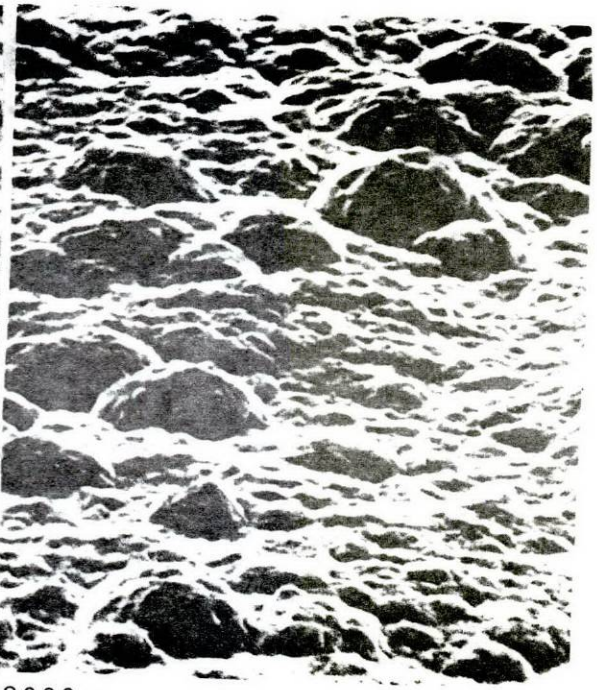

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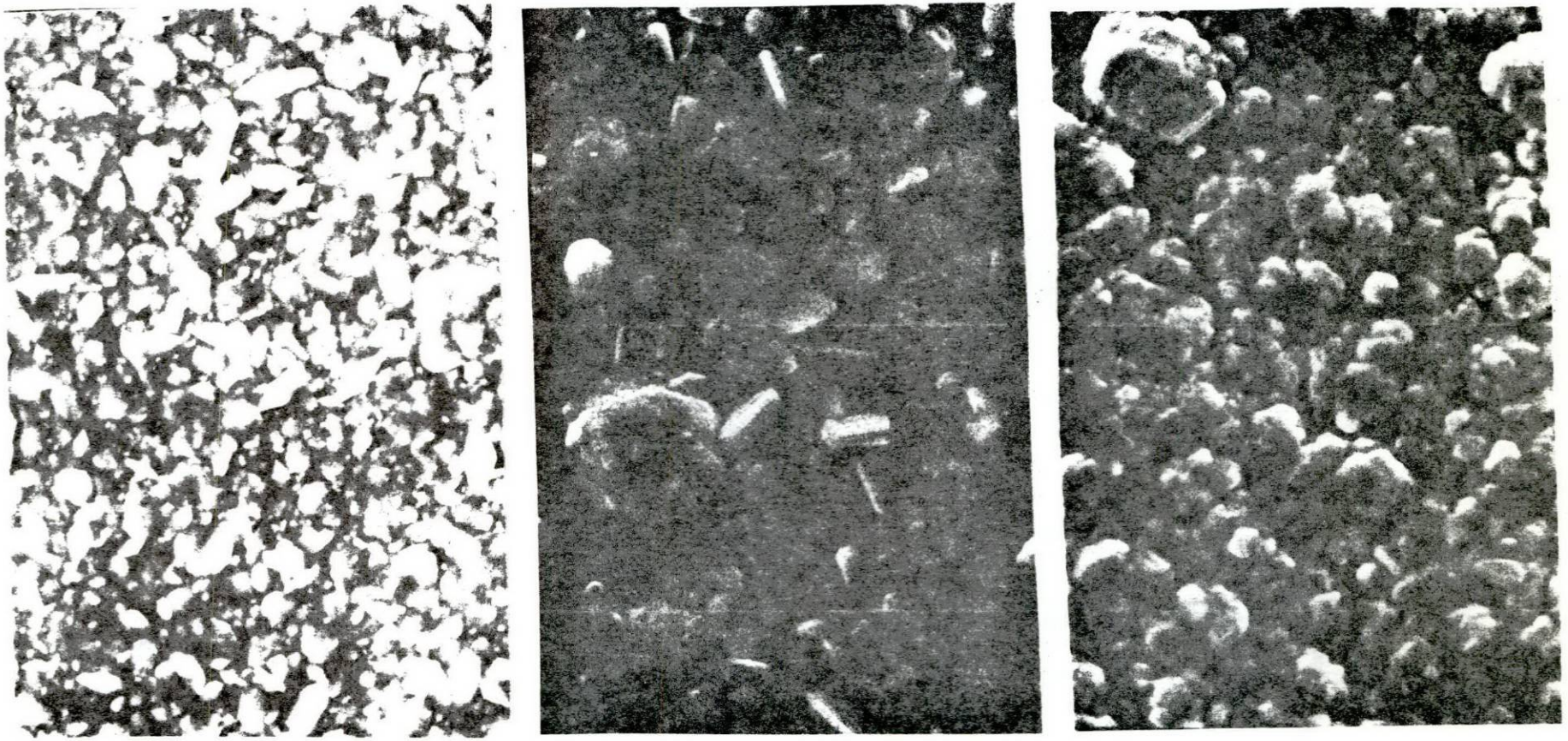
Fig. 17 Gold plate at 80 A/dm^2



8000x 30 A/dm^2 8000x 50 A/dm^2 8000x 80 A/dm^2

Fig. 18 Surface topology of gold plate deposit at various current densities

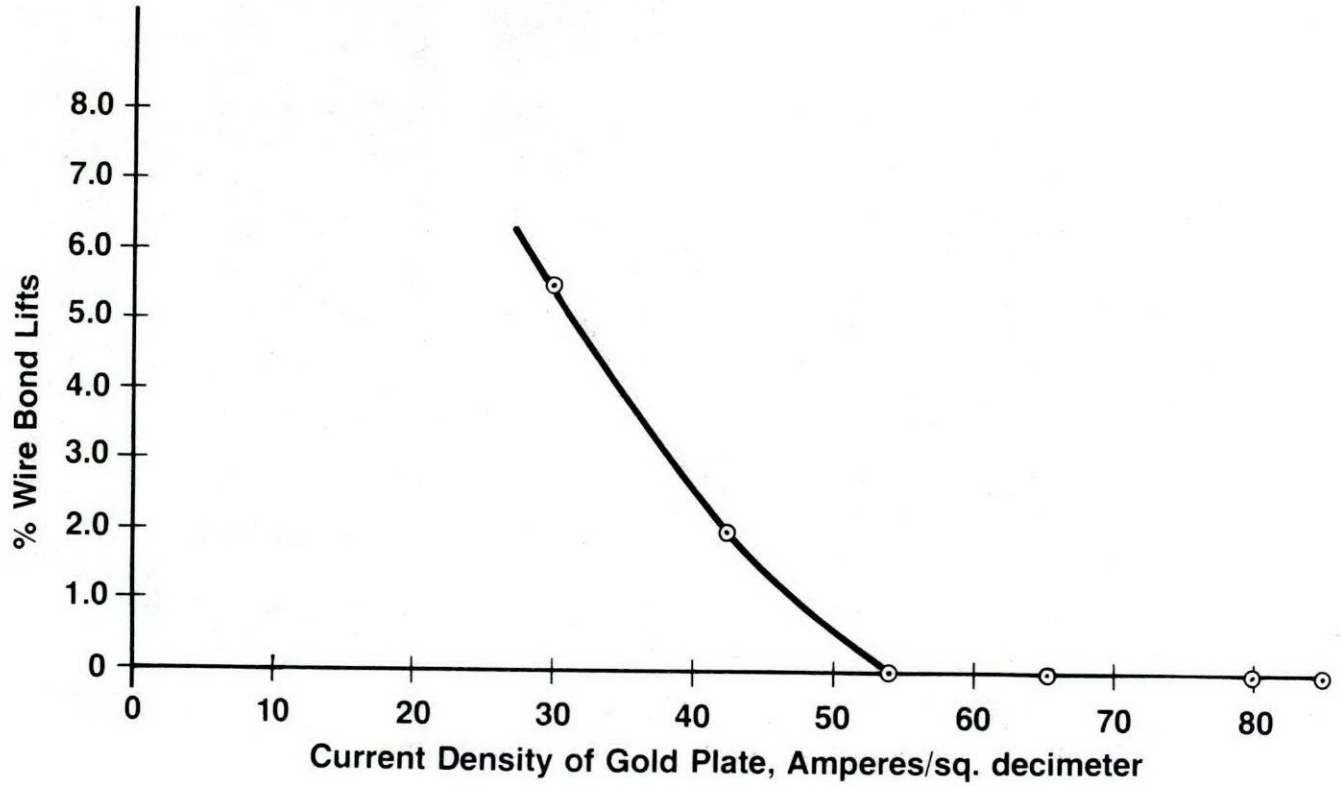


Fig. 19. Frequency of Wire Lifts as a Function of Current Density

E9334

stations between the nickel and gold cells have been effective in preventing gold drag in of nickel. Nickel concentrations do not normally exceed 20 ppm after 12 million units (60,860 meters) of lead frame have been processed. The nickel concentration in the gold plate typically reaches 5 ppm. (See Figure 20.)

In order to protect the gold deposit from accidental solution contamination of substantially higher levels of nickel, the effect of additions of an organic chelating agent (D) on wire bonding was made. Figure 21 is the result of this study. It is believed that concentrations of the chelator substantially higher than 1.5 gm/liter act in the familiar role of an organic contaminant and decrease the density of the gold deposit and thus the reliability for wire bonding. Based on Figure 21, and diffusion studies by Auger spectroscopy which will be discussed in Part II of this report, the concentration of chelator added to the gold strike and plate makeups was established at 0.75 gm/liter. Molar calculations using this concentration of chelator show that 100 ppm of nickel can be complexed. This is deemed adequate for protection of the deposit from accidental contamination of the solution. Further demonstration of the role of the chelator in suppressing the nickel in gold deposit is shown in Figure 22. Here nickel was added to a gold solution which had previously been used to produce 10.8 million acceptable units. Curve A traces the increase of nickel in deposits from the solution which when new had 0.75 gm/liter of chelator. Curve B traces the nickel in deposit from the same solution after adding an additional 0.56 gm/liter of the chelator.

Part II of this report entitled "Control of Surface Quality Utilizing Auger Electron Spectroscopy" continues the solution study and deposit performance when utilizing the surface analysis technique of Auger Spectroscopy.

Conclusions

A dilute gold plating solution has been developed which gives satisfactory deposits for gold-silicon eutectic die attach and thermal compression wire bonding. The solution contains a gold concentration of 9.0 grams per liter as potassium gold cyanide and a specific gravity of 8° Be for bondable deposits. It is operated at 60 - 80 amperes per square decimeter and produces a semibright gold which is deposited at 1 micron thickness over electrolytic nickel.

Continuous reel to reel equipment is utilized which deposits nickel, gold strike and gold plate selectively over stamped copper lead frames at production rates of 1830 cm/min while minimizing solution drag out.

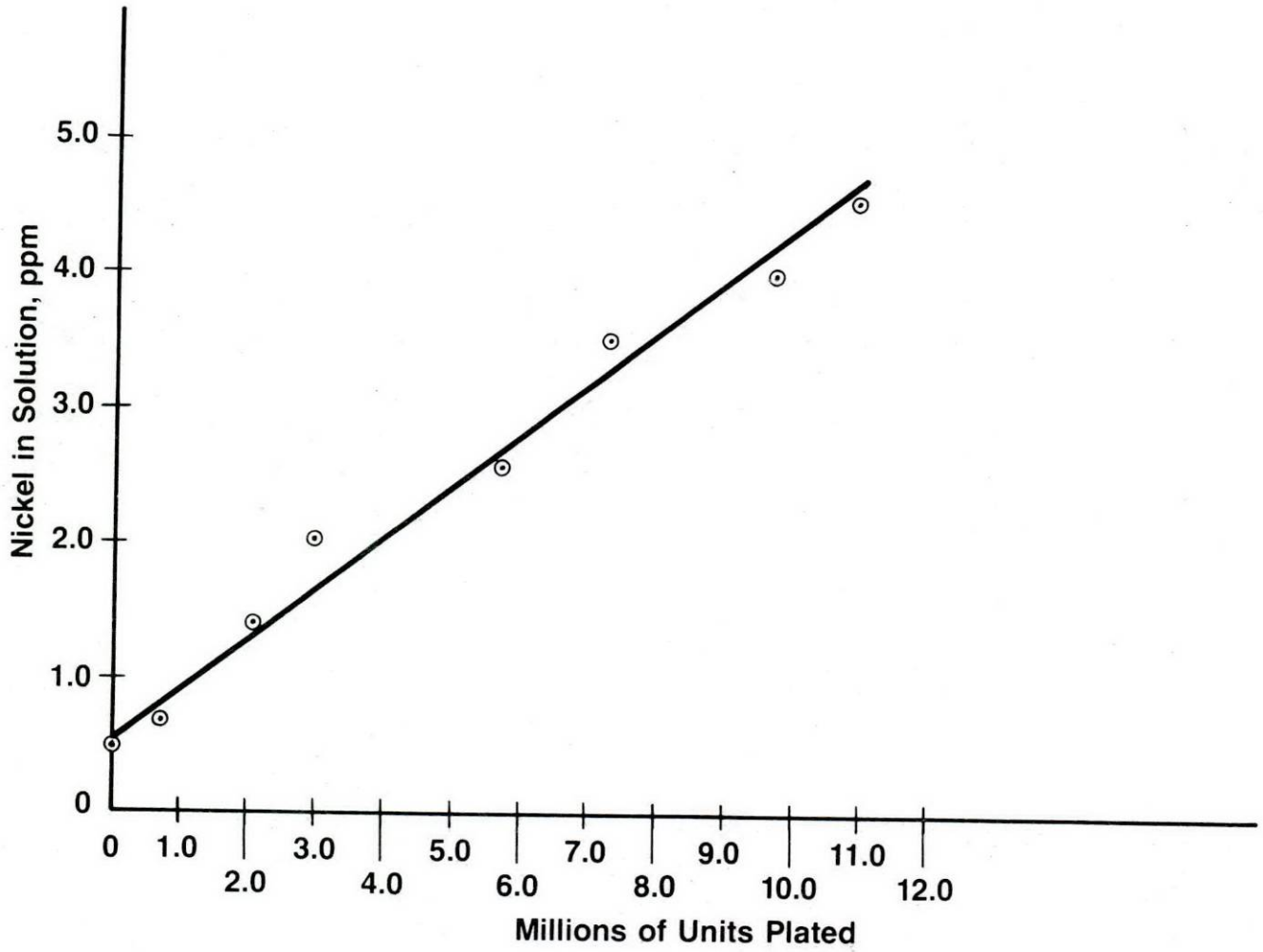


Fig. 20. Nickel Buildup in Gold Plate Solution

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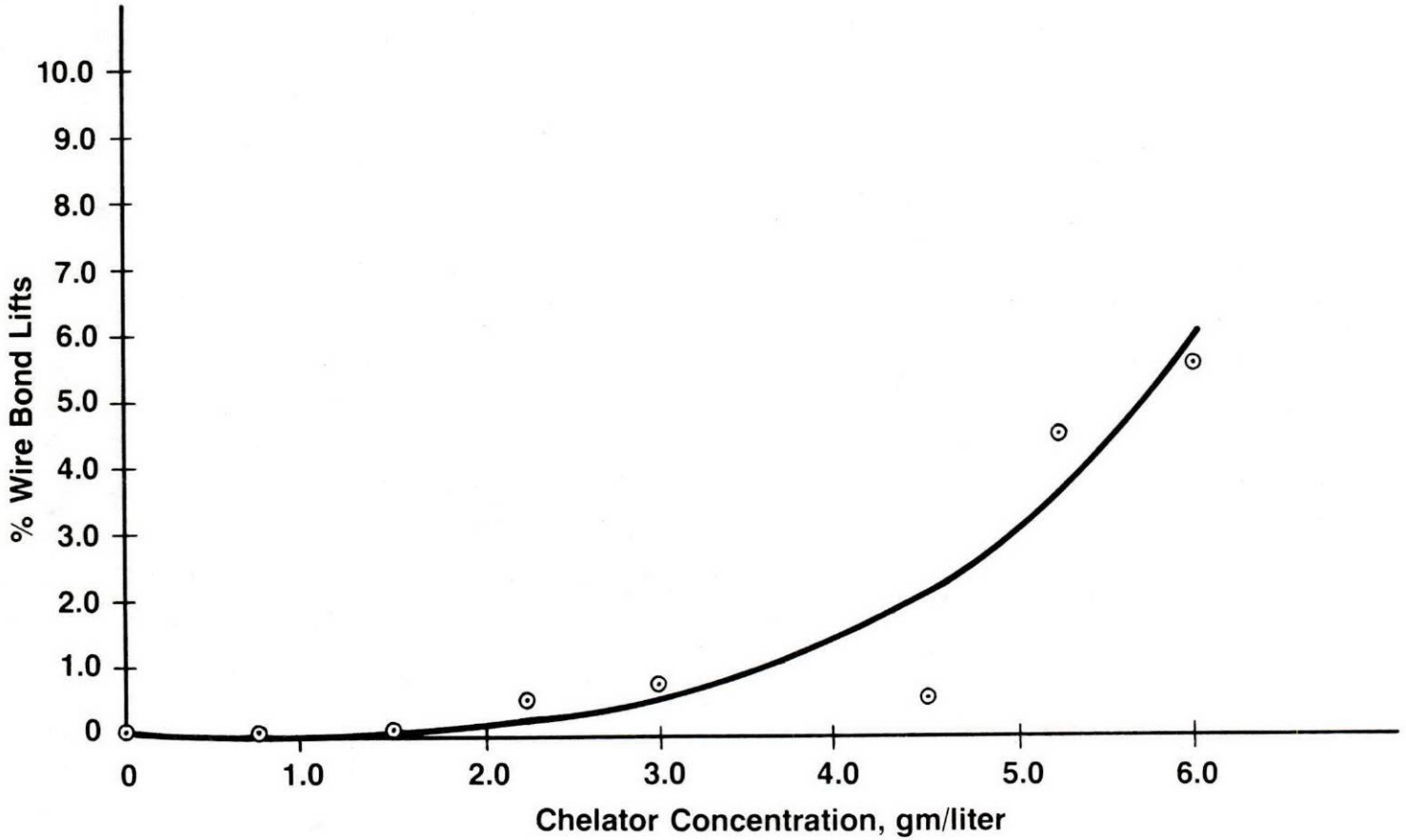

Fig. 21. Wire Bond Performance as a Function of Chelator Concentration

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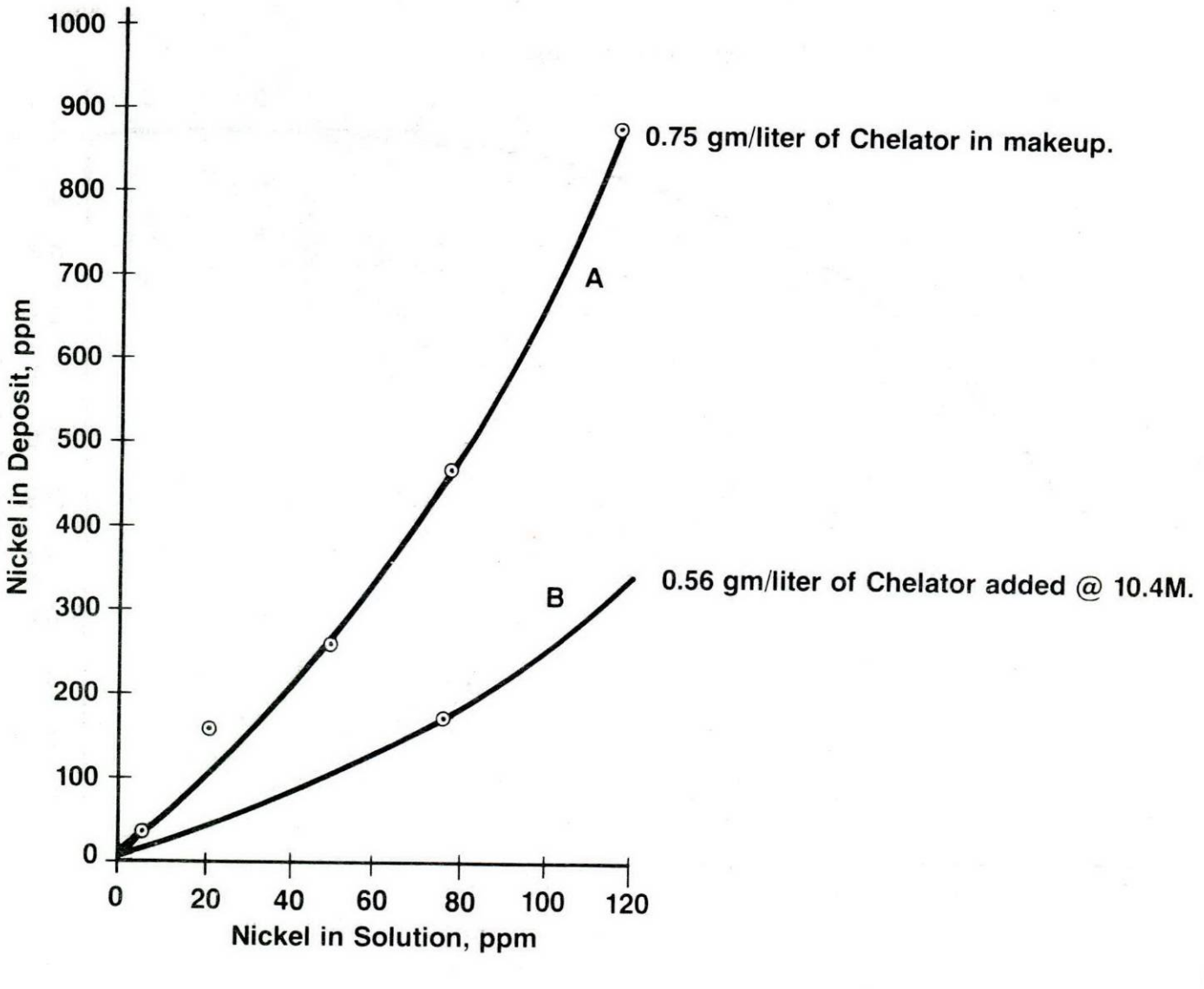

Fig. 22. Effect of Additional Chelator on Nickel in Deposit

Fluidics of solution impingment, current density and concentrations of electrolyte ingredients were found to be critical in minimizing diffusion of nickel and copper substrates during the bonding process. Sufficient surface concentration of these base metals interferes with wire and die bonding.

Solution lives of 66,000 devices per liter of electrolyte have been achieved in production before deposit structures no longer are satisfactory in preventing diffused nickel from interfering with thermal compression wire bonding. S.E.M. photomicrographs were made at 8000X to verify changes in surface topology.

The obvious advantages of such a gold solution for high speed operation include, low dragout of gold metal from the plating cell even at high strip speeds, low precious metal inventories within the plating equipment and easy removal of solution from the plated deposit by air knives and spray rinsing.

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References

1. Hi-Rel Laboratories, Monrovia, Calif., Report No. R-0265, 1976.

2. H. F. Wells response to D. A. Fanner and R. A. F. Hammond, Transactions of Institute of Metal Finishing, 36, 177, 1959.

3. J. L. Jillison, IEEE Transaction on Parts, Hybrids and Packaging, 11 No. 3, 206, 1975.

4. G. E. McGuire, J. V. Jones, and H. J. Dowell, Thin Solid Films, 45, 59, 1977.

5. N. C. MacDonald, Extended Abstract 73-2, Electrochemical Soc., Boston, Mass., Oct. 7-11, 479, 1973.

6. B. C. Johnson, S. Thomas, and L. Richardson, Extended Abstract, Proc. Electrochemical Soc., Pittsburg, Penn., Oct 5, 1978.

7. N. T. Panousis and P. M. Hall, IEEE Transaction on Parts, Hybrids and Packaging, Vol. 12 No. 4, 282, 1976.

8. P. H. Holloway and D. W. Bushmire, 12th Annual Proc. Reliability Physics (IEEE), 180, 1974.

9. A. J. Gonzales, 11th Annual Proc. Reliability Physics (IEEE), 185, 1973.

Meet the Authors

Duane Endicott has been Manager of Metal Finishing Development for domestic and foreign facilities at Motorola's Semiconductor Group since 1974. Prior to this he held various engineering and other managerial positions in the Metal Finishing Department since 1965. Previous industrial experience was with the Bendix Corporation A.E.C. Division as Process Engineer in the Metal Finishing Department.

Duane has a Bachelor Degree in both Physics and Chemical Engineering and completed two years of graduate studies in Chemical Engineering at the University of Kansas. A member of A.E.S. since 1961, Duane is the recipient of the Carl E. Heussner and George B. Hogaboom awards for the best publication by the A.E.S. in 1966. Duane has also served as a member of the Paper's Committee and committee member of A.E.S. Research Projects 34 and 44.

George J. Casey, Jr., CEF, received his B.S. in chemistry from Lebanon Valley College in 1973. After spending two years in the graduate program in chemistry at Iowa State University he transferred to Arizona State University where he obtained a M.S. in Chemical Engineering in 1977. At Arizona State he was affiliated with the late Drs. Samuel E. Craig, Jr. and Russel E. Harr on A.E.S. Research Projects 34 and 44, " Optimization of Barrel Plating Solutions." In 1977 he joined Motorola's Semiconductor Division as a Staff Engineer and is responsible for the development of lead frame plating processes for the Electronic Materials Group. Currently he is again a doctorial candidate at Iowa State, in conjunction with Motorola, where his research is directed towards thin film diffusion in semiconductor applications. Mr. Casey is a member of the Phoenix Branch of the American Electroplaters' Society.

D-4

Electronics I
Session D

High Speed Gold Plating From Dilute Electrolyte Part II

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Phoenix, Arizona

HIGH SPEED GOLD PLATING FROM DILUTE ELECTROLYTES

Part II - "Control of Surface Quality Utilizing Auger Electron Spectroscopy"

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Duane W. Endicott

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ABSTRACT

A brief review of the application of Auger Electron Spectroscopy (AES) to problems in the electronics industry, including grain boundary diffusion, is given. Process control applications to the transistor TO-92 gold electroplating process utilizing a Varian, Inc.[a] digital instrument are presented. C, K, O, Ni, and Cu were found on the surface of the die-bonded parts. Sources of these contaminants, reproducibility of the Auger data, surface nickel contour maps, and Auger data on the gold solution at three stages in its evolution are discussed. Wire bond results are discussed in light of the Auger data.

A companion paper (Part I - Solution Development and Functional Testing) describes the TO-92 process and equipment used in this study.

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a Varian, Inc., Palo Alto, Ca.

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Introduction

Auger Electron Spectroscopy (AES) has become an increasingly important tool for the investigation of surface contamination in the metal finishing industry. A brief description of AES has been published in this Journal by Dini and Musket[1] who reported a study of the effect of platers' tape on aluminum panels (adhesive contamination) and an application of the technique to uranium etching. Reviews of the major applications, limitations, and capabilities of AES are available in the articles by Chang[2,3] and Morabito and Hall.[4]

Recent applications of AES to the investigation of problems associated with metallization in the electronics industry include: several hybrid microcircuit studies of the evaporative tantalum nitride-chromium-gold system;[5-8] an investigation of thermo-compression (TC) gold/aluminum bonding and solder dipping of gold plated Kovar lead frames;[9] a surface analysis study of the transistor TO-5 header TC bond characteristics;[10] and an investigation of contaminants which influence the TC bonding of gold on Kovar lead frames and GaAs substrates.[11] This last application utilized gold plating solutions deliberately contaminated with 500 ppb to 1000 ppm nickel or copper and plated at .5 amp/dm^2. The authors conclude that the metallic surface impurities arise both from diffusion of codeposited impurities as well as diffusion of the substrate material. Adhesion of the TC bond is degraded by the presence of these impurities, especially when they are oxidized.

Several studies on aging of TC bonds to gold metallized thin film circuits in the communications industry exist. Ion sputtering for Auger depth profiling and subsequent diffusion calculations are reported by Hall, Panousis, and Menzel.[12] Hall, Morabito, and Panousis have reported complimentary Auger and conductivity studies for interdiffusion in the Cu-Au thin film hybrid integrated circuit and include bulk diffusion coefficients, ($\tilde{D}$) from 250°C to 25°C (utilizing and 18 year old sample) as well as an appendix for the deconvolution of AES in-depth profiling.[13]

Hall and Morabito have also presented a formalism for determining grain boundary diffusion coefficients (D') for Cu and Pd diffusing through gold on a titanium substrate from AES data.[14,15] These authors also discuss the use of relative sensitivity factors and sputter corrections as applied to the quantitative Auger analysis of gold-copper-oxygen and gold-nickel-oxygen systems on titanium substrates.[16] Nomographs are presented in Reference 14 and 15 for obtaining grain boundary diffusion coefficients while Reference 16 presents nomographs for obtaining atomic percent concentrations from Auger peak height ratios for both binary and ternary alloys.

Panousis and Hall report on the initial characterization[17] and long term reliability[18] of Au plated Cu leads with no diffusion barrier (e.g. nickel or cobalt) utilizing the grain boundary and volume diffusion coefficient studies cited above. These authors also report Arrhenius-type equations to predict failure of solderability and TC bondability of

copper leads plated with .73μm Au.[19] This study presents activation energies for these processes as well as the conclusion that the copper oxide on the surface is Cu_2O.

Tompkins and Pinnel have studied the diffusion of cobalt out of cobalt-hardened gold[20] and present a solution to the diffusion equation as well as low-temperature Arrhenius extrapolations of the diffusion coefficient. These authors also report two investigations on the diffusion of copper and nickel through cobalt-hardened gold.[21,22] The first discusses grain boundary diffusion measurements along with the boundary-value-problem assumptions. Their results indicate that diffusion via the defect structure is not the rate-controlling step in the accumulation of copper and/or copper compounds on the gold surface.[21] The second article reports a grain boundary diffusion coefficient (D') for nickel through gold which is between one and two orders of magnitude smaller than that determined for copper.[22] Results of other investigations are presented, in particular that of Hall and Morabito[23] who conclude that the grain boundary diffusion coefficients (D') of copper and nickel through gold are approximately equal over the temperature range 100 - 250°C, although they conclude that the bulk diffusion coefficient ($\tilde{D}$) for nickel in gold is much lower than that of copper.

The above investigations show that the quantitative use of AES has come of age. A new approach to the use of quantitative AES information as a process control tool is presented in this paper. Even though samples had to be shipped several hundred miles for analysis, turnaround time was still fast enough so that development projects, such as determining the effects of bath constituents or contamination, current density, flow rates, carbon treatment, etc., could be evaluated in conjunction with other information such as Scanning Electron Microphotographs (SEM), die and wire bond results, and solderability. These evaluations are generally concerned with the extension of gold bath lifetime for obvious economic reasons.

Experimental

A Varian Automated Auger Microprobe (A^2M) with digital data acquisition and submicron resolution was used to obtain all spectra and data. The Auger beam current was 5μA at 6 keV with a scan rate of 2.6 ev sec^{-1}, base pressure of 8×10^{-9} torr, and a beam diameter of 10 microns.

The A^2M instrument utilizes a floppy disc data acquisition system and its associated software to calculate an atomic percent for each element of interest by using an area under the curve formalism with Varian-generated sensitivity factors to account for electron cross sections and escape depths. These sensitivity factors are first-order computations based on empirical data and do not include corrections for matrix effects so that the reported atomic percents are accurate only to about 30%, however the precision of these calculated surface concentrations is sufficient to allow the Auger instrument to be used in process control and evaluation of changes in bath chemistry or operating conditions. The precision of the Auger data is discussed further in the Results and Discussion section.

The unique characteristic of the A^2M instrument is its direct acquisition of E•N(E) data instead of the typical derivative mode of data acquistion. Here, N(E) is defined as the number of electrons with energy E per unit energy interval. This allows the area under the curve formalism which has one advantage over derivative peak height measurements in that the former is not affected by changes in integral peak shape whereas the latter is. Thus, chemical shifts in the Auger spectra should not affect the reported atomic percents. However, disadvantages of the integral approach includes less versatility in handling background shifts and lack of an historical connection to the literature due to the newness of the integral approach.

The use of a high energy Auger gold peak (2024 ev) avoids the possible spectral interference problems associated with a low energy peak. However, the calculated nickel and oxygen values will be lower with the higher energy gold peak since the escape depth of the 2024 ev Auger electrons is about 20A whereas that of a 69 ev gold Auger electron is only about 5A.[24]

Results and Discussion

The transistor TO-92 technology used by Motorola's Semiconductor Group has already been described (Part I). A typical E•N(E) vs E Auger spectrum of the die bonded wire bond pad of this device is shown in Figure 1 while the $\frac{dN(E)}{dE}$ vs E spectrum is shown in Figure 2. AES peaks corresponding to C, K, O, Ni, Cu, and Au were detected.

Possible sources of the carbon would be either adsorbtion of hydrocarbons from the atomosphere with subsequent cracking in the Auger beam[7] or incorporation of the organic chelating material, which is the only solution constituent containing carbon other than potassium gold cyanide, into the electrodeposit with subsequent migration to the surface during the die attach heat cycle.[25] Cyanide polymer formation has been ruled out since the Auger investigation revealed no nitrogen peaks. Since an unheated wire bond pad yielded the same atomic percent carbon (24) and argon ion sputtering with subsequent Auger analysis of a heat treated part indicated that carbon was not present throughout the deposit, the adsorbed carbon hypothesis is preferred. Whether this carbon is from hydrocarbons in the atomosphere, as indicated in the literature[7] or from incomplete rinsing of entrapped gold solution from the surface grains has yet to be determined.

Potassium is present as the cation of the conductivity salt in the gold solution so it's presence (.05-.30 atomic %) in the deposit is not surprising. Likewise, since a copper lead frame is used, the presence of a trace amount (.03-.10 atomic %) of copper is also expected.

Nickel on the surface may occur either as a result of codeposition or substrate diffusion as mentioned earlier.[11] Since the organic chelating material is present to inhibit codeposition of nickel the source of the surface nickel is considered to be primarily from the substrate diffusion via grain boundaries. This is confirmed by Auger data obtained on Motorola's

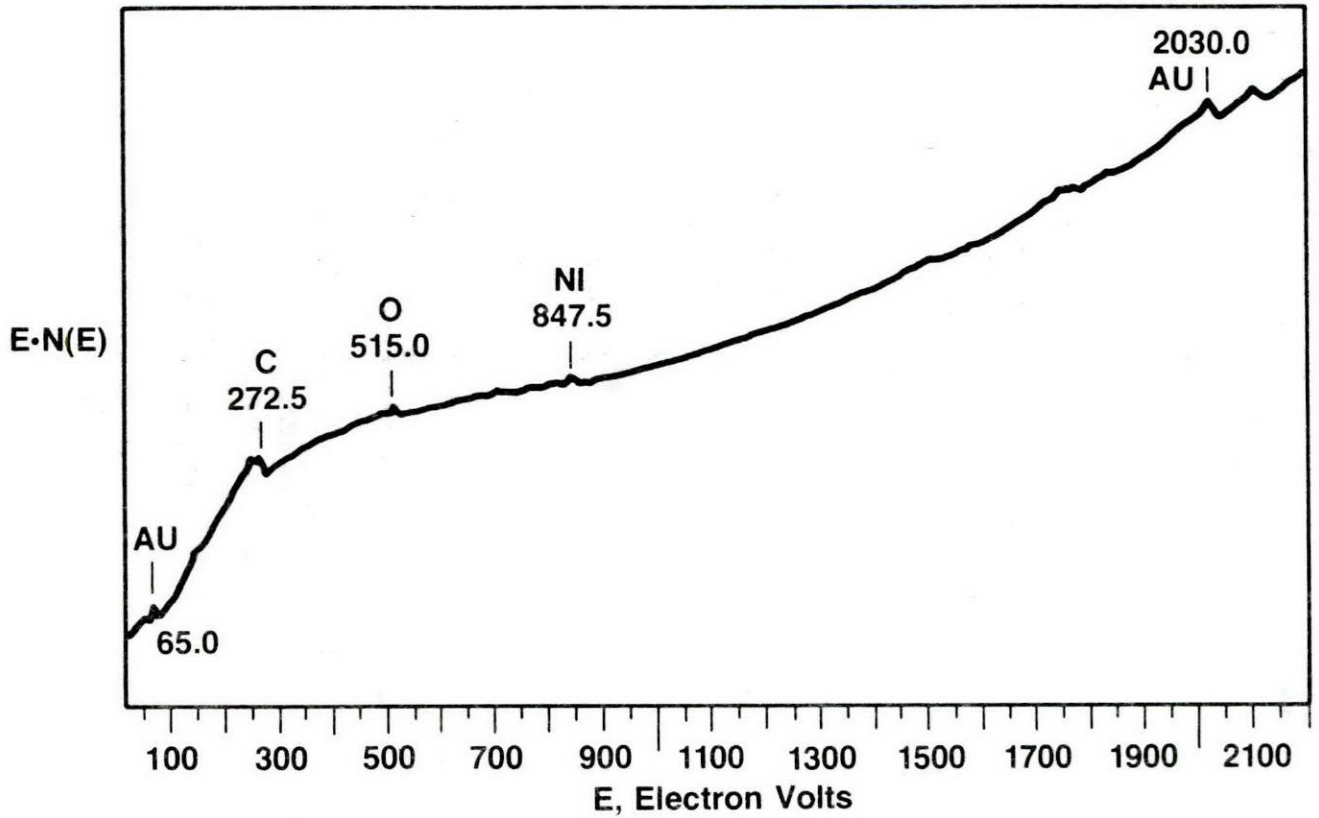

Figure 1. E•N(E) vs E Auger Spectrum of Wire Bond Pad

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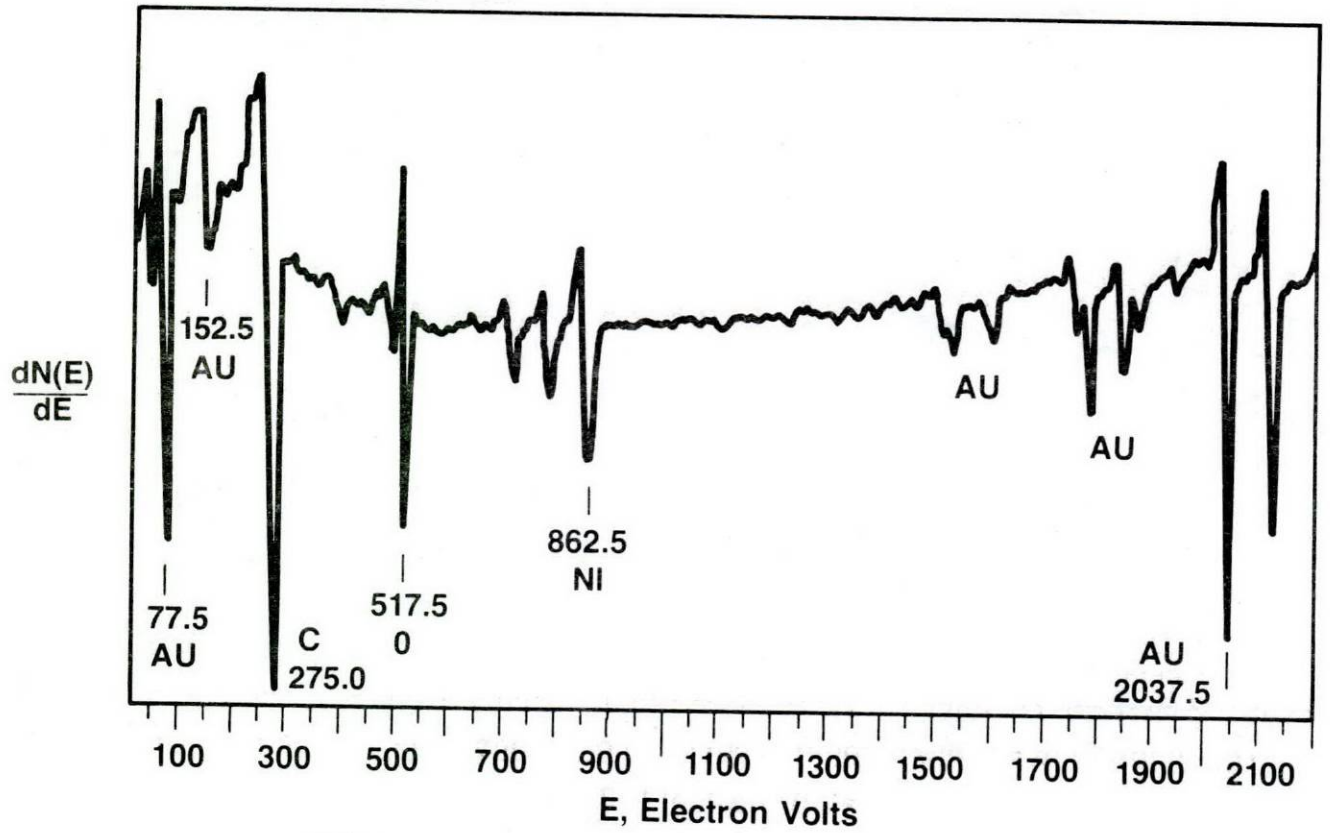

Figure 2. $\frac{dN(E)}{dE}$ vs E Auger Spectrum of Wire Bond Pad

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Central Research PHI[b] Auger system.[26] Nickel plated copper and tantalum blanks were processed on the ACR[c] machine and the gold deposits analyzed by AES. The tantalum blank had only 20% of the nickel compared to the nickel substrate blank. This is to be expected since both grain boundary and bulk diffusion can occur at the die bonding temperature of 460°C, which is about .55 T_m. It is generally accepted that bulk diffusion appears above .3 - .5 T_m, where, in this case, T_m is the melting point of gold in absolute degress.[21,27] That is, bulk diffusion can result from diffusion of the substrate material into gold grains with subsequent diffusion into gold grain boundaries, or from diffusion of codeposited nickel out of the gold grains and into the gold grain boundaries. Diffusion via grain boundaries are from two to four orders of magnitude greater than the corresponding bulk diffusion rates.[22]

The amount of observed oxygen is usually between 1/3 to 1/2 of the amount of nickel. It is generally accepted that the oxygen is in the form of a metallic oxide[9], in this case probably NiO, particularly since the oxygen content follows the nickel content rather closely. Formation of the oxide of nickel is very detrimental to TC bonding since gold will not adhere well to oxides.[28]

Table I lists the Auger data for an early gold solution as a function of temperature, while Figure 3 displays the Auger nickel data in graphical form. Note that the average O/Ni ratio decreased with increasing temperature.

TABLE I
TEMPERATURE EFFECT ON AUGER DATA

TEMP (°C)	UNITS PLATED (X10^6)	ATOMIC % Ni	O	O/Ni	C	Au
440	0.00	.45	.22	.49	20.5	77.8
	1.10	.60	.26	.43	20.8	77.2
	2.75	1.4	.40	.29	20.3	76.2
			Average	.40	20.5	
460	0.00	.58	.25	.43	21.0	77.3
	1.10	1.2	.47	.39	21.1	76.2
	2.75	2.4	.72	.30	19.5	75.7
			Average	.37	20.5	
480	0.00	.95	.38	.40	21.7	75.9
	1.10	1.4	.52	.37	21.5	75.5
	2.75	3.6	1.0	.28	18.6	74.9
			Average	.35	20.6	
500	0.00	1.7	.54	.32	21.2	75.4
	1.10	1.7	.56	.33	20.6	76.1
	2.75	4.0	1.2	.30	19.5	73.5
			Average	.32	20.4	

b Physical Electronics Inc., Division of Perkin-Elmer, Minneapolis, Mn.
c American Chemical and Refining, Los Angeles, Ca.

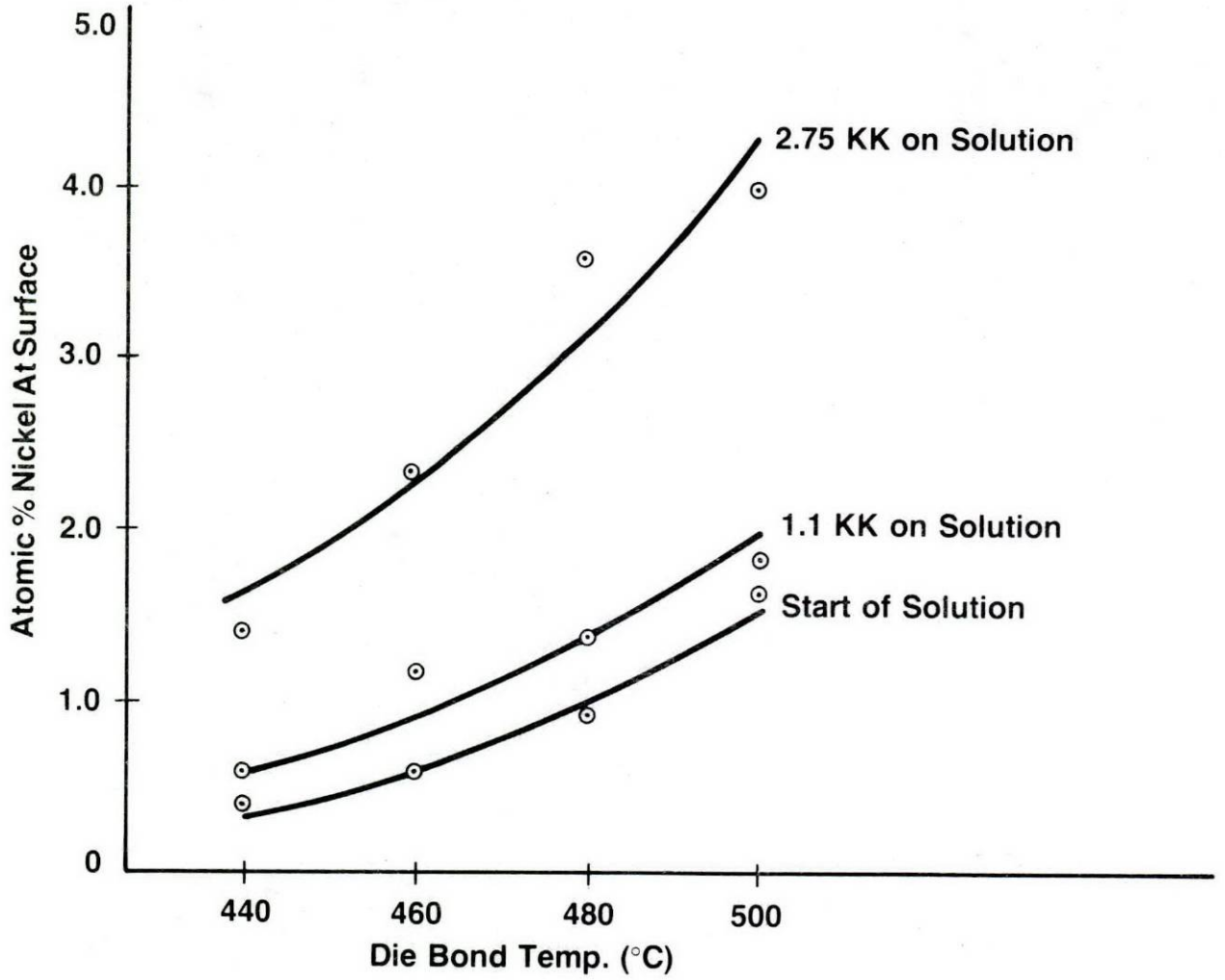

Figure 3. Auger Atomic Percent Nickel vs Die Bond Temperature for Early Production Gold Solution

This effect may be explained in several ways. Unfortunately, none of the explanations can be considered conclusive, without further investigation with such tools as Auger depth profiling and secondary ion mass spectroscopy (SIMS).[29-31] Several factors can cause inhomogeneity in the sputtering process, one of these is the preferential sputtering of oxygen atoms over the nickel atoms.[16,32] The reader is referred to Reference 32 for a discussion of the problems encountered in obtaining corrected Auger depth profiles.

One explanation for the observed O/Ni ratios is that, at the higher temperatures, nickel is diffusing faster than it can be oxidized. This conclusion is of interest, since many diffusion models assume that a surface sink exists whereby the metallic contaminant is immediately oxidized upon arrival at the gold surface.[20,33,34] This explanation is probably unlikely, since the Auger signal comes from only 7 Å into the surface, and as a 7 Å thickness of nickel is only about a monolayer, there should be no physical barrier to the oxidation process although a kinetic barrier may exist.[19,21,22]

Several depth profiles obtained on Motorola's PHI Auger equipment indicate that the concentration of nickel decreases to almost zero in the first 100 Å of the surface.[35] This result would also suggest that the surface-sink assumption be re-examined.

A second explanation for the observed O/Ni ratios would be the preferential reaction of carbon with oxygen at the higher temperatures. If this is the case, the amount of carbon on the surface should be less at the higher temperatures, which is not observed.

Additional work is currently being done at Motorola to more clearly explain the observed O/Ni ratios.

As mentioned in Part I, the Auger technique was used in the determination of the operating concentration of the organic chelating agent, ingredient D. Gold strike and plate solutions were made without the organic chelating material so that the effect of nickel contamination could be studied both before and after addition of the chelator. The results are summarized in Table II which lists the Auger atomic percent nickel for the various nickel and chelator levels. All wire bond results were acceptable, that is, no full or partial lifts were observed.

TABLE II

NICKEL CONTAMINATION AND CHELATOR TESTS

Nickel in Solution, ppm		Chelator Concentration Grams/Liter		Auger Atomic %
Gold Strike	Gold Plate	Gold Strike	Gold Plate*	Nickel
0	0	0	0	3.3
0	5	0	0	1.5
0	10	0	0	0.72
0	15	0	0	1.1
0	20	0	0	1.4
0	30	0	0	1.6
0	30	0	0.47	0.78
10	30	0	0.47	2.0
15	30	0	0.47	1.7
20	30	0	0.47	1.0
25	30	0	0.47	1.0
30	30	0	0.47	0.67
50	50	0	0.47	1.3
50	50	0.75	0.75	1.4
50	50	0.75	0.75	1.4

*Current density: 86.1 amperes/dm^2

With no nickel in the gold strike solution and no chelator present, the amount of surface nickel decreased as the nickel level in the gold plate solution increased from 0 to 10 ppm. Further increasing the nickel level in the plate solution from 15 to 30 ppm increased the amount of surface nickel. It is possible that the nickel, at concentrations less than 10 ppm, acts as an agent which increases the deposit density. The effect of the chelator is seen when .47 g/l are added to a plate solution containing 30 ppm nickel. The atomic percent nickel is halved from 1.6 to 0.78.

With chelator present in the plate solution, the initial addition of nickel to the strike solution increases the amount of surface nickel but further addition of nickel to the strike solution results in a decrease in the amount of surface nickel.

No reason is offered for the initial increase, although evidence is presented in a later section which shows that the surface distribution of nickel is not uniform. The subsequent decrease in surface nickel could again be due to increased deposit density.

Above 30 ppm nickel in both the strike and plate solutions an increased level of nickel contamination results in increased surface nickel. At 50 ppm nickel in both the strike and plate, increasing the chelator concentration from .47 to .75 g/l has no effect, either deleterious or beneficial on wire bonding or on the amount of surface nickel.

Thus it appears that a low level of nickel contamination in the gold solutions is actually beneficial although this conclusion can not be obtained from wire bond results. Data not presented here indicates an increase in the amount of surface nickel when the chelator level is above 1.50 g/l. At this level of concentration, the chelator is probably acting as an organic contaminant. Thus, the operating level of chelator was fixed at .75 g/l since this will allow for drag out effects and initially be capable of complexing up to 100 ppm of nickel. Nickel levels in production solutions have never exceeded 40 ppm for the strike or 20 ppm for the plate and typically are not above 20 and 5 ppm respectively.

As mentioned earlier, the precision of the Auger data is such that it may be used to evaluate process changes in the gold bath. Table III illustrates the reproducibility of the calculated atomic percents. Ten parts from a 20 inch section of lead frame were selected at random for Auger analysis. With the exception of one part, the reproducibility was quite good. Of interest is the O/Ni ratio, it is reproducible within $\pm 2\sigma$, where σ is the relative standard deviation of the sample. In this case it means that the O/Ni ratio is .36 ± .05. This lends further support to the conclusion drawn from the data in Table I. The differences in the O/Ni ratio as a function of temperature are indeed real differences and not experimental artifacts.

TABLE III

REPRODUCTIBILITY OF AUTOMATED MACHINE AUGER DATA

Atomic %

Sample	Ni	O	O/Ni	C	Au
A	2.7	.99	.37	32.7	62.7
B	2.4	.91	.38	29.0	66.6
C	2.5	.91	.36	26.4	69.2
D	3.0	1.0	.33	30.8	64.1
E	2.6	.97	.37	26.4	69.1
F	2.1	.83	.40	28.3	67.9
G	2.5	.94	.38	26.3	69.4
H	6.2	1.9	.31	38.3	52.6
I	3.8	1.3	.34	26.6	67.2
J	4.0	1.3	.33	30.8	62.8
*Avg.	2.8	1.0	.36	28.6	66.6
σ, Sample Rel. Std. Dev. (%)	23.0	16.9	6.8	8.4	4.1

*not including H

Although the precision of the Auger data is quite good, the calculated atomic percents are not of an absolute nature, due to the matrix effects. However, the same matrix was used throughout this study, so that relative differences in the Auger data are clearly defined, although the absolute

differences are not. In order to accurately calculate an atomic percent, standards consisting of the same matrix would have to be prepared with ion implantation or diffusion techniques.

An explanation for the "outlier," sample H, in Table III may be found be referring to Figures 4a and 4b which are surface contour maps of the nickel on the surface of the gold obtained with an Auger beam diameter of 4 microns.

The rack control is shown in 4a while that of a typical part from the automated machine (number 143-168) is shown in 4b. The area of interest is 99 X 99 micrometers and was taken from the center of an unbonded post. The maps were computer generated by manipulation of the difference between the nickel Auger signal at 843 ev and the background signal at 870 ev. The contour lines are at the 50% level. That is, those areas shaded dark grey represent a surface concentration of nickel between the maximum local value of the above difference and 50% of this value, while the light grey areas represent a concentration below 50% of the maximum local value.

Both the rack plated part and automated machine part exhibit an uneven surface distribution of nickel. Since the reproducibility of the contour maps has not yet been investigated the only conclusion that can be drawn is that the 10 micron Auger beam could be occasionally positioned to yield an unusually high or low atomic percent of nickel. This could also result in an occasional unexplained wire bond lift result.

The percentage of TC bond failures is directly related to the amount of nickel diffused to the surface of the gold. Figure 5 is a typical plot of the amount of nickel versus the percentage of complete wire bond lifts. The reader is referred to the companion paper for definitions of the various modes of bond failure.

No attempt was made to correlate the bond strength with the level of nickel contamination, since, for the TO-92 transistor, the pass-fail criteria for a bond is if it yields a complete lift. The product specification is met only by product with no more than 1% complete lifts. Above approximately two atomic percent nickel, the number of complete wire lifts exceeds production specifications, although acceptable product has been produced with nickel contamination between two and three atomic percent. Avove three atomic percent nickel, the percentage of complete wire lifts is nearly always outside the product specification.

This grey area of lifts between two and three atomic percent nickel can probably be attributed to an uneven surface distribution of nickel as mentioned earlier.

Before discussing the Auger data associated with the evolution of the gold process on the ACR machine, the controlled-depth rack process Auger data will be presented in Table IV, since the rack-plated parts are the control samples for the automated process. This rack process has been in use since 1971 and the Auger data were obtained from rack samples plated between December 1977 and November 1978. Rack samples were chosen at random over this time period. Furthermore, the samples were obtained at

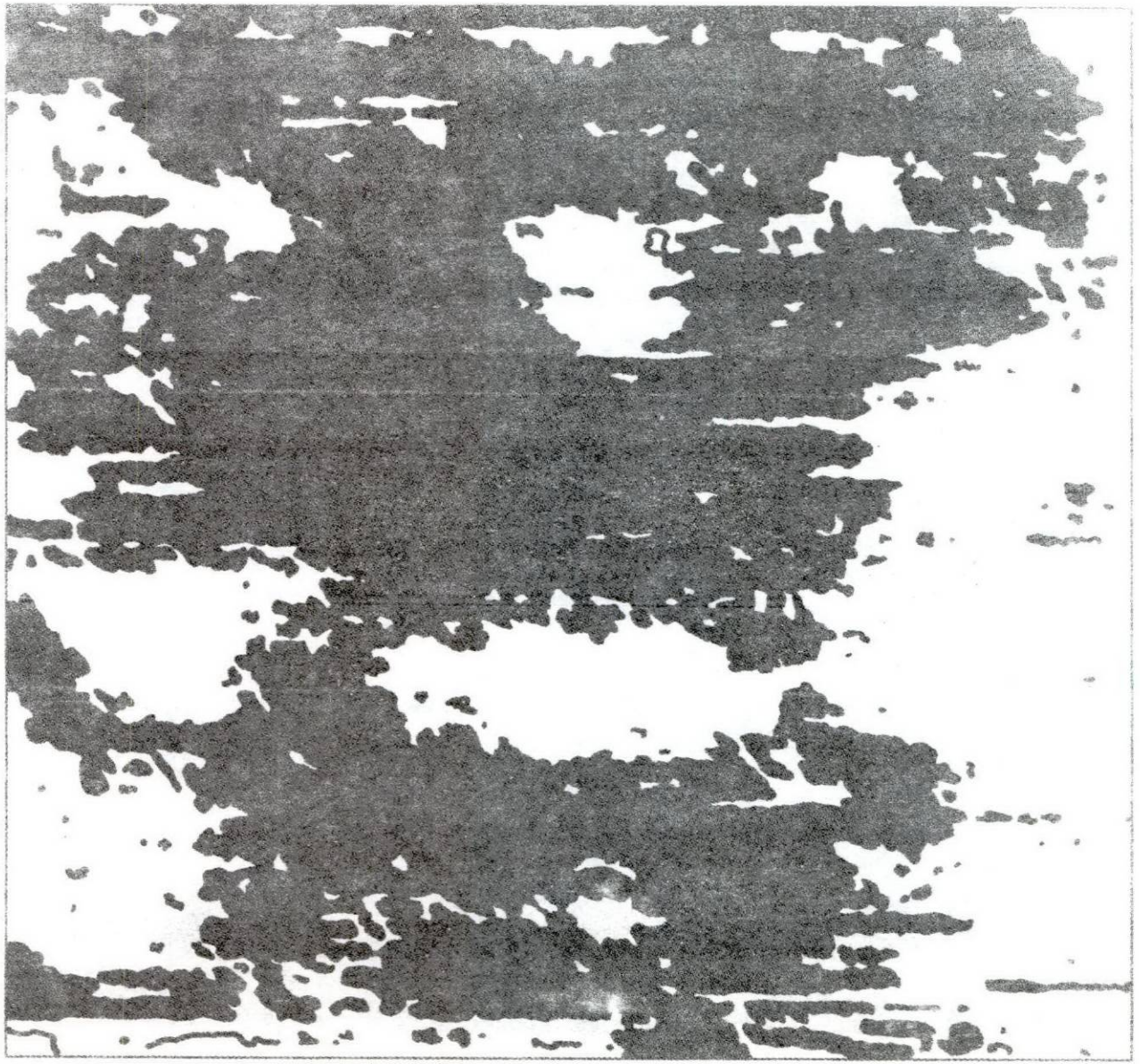

Figure 4a. Rack Plated Surface Nickel Contour Map

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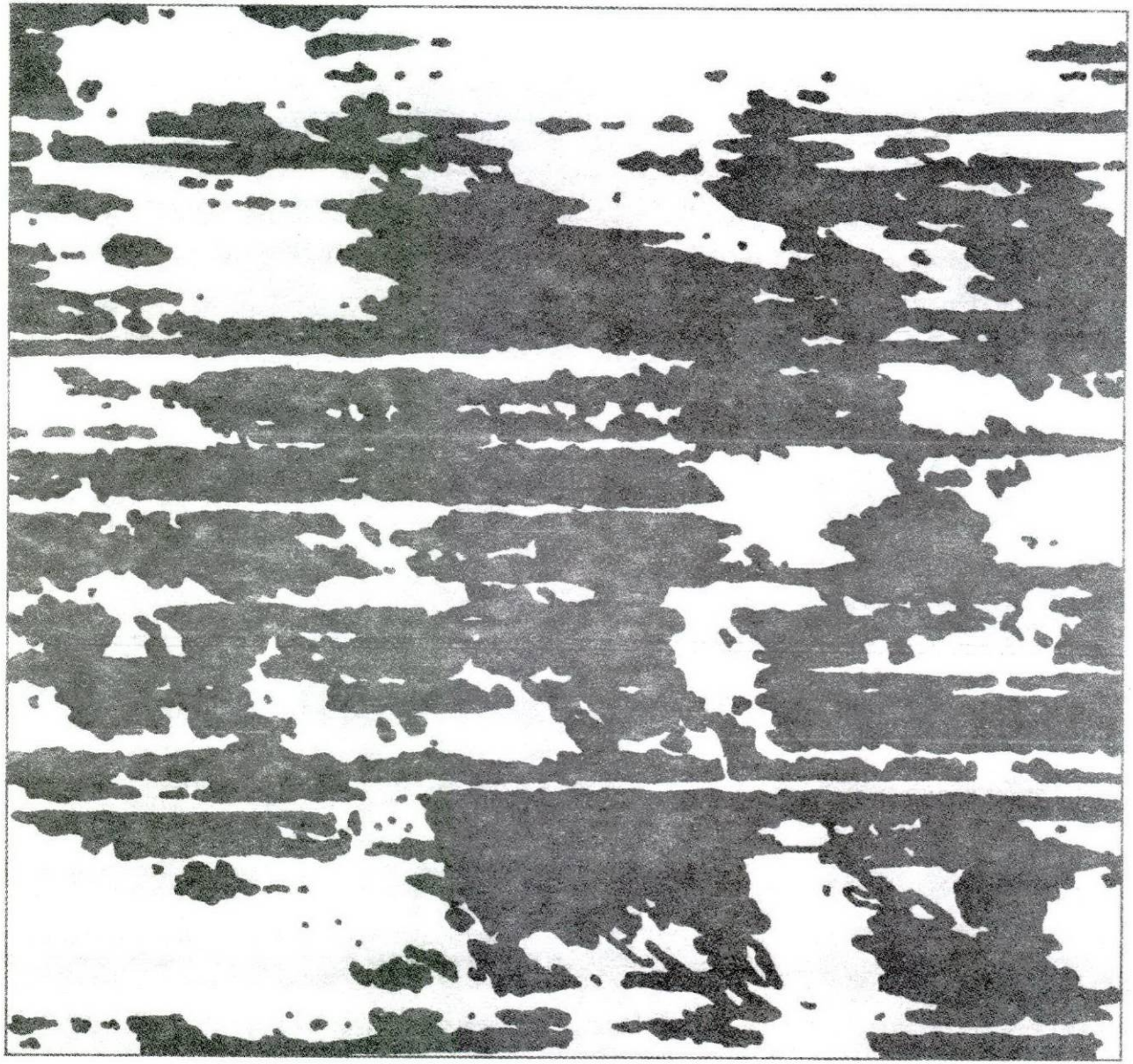

Figure 4b. Continuous, Selectively Plated Surface Nickel Contour Map

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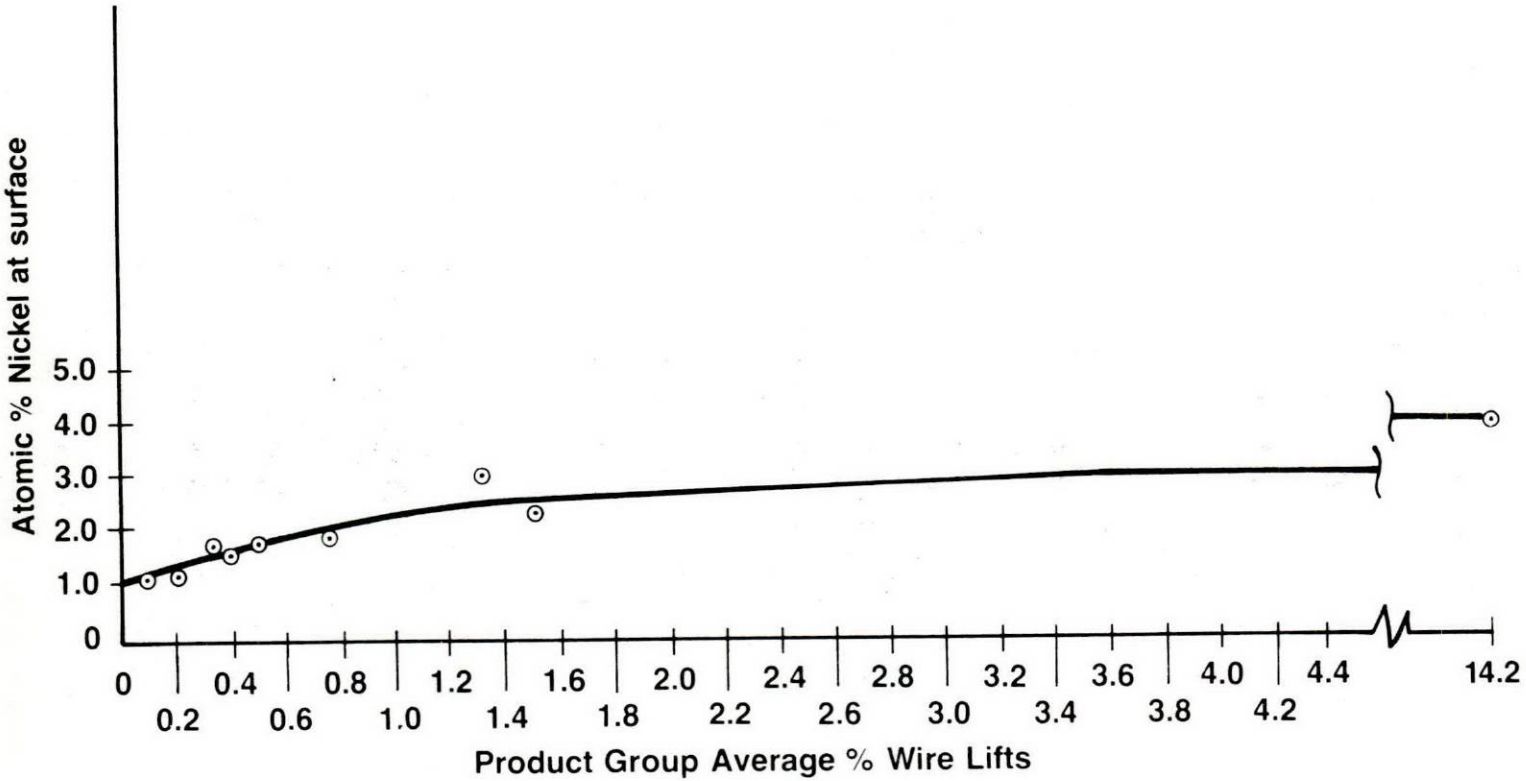

Figure 5. Auger Atomic Percent Nickel vs Complete Wire Bond Lifts

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various stages in the lifetime of the rack final gold solution. Note that there is no dependence of nickel content on solution life, which has varied between one and two years depending upon production requirements. Again, the average O/Ni ratio is about .40. Data was taken after a 460°C die bond heat excursion.

TABLE IV

RACK AUGER DATA

Atomic %

Sample No.	Ni	O	O/Ni	C	Au
1	3.2	.78	.24	40.0	56.6
2	.99	.42	.42	36.6	62.8
3	1.3	.46	.35	31.9	67.6
4	1.2	.34	.28	34.2	64.7
5	.98	.52	.53	36.0	62.8
6	1.9	.56	.29	28.4	68.8
7	1.7	.77	.45	36.3	61.2
8	1.5	.56	.37	30.1	67.8
9	1.6	.65	.40	29.9	67.6
10	2.0	.89	.45	31.4	65.5
11	2.1	.75	.36	28.2	62.7
12	1.7	.69	.41	28.1	69.1
13	2.0	.73	.37	25.2	71.6
*Avg.	1.6	.61	.39	31.4	66.0
σ, Sample Rel. Std. Dev. (%)	24.7	26.6	17.9	11.9	4.9

*not including sample #1

Table V lists the Auger data as a function of gold solution life for a preliminary production solution, while Figure 6 plots the Auger nickel level as a function of solution life. While this solution was contaminated by stamping oil from the raw parts, due to drag-in caused by failure of the degreaser pump, the rise in nickel content at the 2 million level is not atypical. Carbon treatment of the gold solution at 3.5 million units lowered the Auger nickel content to 2.0 atomic percent which also supports the organic contamination theory. At this point, the nickel level again began to rise, and the wire bond results were again unacceptable. Future gold solutions were operated until 2 million units were accumulated at which point the gold was reclaimed and a new solution made up.

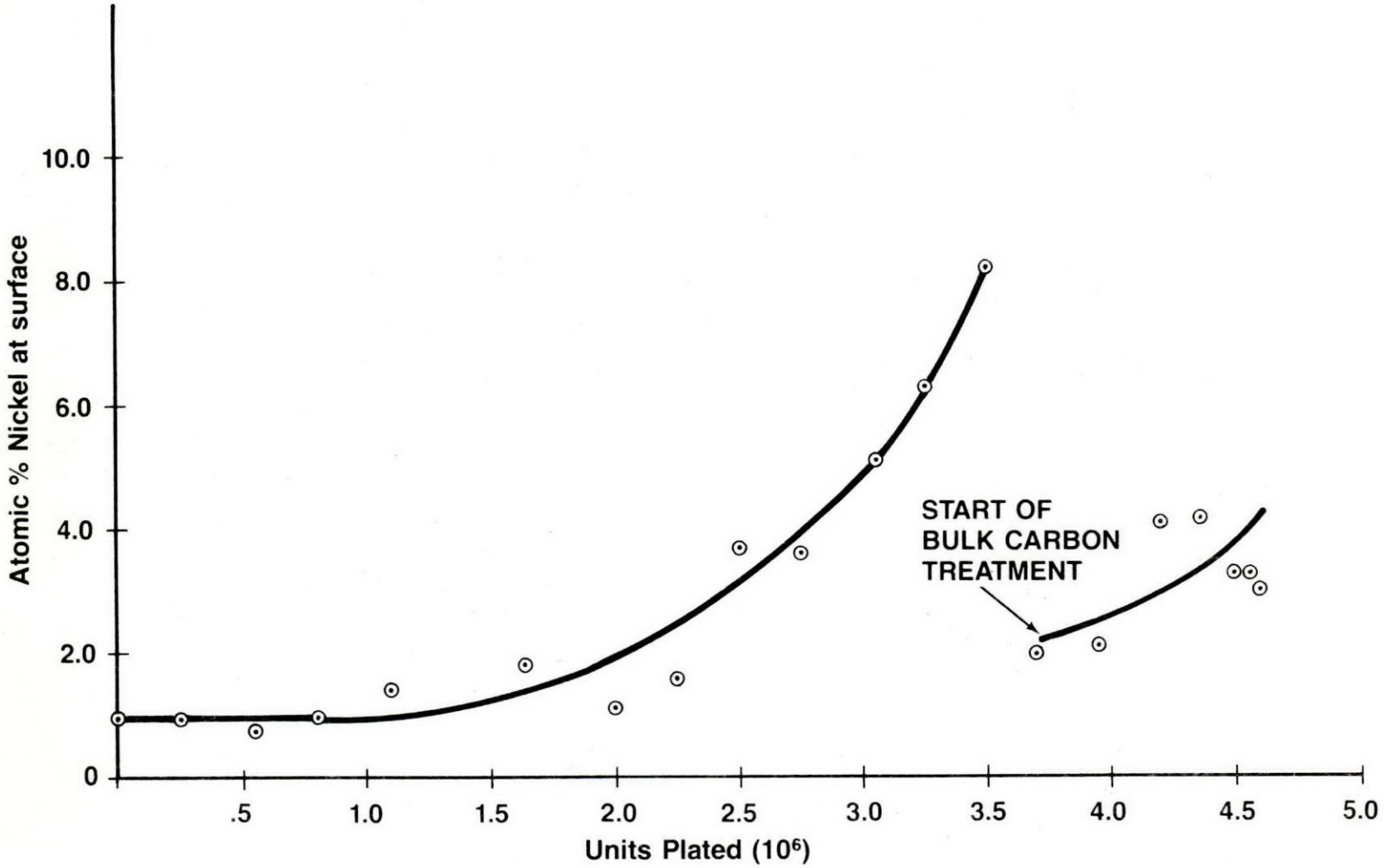

Figure 6. Auger Atomic Percent Nickel vs Solution Life for Early Production Cold Solution

E9337

TABLE V

PRELIMINARY GOLD SOLUTION AUGER DATA

Atomic %

# Units ($X10^6$)	Ni	O	O/Ni	C	Au
0.00	0.95	.38	.40	21.7	75.9
0.25	0.92	.36	.39	21.7	75.7
0.55	0.73	.40	.55	21.5	76.3
0.80	0.97	.21	.22	20.8	76.9
1.10	1.4	.52	.37	21.5	75.5
1.65	1.8	.23	.13	21.1	75.1
2.00	1.1	.30	.27	20.3	76.6
2.25	1.6	.46	.29	21.0	75.1
2.50	3.7	1.3	.35	18.1	75.0
2.75	3.6	1.0	.28	18.6	75.0
3.05	5.1	1.5	.29	16.1	75.1
3.25	6.3	1.8	.29	18.9	71.2
3.50	8.2	2.3	.28	16.2	70.2
*3.70	2.0	.82	.41	17.5	77.4
3.95	2.1	.56	.27	25.0	71.4
4.20	4.1	1.1	.27	28.1	65.1
4.35	4.2	1.2	.29	23.8	69.8
4.50	3.3	.95	.29	26.0	68.8
4.55	3.3	1.0	.30	25.5	69.3
4.60	3.0	1.1	.37	34.1	61.4
		Average	.32		

*start of bulk carbon treatment

This practice continued for five months at which time the freshly made-up solution was carbon treated and the content of additive C, the ingredient controlling deposit density and brightness was increased from 1.0 to 3.0 g/liter. These changes allowed a gold solution to plate over 4 million units before failure of wire bonds due to increased nickel levels occurred. Auger data for this type of solution is presented in Table VI. Again, the average O/Ni ratio is about .44.

TABLE VI

MIDDLE GOLD SOLUTION AUGER DATA

Atomic %

# Units ($X10^6$)	Ni	O	O/Ni	C	Au
.08	2.8	.80	.29	34.5	62.3
.45	1.4	.59	.42	35.2	63.5
.83	1.2	.83	.69	32.9	65.4
1.02	.84	.38	.45	33.7	65.7
1.20	1.2	.56	.47	34.2	64.5
1.63	1.1	.57	.52	34.7	64.1
2.03	1.4	.39	.28	32.5	65.9
2.30	.84	.51	.61	37.4	61.6
3.02	.87	.30	.34	34.1	65.0
3.90	.79	.27	.34	40.0	59.3
4.29	.73	.42	.58	42.1	57.1
4.34	1.6	.44	.28	35.2	62.9
Avg.	1.2	.51	.44	35.5	63.1

An additional increase in the production schedule required an extension of the solution life to at least 10 million units. This objective was realized by continuing the initial carbon treatment of the gold solution, keeping the initial concentration of ingredient C at 3.0 g/l, and further carbon treatment at 4.5 and 9.0 million units, along with an increasing concentration of ingredient C such that the solution contained 9.0 g/l at the end of its useful life. The additional carbon treatments were done using two, ten inch activated carbon filter cartridges so that production would remain uninterrupted. These improvements to the operation of the solution allowed over 12 million units to be plated before unacceptable wire bonds occurred. The effect of the additional carbon treatment is best seen in Figure 7, which plots the Auger nickel data from Table VII versus the number of units plated. Again, the O/Ni ratio was about .43. Note the decrease in the amount of surface nickel concommitant with the carbon treatment.

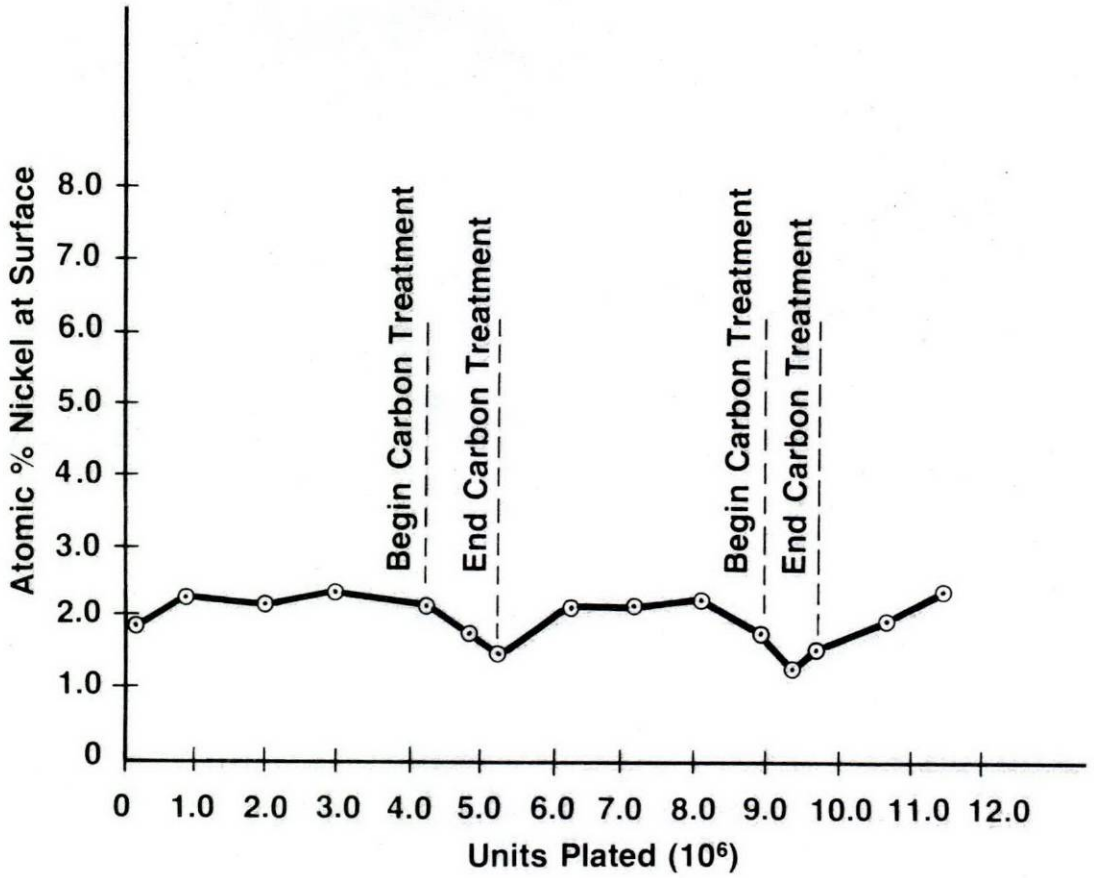

Figure 7. Auger Atomic Percent Nickel vs Solution Life for Final Production Cold Solution

E9324

TABLE VII

FINAL GOLD SOLUTION AUGER DATA

Atomic %

# Units ($X10^6$)	Ni	O	O/Ni	C	Au
.18	1.9	.63	.33	25.7	71.5
.88	2.3	.83	.36	27.1	69.5
2.02	2.2	.77	.35	23.2	73.4
2.98	2.4	.75	.31	18.7	77.7
4.28	2.2	.77	.35	27.2	69.8
4.90	1.8	.68	.38	24.2	73.1
5.26	1.5	.65	.43	24.2	73.3
6.20	2.2	.76	.35	25.5	71.1
7.20	2.2	.83	.38	25.6	71.2
8.10	2.3	.92	.40	28.0	68.4
9.00	1.8	.82	.46	24.8	71.8
9.40	1.3	1.2	.92	24.2	71.6
9.70	1.6	.98	.61	32.8	63.4
10.70	2.0	.87	.44	26.4	70.2
11.50	2.4	.98	.41	31.6	64.9
Avg.	2.0	.83	.43	25.9	70.7

Conclusions

The use of Auger Electron Spectroscopy as a process control tool in the evolution of a gold plating solution has been demonstrated. Carbon has been shown to be a surface contaminant only and most of the nickel responsible for wire bond failure is due to diffusion of the substrate and not codeposited nickel. The temperature dependence of the oxygen to nickel ratio suggests that the surface sink assumption inherent in some diffusion models should be re-examined.

Progressively increasing the concentration of ingredient C, which controls deposit density and brightness, along with periodic carbon treatment increases the useful life of the gold solution to over 12 million units. The chelator concentration was optimized by consideration of Auger data since wire bond results alone could not. A small amount of nickel contamination (less than 10 ppm) is beneficial in the gold solution. Finally, the surface nickel contour maps indicate an uneven surface distribution of nickel.

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References

1. J. W. Dini and R. G. Musket, This Journal, 60, 811, 1973.

2. C. C. Chang, Surface Science, 25, 53, 1971.

3. C. C. Chang, Surface Science, 48, 9, 1975.

4. P. M. Hall and J. M. Morabito, Scanning Electron Microscopy/1976. Proc. 9th Annual Scanning Electron Microscope Symp. IIT Research Institute, Chicago, Il. p 221-230.

5. J. L. Jellison, IEEE Trans. PHP-11, 206, Spt. 1975.

6. N. T. Panousis and H. B. Bonham, 11th Annual Proc. Reliability Physics (IEEE), 21, 1973.

7. P. H. Holloway and D. W. Bushmire, 12th Annual Proc. Reliability Physics (IEEEE), 180, 1974.

8. J. M. Morabito, Thin Solid Films, 19, 21, 1973.

9. A. J. Gonzales, 11th Annual Proc. Reliability Physics, (IEEE), 185, 1973.

10. N. C. MacDonald, Extended Abstracts, Electrochemical Society, 73-2, Boston, Mass., Oct. 7-11, 479, 1973.

11. G. E. McGuire, J. V. Jones, and H. J. Dowell, Thin Solid Films, 45, 59, 1977.

12. P. M. Hall, N. T. Panousis, and P. R. Menzel, IEEE Trans. PHP-11, 202, Sept. 1975.

13. P. M. Hall, J. M. Morabito, and N. T. Panousis, Thin Solid Films, 41, 341, 1977.

14. P. M. Hall and J. M. Morabito, Surface Science, 59, 624, 1976.

15. P. M. Hall and J. M. Morabito, Surface Science, 54, 79, 1976.

16. P. M. Hall and J. M. Morabito, Surface Science, 67, 373, 1977.

17. N. T. Panousis and P. M. Hall, IEEE Trans. PHP-13, 305, Sept. 1977.

18. N. T. Panousis and P. M. Hall, IEEE Trans. PHP-13, 309, Sept. 1977.

19. N. T. Panousis and P. M. Hall, Thin Solid Films, 53, (2), 183, 1978.

20. H. G. Tompkins, J. Electrochem. Soc. 122, 983, 1975.

21. H. G. Tompkins and M. R. Pinnel, J. Applied Physics, 47, 3804, 1976.

22. H. G. Tompkins and M. R. Pinnel, J. Applied Physics, 48, 3144, 1977.

23. P. M. Hall and J. M. Morabito, Thin Solid Films, 53, 175, 1978.

24. P. W. Palmberg, G. E. Riach, R. E. Weber, and N. C. MacDonald, "Handbook of Auger Electron Spectroscopy," Physical Electronics Industries, Minnesota, 2nd Edition, 1976.

25. S. Nakahara and Y. Okinaka, Extended Abstracts, Electrochemical Society, 75-2, Dallas, Texas, Oct. 5-10, 398, 1975.

26. B. C. Johnson, S. Thomas, and L. Richardson, Extended Abstract, Proc. Electrochemical Soc., Pittsburgh, Pa., Oct. 5, 1978.

27. R. W. Balluffi, Phys. Status Solidi, 42, 11, 1970.

28. K. E. Haq, K. H. Behrndt, and I. Kobin, J. Vac. Sci. Technol., 6, 148, 1969.

29. J. M. Morabito and R. K. Lewis, Anal. Chem., 45, #6, 869, 1973.

30. J. M. Morabito, Anal. Chem., 46, #2, 189, 1974.

31. J. M. Morabito and M. J. Rand, Thin Solid Films, 22, 293, 1974.

32. P. M. Hall and J. M. Morabito, CRC Critical Reviews in Solid State Sciences and Materials Sciences, 8, 53, 1978.

33. A. D. LeClaire, Brit. J. Appl. Phys., 14, 351, 1963.

34. R. F. Canon and J. P. Stark, J. Appl. Phys., 40, 4361, 1969.

35. B. Johnson, Motorola Semiconductor Group, Central Research, Private Communication.

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George J. Casey, Jr., CEF, received his B.S. in chemistry from Lebanon Valley College in 1973. After spending two years in the graduate program in chemistry at Iowa State University he transferred to Arizona State University where he obtained a M.S. in Chemical Engineering in 1977. At Arizona State he was affiliated with the late Drs. Samuel E. Craig, Jr. and Russel E. Harr on A.E.S. Research Projects 34 and 44, " Optimization of Barrel Plating Solutions." In 1977 he joined Motorola's Semiconductor Division as a Staff Engineer and is responsible for the development of lead frame plating processes for the Electronic Materials Group. Currently he is again a doctorial candidate at Iowa State, in conjunction with Motorola, where his research is directed towards thin film diffusion in semiconductor applications. Mr. Casey is a member of the Phoenix Branch of the American Electroplaters' Society.

Duane Endicott has been Manager of Metal Finishing Development for domestic and foreign facilities at Motorola's Semiconductor Group since 1974. Prior to this he held various engineering and other managerial positions in the Metal Finishing Department since 1965. Previous industrial experience was with the Bendix Corporation A.E.C. Division as Process Engineer in the Metal Finishing Department.

Duane has a Bachelor Degree in both Physics and Chemical Engineering and completed two years of graduate studies in Chemical Engineering at the University of Kansas. A member of A.E.S. since 1961, Duane is the recipient of the Carl E. Heussner and George B. Hogaboom awards for the best publication by the A.E.S. in 1966. Duane has also served as a member of the Paper's Committee and committee member of A.E.S. Research Projects 34 and 44.

D-5

Electronics I
Session D

Evaluation of an Improved Ruthenium Plating Process

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EVALUATION OF AN IMPROVED RUTHENIUM PLATING PROCESS

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ABSTRACT

Electroplated ruthenium is a prime candidate for electrical contact applications but has not been widely used because of the difficulty in consistently obtaining sound deposits. An improved ruthenium plating process utilizing a buffered acid solution of the ruthenium compound $K_3[Ru_2N(H_2O)_2Cl_8]$ in a compartmented plating cell has been evaluated in the small scale manufacture of sealed reed contacts. The process produces pure deposits that have lower stresses than those from conventional solutions and operates with a cathode efficiency that remains constant throughout several metal turnovers of the solution.

Introduction

Electroplated ruthenium is an attractive alternate for electroplated gold as an electrical contact material. Compared with gold, its lower density and selling price result in a roughly sixfold cost advantage for equal deposit thicknesses. While ruthenium will oxidize in air at ambient temperatures, the thin oxide layer (RuO_2) is adherent and protective, much like the oxide layer on titanium. However, unlike titanium dioxide, ruthenium dioxide has a conductivity essentially the same as the parent metal.[1,2] In addition, ruthenium dioxide is not attacked by hot or cold acids or aqua regia.[3] Ruthenium is very hard and when tested in a slip ring application was found to have better wear resistance than electrodeposited rhodium.[4]

With all of these positive properties, the question arises as to why electrodeposited ruthenium has not had widespread application. The answer to this is that the electrolytes that have been reported in the literature suffer from one or more of the following limitations: low and variable cathode current efficiency, sensitivity to solution agitation, production of highly stressed impure deposits, instability of the ruthenium compounds used, and formation of volatile toxic compounds during electrolysis.[5,6,7]

The issuing of three patents[8,9,10] covering ruthenium electrodeposition on April 4, 1978 indicates the degree of interest in overcoming the deficiencies discussed above. The patent issued to Heller, Miller, and Vadimsky[9] describes the synthesis of a pure ruthenium salt and its use in an electroplating process capable of producing crack free deposits at a constant cathode efficiency, and it was this system that was studied here.

In order to evaluate this process for production, a pilot ruthenium electroplating line was set up to plate the contact surfaces of sealed reed contacts. The reed contact consists of two Remendur (49% Co, 49% Fe, 2% V) reeds sealed in a glass envelope, as shown in Fig. 1. Currently, the contact area of the reed is electroplated with two microns of a hard gold-cobalt alloy. For this evaluation, the reeds were electroplated with one micron of ruthenium over one micron of pure gold, as shown in Fig. 2.

Equipment and Solutions

To simulate production conditions, the pilot plating line was designed to accommodate a standard production plating rack holding 2016 reeds. An overall view of the rack is given in Fig. 3 and a closer view of the reeds in the rack in Fig. 4. During the production plating process, only the reed tips are immersed in the cleaning, rinsing, and electroplating solutions. The pilot plating line, consisting of four tanks each having liquid height and level controls, was designed to duplicate this method of processing. The two electroplating solutions, gold and ruthenium, were circulated to provide mild agitation, and a flowing deionized water rinse was used between each processing step. The basic processing steps for both production (hard gold-cobalt alloy) and experimental (ruthenium over gold) plating are outlined in Table I.

The electrocleaning solution is a mixture of potassium hydroxide and potassium cyanide. The pure gold underplate was deposited from a citrate buffered solution.[11] In both the electrocleaning and gold plating steps, insoluble counterelectrodes were used. These were planar and were located 2 1/2 inches below the horizontal plane of the reed array. A stainless steel electrode was used in the electrocleaning and a platinum anode in the gold electroplating.

Work by Vadimsky, Menezes, Heller, and Miller[12] has shown that the anolyte and catholyte must be separated in the ruthenium plating solution in order to maintain the ruthenium complex in a stable valence state and to prevent the formation of toxic RuO_4. This was accomplished using an anode compartment with a membrane that allows only the transfer of cations. The anode compartment, containing a platinum anode grid, is shown in section in Fig. 5. As indicated in Fig. 6, it was constructed of polypropylene, and the membrane consisted of a polymeric perfluorinated polysulfonic acid material, DuPont Nafion® A Teflon® restraining grid was stretched over the membrane to minimize bulging due to the evolution of gas.

The ruthenium plating system uses an acid phosphate buffer in both the anode and cathode compartments. The ruthenium plating salt, $K_3Ru_2NCl_8(H_2O)_2$, is added to the cathode compartment only. The compositions of anolyte and catholyte are given in Table II.

Results

During the course of this evaluation, approximately 50,000 reeds were ruthenium plated and more than 12,000 contacts were assembled. Three separate plating baths were used, one made up using ruthenium salts prepared at Bell Laboratories and the others made up using two separate lots of ruthenium salts prepared by an outside processor using the Bell Laboratories' method of synthesis. There was no detectable difference in the performance of the three electrolytes.

Laboratory studies by Vadimsky et al.[12] have indicated a cathode efficiency of 60% through eight turnovers of the metal content of the bath and a reduction in cathode efficiency to approximately 40% after ten turnovers. Except for one case where the catholyte was inadvertently contaminated with cyanide from the electrocleaner, the cathode efficiency remained constant at about 60% during these evaluation experiments. While the cathode efficiency was reduced to 20% by the cyanide contamination, it was not affected by metallic contamination caused by dissolution of the Remendur reeds at the levels indicated in Table III. Also, unlike the electrolytes described in the literature, solution agitation had no effect on the cathode efficiency.

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During contact assembly, the plated reeds are sealed into the glass envelope using infrared heating. To simulate the severe thermal shock that this causes, the ruthenium plated reeds were tested by inserting them into a 500°C furnace for 30 seconds and then rapidly removing and cooling them to room temperature.

It has been found[12] that if the ruthenium electrodeposit is not otherwise embrittled, the soft gold underplate compensates for the difference in thermal expansion between the Remendur and the ruthenium, thus preventing cracking of the electroplate. Figure 7 shows the surfaces of two reeds after thermal shock testing, both reeds having been plated with one micron of ruthenium over one micron of soft gold. The top reed was plated with ruthenium from a commercially available solution, while the lower reed was plated using the process described herein. The lower reed is representative of the quality of the deposits obtained during this evaluation. No cracking was observed even when the catholyte was contaminated with dissolved Remendur at the level shown in Table III.

The pilot plating line was operated over a period of several months, during which time the solutions were subjected to many cycles of heating and cooling. There was no evidence of physical degradation or change in the permeability of the membrane material and no detectable formation of RuO_4.

Conclusions

Throughout the evaluation experiments, the ruthenium electrolyte remained stable and had a constant cathode efficiency unaffected by either solution agitation or metallic contamination. When one micron of ruthenium was electrodeposited over one micron of soft gold, it remained crack free after thermal shock testing. The membrane material used in the anode cell was stable and performed satisfactorily. This evaluation has shown that the ruthenium plating process described in the patent of Heller, Miller, and Vadimsky[9] can be used under the production conditions simulated during this investigation.

References

1. D. B. Rogers, R. D. Shannon, A. W. Sleight, and J. L. Gillson, Inorg. Chem., 8, 841 (1969).

2. H. Schäfer, G. Schneidereit, and W. Gerhardt, Anorg. Allgem. Chem., 319, 327 (1963).

3. "Handbook of Chemistry and Physics", The Chemical Rubber Co., 1971, p. B-28.

4. H. C. Angus, Trans. Inst. Metal Finishing, 43, 135 (1965).

5. F. H. Reid and J. C. Blake, Trans. Inst. Metal Finishing, 38, 45 (1961).

6. G. A. Conn, Plating, 1038 (1969).

7. G. S. Reddy and P. Taimsalu, Trans. Inst. Metal Finishing, 47, 187 (1969).

8. B. G. Gebaur, US 4,082,622 (1978).

9. A. Heller, B. Miller, R. G. Vadimsky, US 4,082,624 (1978).

10. J. N. Crosby, US 4,082,625 (1978).

11. R. A. Ehrhardt, Proc. Am. Electroplaters' Soc., 47, 78 (1960).

12. R. G. Vadimsky, S. Menezes, A. Heller, and B. Miller, Bell Laboratories, Murray Hill, N.J., unpublished work.

TABLE I

ELECTROPLATING CYCLES

Production	Experimental
Electroclean	Electroclean
Soft Au Strike	Soft Au Plate
Hard Alloy Au Plate	Ru Plate
Dry	Dry

Deionized water and reclaim rinses omitted for clarity.

TABLE II

RUTHENIUM PLATING SOLUTION COMPOSITION

	Anolyte	Catholyte
H_3PO_4	50 ml/l	50 ml/l
KH_2PO_4	110 g/l	110 g/l
$K_3[Ru_2N(H_2O)_2Cl_8]$	-	32.5 g/l
Ru as Metal	-	10.0 g/l

OPERATING CONDITIONS

Temperature	70°C	70°C
pH	1.7	1.7

Cathode Current Density	10 mA/cm^2
Cathode Current Efficiency	60-70%

TABLE III

RUTHENIUM CATHOLYTE ANALYSIS

Metal	Concentration, g/l
Ru	10.5
Fe	0.20
Co	0.036
V	ND(<0.3)

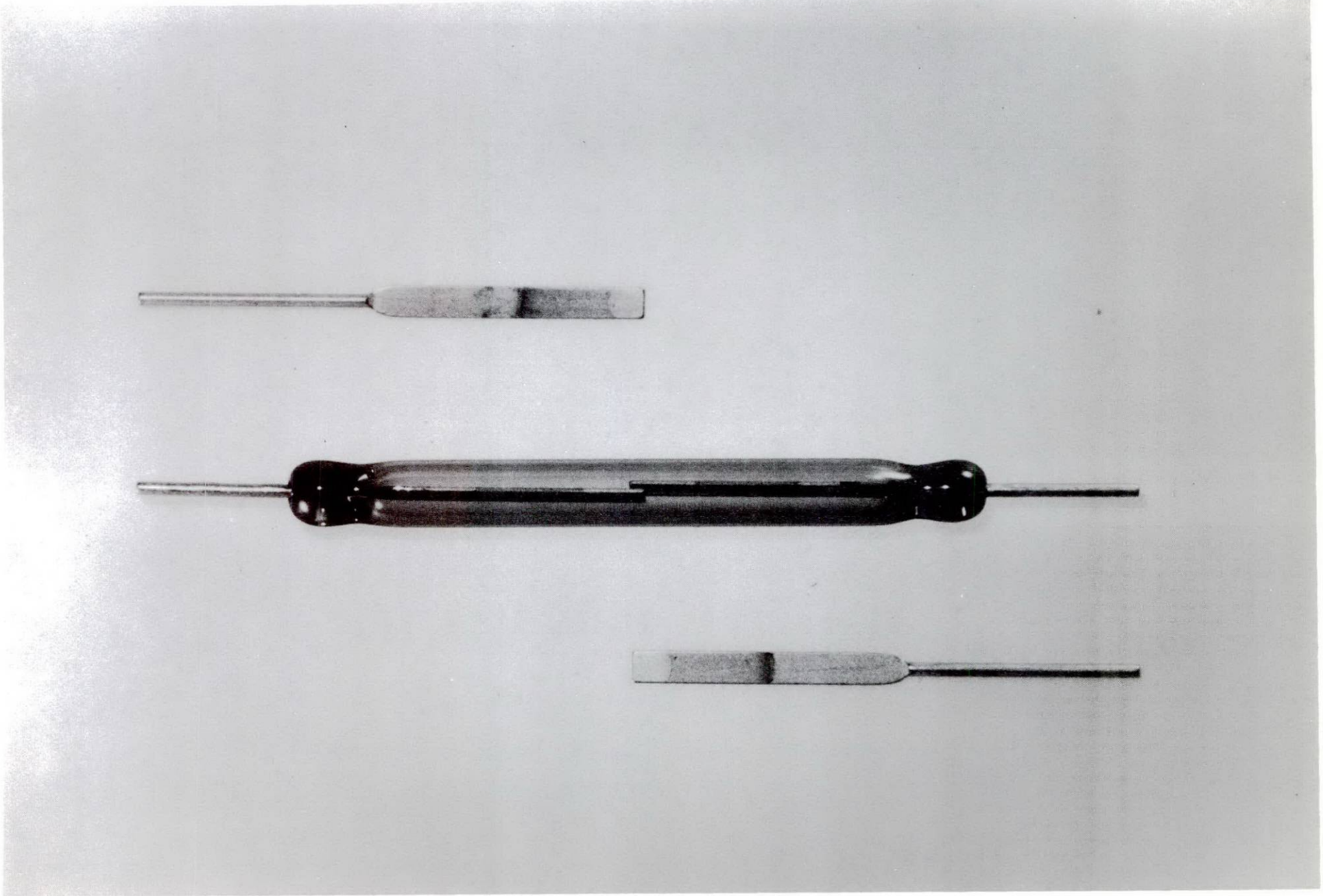


FIGURE 1

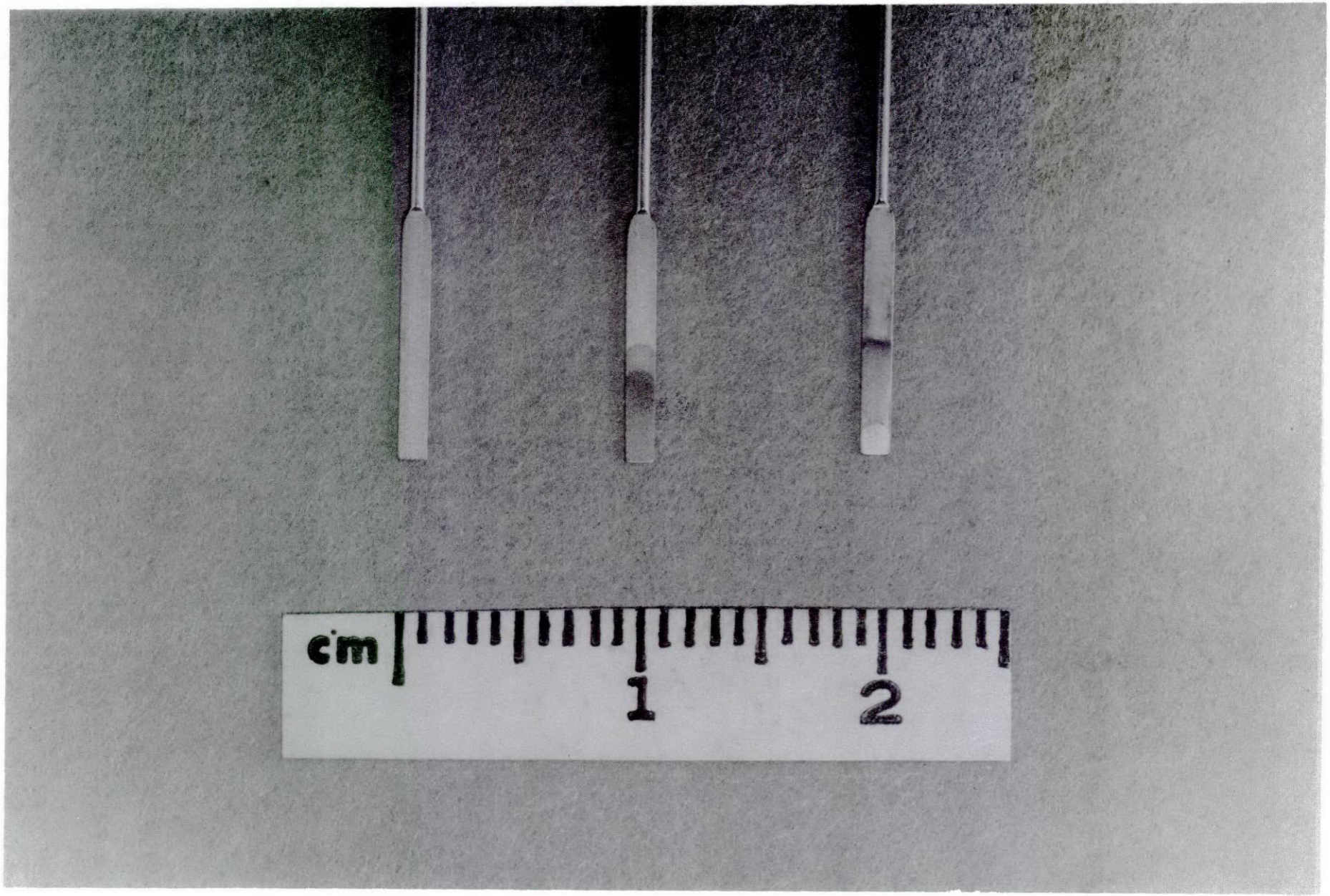


FIGURE 2

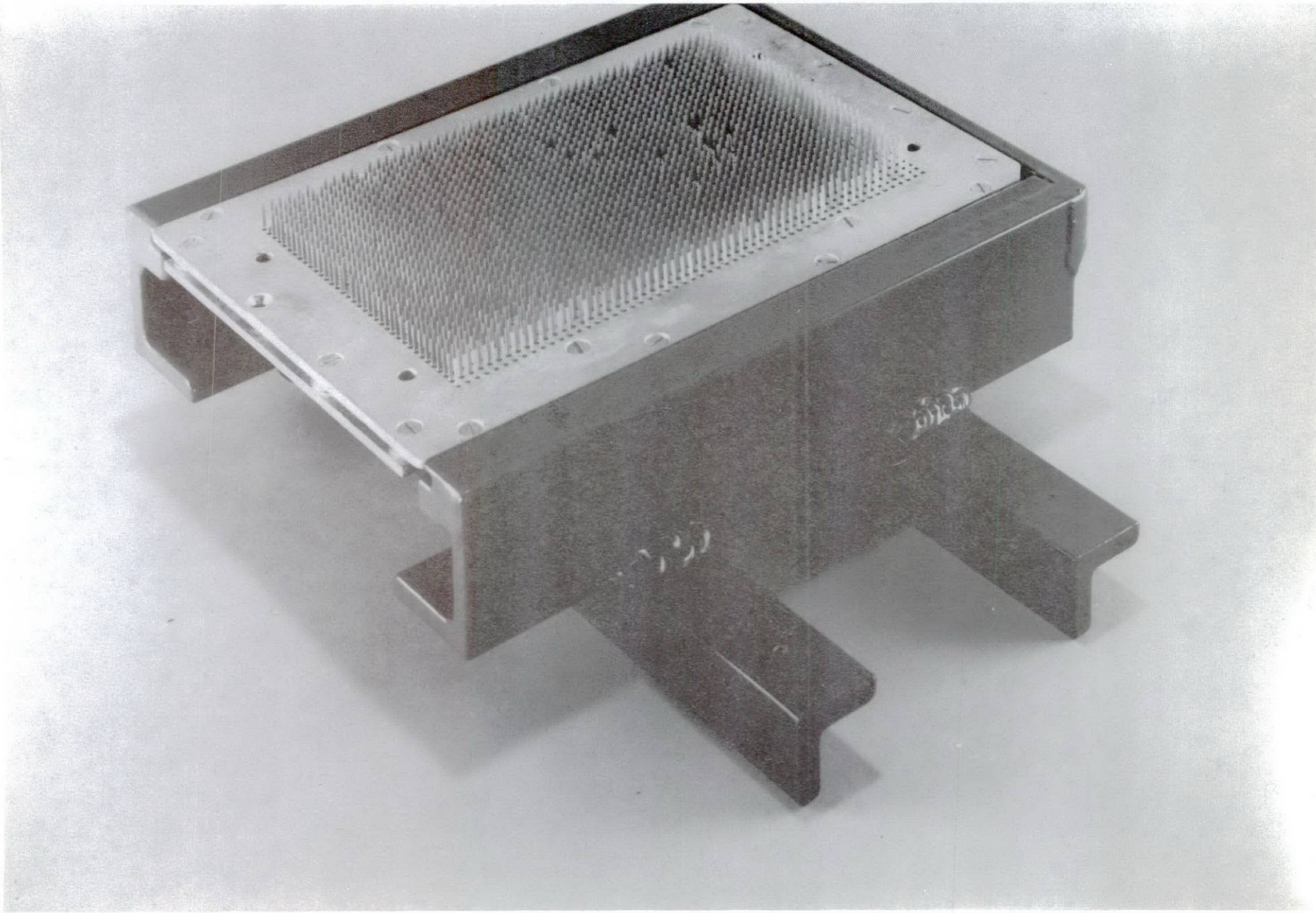


FIGURE 3

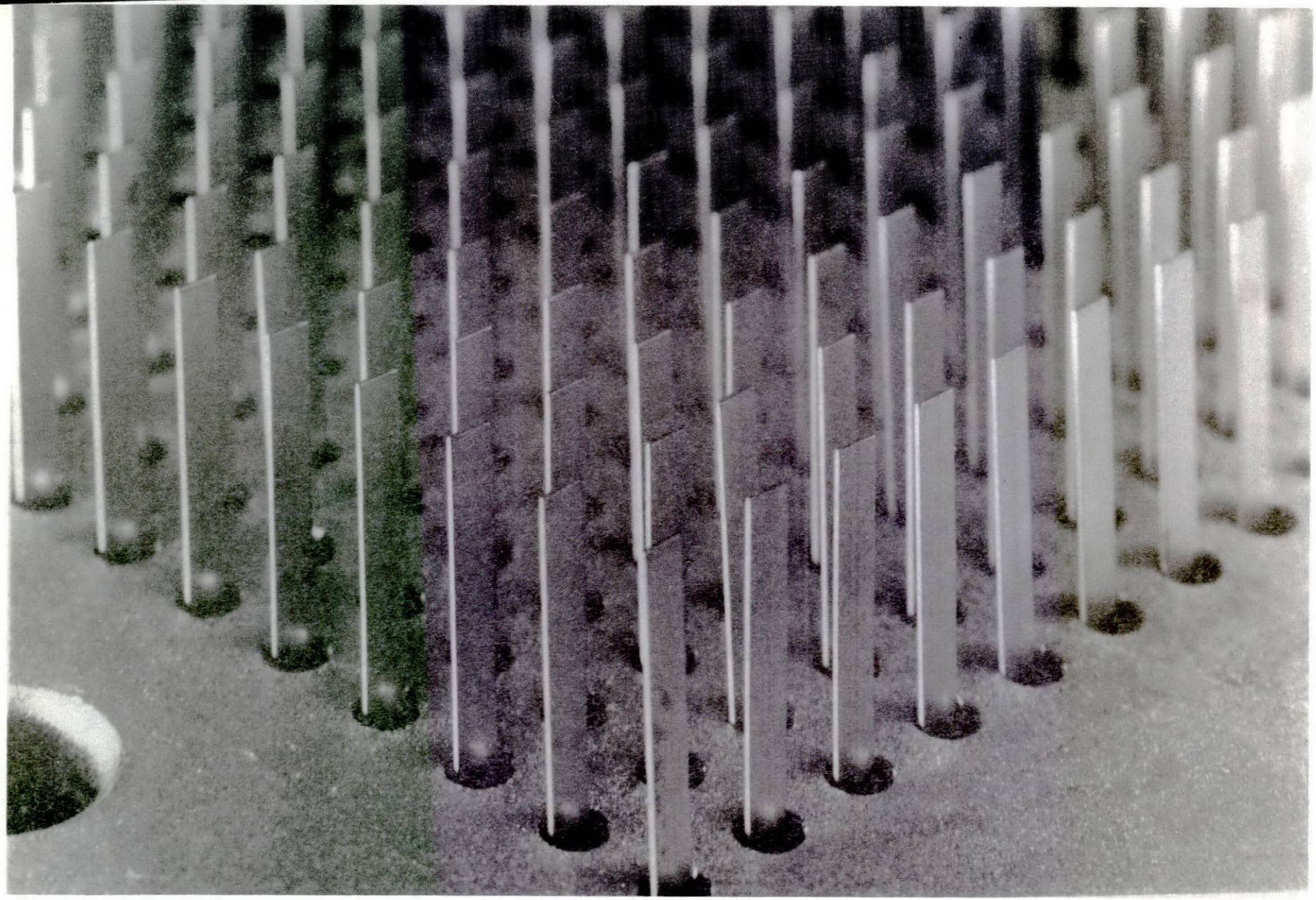


FIGURE 4

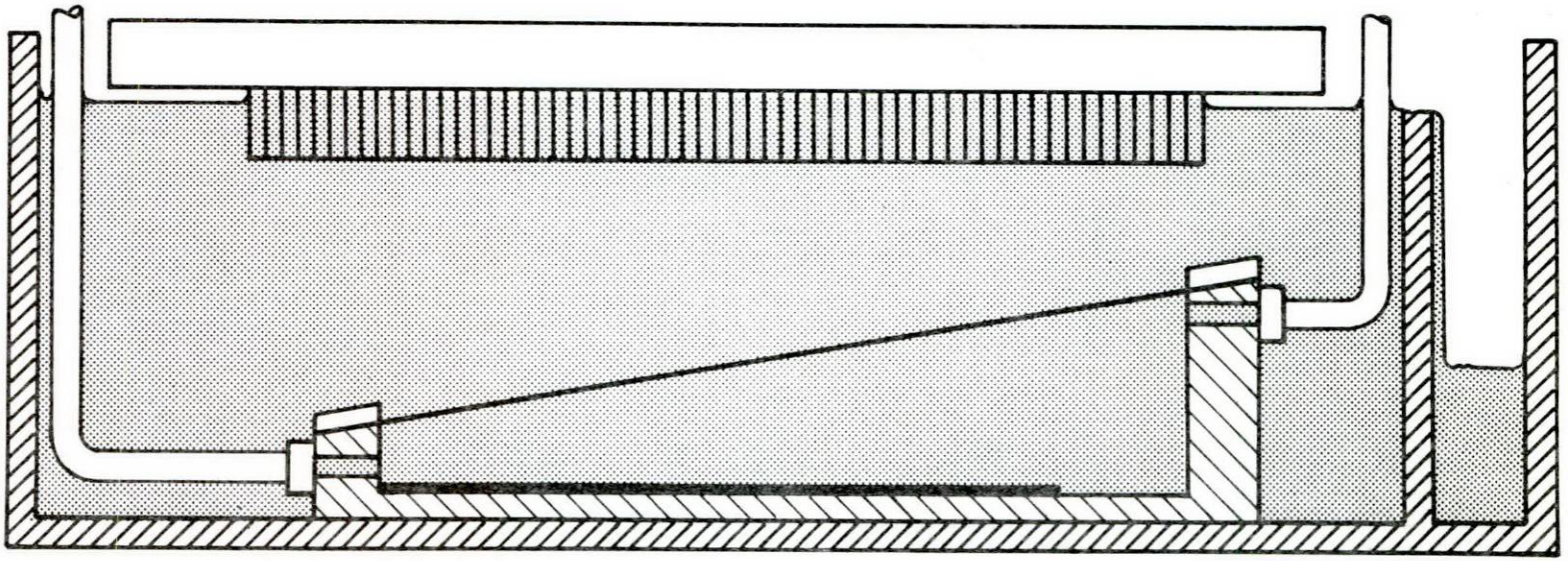


FIGURE 5

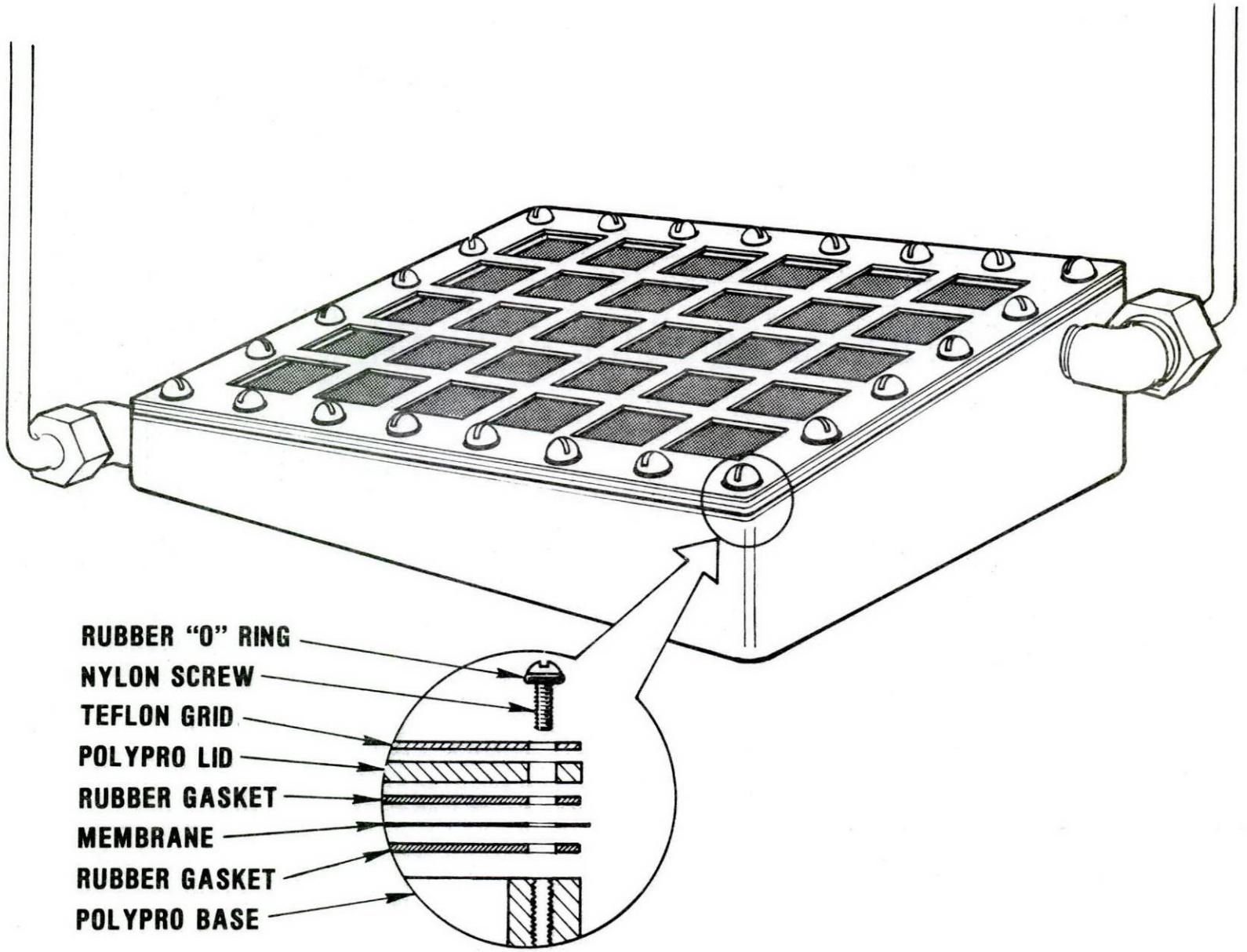
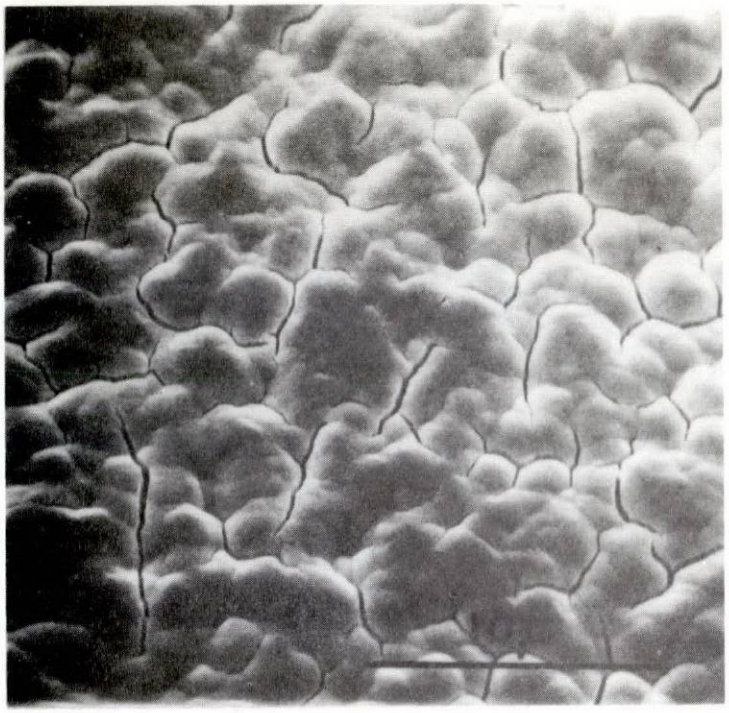

RUBBER "O" RING
NYLON SCREW
TEFLON GRID
POLYPRO LID
RUBBER GASKET
MEMBRANE
RUBBER GASKET
POLYPRO BASE

FIGURE 6



a



b

FIGURE 7

E-1

Electroforming I
Session E

Introduction to Electroforming

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AN ELECTROFORMER IS A VERY SPECIAL BREED IN INDUSTRY. HE MUST HAVE THREE SPECIAL SKILLS ALL COMBINED TO PRODUCE A GOOD ELECTROFORM. HE MUST HAVE VERY DEFINITE CHEMICAL, ELECTRICAL AND MECHANICAL SKILLS IF HE IS GOING TO SUCCEED. HE MUST ALSO HAVE AN IMMAGINATIVE MIND AND THE ABILITY TO THINK IN THREE DIMENSIONS IN BOTH A POSITIVE AND A NEGATIVE IMAGE IN ORDER TO VISULIZE AN END PRODUCT. ELECTROFORMING HAS COME A LONG WAY JUST IN THE LAST TWENTY YEARS AND IS DEFINITELY NOT AN ART, BUT A DISTINCT PRECISION METHOD BASED ON SOUND CHEMICAL, ELECTRICAL AND MECHANICAL KNOWLEDGE.

OUR WHOLE INTRICATE WORLD IS MADE UP OF EXTREMELY SMALL BITS OF MATTER, KNOWN AS MOLECULES. WHAT BETTER WAY COULD WE HAVE OF FORMING EITHER SIMPLE OR COMPLEX PARTS THAN BY JOINING MOLECULES OF A PARTICULAR METAL THROUGH AN ELECTROCHEMICAL PROCESS. THIS ELECTRODEPOSITION PROCESS IS THE BASIS FOR ALL ELECTROFORMING. OVER THE YEARS ELECTROFORMING HAS BEEN DESCRIBED IN MANY MANY DIFFERENT WAYS AND HAS BEEN REFERRED TO AS COLD CASTING, IONIC FABRICATION, GALVANOPLASTY FROM THE FRENCH WORD GALVANOPLASTIQUE, AND FINALLY A RATHER COMMON USAGE OF THE WORD "ELECTRO" AS USED BY THE ENGLISH. REGARDLESS OF WHAT TERM WE USE TO DESCRIBE THIS ELECTROCHEMICAL PROCESS, I THINK THE MOST APT DEFINITION IS ONE GIVEN BY MR. A. KENNETH GRAHAM, A NOTED ELECTROFORM CONSULTANT WHO DEFINES ELECTROFORMING AS (QUOTE) "THE ART OF PRODUCING OR REPRODUCING METALLIC OBJECTS BY ELECTRODEPOSITION UPON A MASTER FORM, MANDREL OR MATRIX, WHICH IS THEN REMOVED IN WHOLE OR IN PART." (UNQUOTE) ALTHOUGH ELECTROFORMING AND ELECTROPLATING ARE FUNDAMENTALLY SIMILAR IN THEIR TECHNOLOGY AND SEQUENCE OF OPERATION THEY DO DIFFER IN THEIR END PRODUCT. THIS POINT WILL BE BROUGHT OUT IN A FILM ON ELECTROFORMING DURING THIS PRESENTATION.

ELECTROFORMING IS NOT NEW, AND IT IS DEFINITELY NOT AN "EXOTIC" FABRICATION TECHNIQUE. IT IS A PRECISION FABRICATION TECHNIQUE WHICH PROVIDES THE DESIGN ENGINEER WITH A VERY VALUABLE TOOL WITH WHICH HE CAN FABRICATE A SINGLE PART OR AN ASSEMBLY. TODAY WITH OUR CLOSELY CONTROLLED SOLID STATE POWER SUPPLIES AND THE VAST NUMBERS OF PROPRIETARY ELECTRO-PLATING FORMULAS AVAILABLE, ELECTROFORMED PARTS ARE LIMITED ONLY BY THE SKILLS AND IMAGINATION OF THE ELECTROFORMER IN ADAPTING HIS KNOWLEDGE OF ELECTROCHEMISTRY. HIS FABRICATED PART CAN BE AS SMALL AS THE HEAD OF A PIN OR THE SIZE OF A FULL SCALE WIND TUNNEL MODEL -- LIMITED ACTUALLY ONLY BY THE SIZE OF HIS ELECTROFORM TANK. MANY APPLICATIONS OF ELECTROFORMING HAVE COME TO LIGHT IN OUR FAST MOVING PRESENT DAY SPACE AGE, DUE IN PART TO NEW ELECTROCHEMICAL KNOWLEDGE AND IMPROVED TECHNIQUES, BUT LARGELY DUE TO THE UNINHIBITED IMAGINATIONS OF DESIGN ENGINEERS AND PLANT MANAGERS WHO CALL FOR THE FABRICATION OF ITEMS WHICH DEFY CONVENTIONAL FABRICATION TECHNIQUES. THE ENGINEER RESPONSIBLE FOR THE METHOD OF FABRICATION SHOULD CONTACT THE ELECTROFORMER AT THE VERY CONCEPT OF HIS DESIGN IDEA. THIS WILL INDEED ESTABLISH AT ONCE IF ELECTROFORMING IS THE MOST INEXPENSIVE WAY TO GO ---- OR IF IT IS THE ONLY WAY IN WHICH TO MEET ALL THE PHYSICAL AND METALLURGICAL PROPERTIES NEEDED IN THAT PRODUCT. NO, ELECTROFORMING IS NOT A "CURE ALL" BUT IT CERTAINLY IS AN EXCELLENT PROBLEM SOLVER -- IF GIVEN THE PROPER CHANCE IN THE HANDS OF A QUALIFIED ELECTROFORMER.

WE'VE COME A LONG WAY TOWARD MAKING ELECTROFORMING AN ACCEPTED FABRI-CATION METHOD AND THE FULL USAGE OF THIS TECHNIQUE IS STILL YET TO COME. WHATEVER YOUR PRODUCT IS, TO MAKE ELECTROFORMING A COMPETITIVE METAL WORKING PROCESS YOU MUST ASK YOURSELF "WHEN SHOULD YOU CONSIDER

ELECTROFORMING?" THERE ARE FIVE BASIC STATEMENTS, ANY ONE OF WICH WILL BE REASON ENOUGH TO CONSIDER ELECTROFORMING:

1. WHEN A PART DEFIES CONVENTIONAL FABRICATION METHODS, SUCH AS AN INTERNAL TAPERED SECTION OR A CORNER CUBE REFLECTOR WITH OPTICAL TOLERANCES.
2. WHEN BETTER THAN A 16 MICRO-INCH INSIDE SURFACE IS REQUIRED. (THAT KIND OF SURFACE IS EASY TO PUT ON THE OUTSIDE OF A MANDREL.)
3. WHEN A SEAMLESS, CORROSION FREE AND LIGHTWEIGHT BUT STRONG STRUCTURE IS REQUIRED. (A .020" THICK NICKEL WALL WILL USUALLY GIVE YOU ALL THE STRENGTH YOU'LL NEED FOR AN AVERAGE PART.)
4. WHEN CONVENTIONAL TOOLING COST ARE TOO HIGH FOR SHORT RUNS. (TOOLING FOR A DEEP DRAW WOULD BE EXPENSIVE FOR ONLY 50 OR 100 PIECES.)
5. WHEN A DESIGN HAS NOT BE FROZEN, THEN SMALL CHANGES ARE NOT EXPENSIVE. FOR INSTANCE -- GROWN ON BOSSES, THREADED PARTS, GROWN IN PLACE HOLES.

AFTER CONSIDERING THOSE FIVE POINTS DON'T OVERLOOK THE POSSIBILITIES WITH ELECTROFORMING AND BY ALL MEANS DO NOT DISMISS A WILD OR INTRIGUING IDEA WITHOUT CONSULTING AN ELECTROFORMER.

GENTLEMEN I COULD STAND HERE AND TALK TO YOU ALL DAY ABOUT ELECTRO-FORMING BUT I STILL THINK A PICTURE IS WORTH A THOUSAND WORDS. WE HAVE A FILM THAT WAS MADE AT MARTIN MARIETTA AEROSPACE IN OUR ELECTROCHEMICAL LAB THAT I THINK YOU WILL FIND INTERESTING. THIS FILM GIVES A BASIC HISTORY AND EXPLANATION OF ELECTROFORMING, AS WELL AS A GOOD OVERALL VIEW OF THE MANY ITEMS BEING PRODUCED IN MARTIN MARIETTA'S ELECTROFORM LAB.

E-2

Electroforming I
Session E

Electroforming with Heat Resistant, Sulfur-Hardened Nickel

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Birmingham, England

ELECTROFORMING WITH HEAT RESISTANT, SULPHUR-HARDENED NICKEL

by

W.R. WEARMOUTH AND K.C. BELT*

ABSTRACT

Nickel electroforms containing sulphur incorporated from organic stress reducing addition agents, are susceptible to catastrophic embrittlement on exposure to elevated temperatures. The effect of co-deposited manganese on the hardness and ductility of sulphur-containing nickel electrodeposits has been determined, as deposited, and after heat treatment up to 500°C. The results indicate that in the presence of greater than 0.1 weight percent manganese, there is no catastrophic embrittlement on heat treatment. Metallographic evidence shows that the manganese preferentially combines with the sulphur on heat treatment, and prevents the formation of brittle grain boundary films of nickel sulphide. Potential electroforming applications are discussed.

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INTRODUCTION

One of the main requirements for successful electroforming is that the internal stress in the deposit is kept as close to zero as possible. With many mandrel materials there is no adhesion between the electroform and the mandrel, and internal stress in the deposit will tend to distort the electroform. In severe cases internal stress may lead to premature detachment of the electroform from the mandrel. However, there are applications, for example, rotary screen printing cylinders, where the stress in the deposit is deliberately made compressive, in order to facilitate separation from the cylindrical mandrel.

Sulphamate baths, both conventional and concentrated (NI-Speed), find wide application in electroforming, since the deposits produced generally have a lower internal stress than deposits from the Watts bath. In fact, the internal stress in deposits from the NI-Speed bath can be made either compressive, zero, or tensile, by varying the current density and solution temperature[1]. To enable the Watts bath to be used for electroforming, it is necessary to add a stress-reducing addition agent to the solution. Most of these agents are aryl sulphonates or their derivatives, e.g. saccharin or the sodium salt of naphthalene tri-sulphonic acid, and the sulphur present is incorporated into the deposit. The incorporated sulphur also refines the grain size of the deposit and greatly increases its hardness. This is important for applications such as electroformed moulds and dies, where the hardness of pure nickel is insufficient to withstand the conditions of usage. However, such sulphur-containing deposits are susceptible to embrittlement on exposure to temperatures in excess of 200°C[2].

The embrittlement of nickel caused by the presence of sulphur is well-known[3,4], due to the formation of brittle grain boundary films of nickel sulphide. In commercial nickel, the brittleness is usually eliminated by additions of manganese or magnesium to the molten nickel just prior to casting[4,5]. These elements preferentially combine with the sulphur and prevent the formation of the brittle nickel sulphide. The manganese sulphide forms a high melting point eutectic which melts at 1325°C and is precipitated as globules along the grain boundaries, whereas the magnesium sulphide is insoluble in the nickel and forms particles which are entrapped within the grains during solidification.

Most of the work on electrodeposited nickel-manganese alloys has been in the sulphate or chloride bath[6,7], although Stephenson[8] reported on the excellent properties of nickel deposits containing less than 1% manganese, deposited from a sulphamate bath. Recently, Dini[9] reported the co-deposition of manganese from a sulphamate bath containing up to 5 g/l manganese, added as manganese sulphamate. His results are pertinent to the work in the present investigation, and will be discussed more fully later in the paper.

Preliminary results describing the heat resistance of sulphur-containing nickel-manganese electrodeposits from the NI-Speed bath, have been published by the authors[10]. The results demonstrated the feasibility of preventing the embrittlement of such deposits on heat treatment, by co-depositing a sufficient amount of manganese. However, metallographic examination, using the optical microscope and the electron microscope, failed to

show evidence supporting the hypothesis that the manganese preferentially combines with the sulphur, as in the case of commercial nickel alloys. The present investigation describes the deposition of sulphur-containing nickel-manganese alloys with varying magnanese concentrations, from Watts and sulphamate type solutions[11]. The properties of the deposits, as plated, and after heat treatment, for varying times, between 200°C and 500°C, are given. Also analytical results from the scanning electron microscope are shown, which support the proposed mechanism of embrittlement prevention.

EXPERIMENTAL PROCEDURE

Three basic solutions were used, whose compositions are given in Table 1. All the solutions were made up in 4 l. batches carbon-permanganate purified, plated-out, and saccharin sodium (o-benzoic sulfimide sodium salt) added to a concentration of 0.25 g/l. Manganese ions were added to the solution as an aqueous solution of manganese sulphate, which was carbon-treated, before use.

Samples, in the form of electroformed cylinders, were plated from the solutions at a temperature of 60°C and a pH of 4.0. The cylinders, 35 mm long and 30 mm diameter x 100 microns thick, were formed on a stainless steel mandrel, which was rotated vertically in the solution at approximately 200 rpm with air agitation, using a concentric anode.

Hardness measurements were made on a Vickers diamond pyramid indentation machine at a load of 1.0 kilogramme. The sulphur content of the deposits was determined using a combustion method, and the manganese content by atomic absorption spectrometry after dissolving a known weight of the sample in an acidic solution

Internal stress was measured in deposits 25 microns thick, using a modified Brenner-Senderoff spiral contractometer.

Ductility measurements were made on strips cut from the electroformed cylinders. After clamping the strip between flat ended supports, the number of reverse bends through 90° beforefracture, was recorded. This technique is not recommended for, and can not be compared with the results from, standard quantitative elongation determination methods. However, in the context of the present investigation, where the distinction between embrittled deposits and deposits possessing some ductility, is of paramount importance, the method is satisfactory, and provides results which are self-consistent if not absolute.

RESULTS

Deposit Properties - Ambient Temperature

Table 2 shows the effect of current density on the composition of deposits from the Watts, conventional sulphamate, and NI-Speed solutions. The manganese concentration increases with increase in current density, more manganese being deposited from the Watts solution than the sulphamate based solutions at current densities higher than 6.5 A/dm^2.

It is noticeable that the percentage of co-deposited manganese is very low. This is due to the highly negative potential of manganese in aqueous solutions making its co-deposition with other depositable metals difficult. However, in accordance with the atomic weights of sulphur and manganese, a weight ratio of S:Mn = 1:1.7 is required for the formation of manganese sulphide.

Earlier results[9] showed that a manganese content of approximately 0.1% is sufficient to prevent embrittlement on heat treatment at 450°C. This is somewhat greater than that calculated stoichiometrically, but it has been shown by previous workers[12] investigating additions of manganese to cast iron, that manganese contents in excess of those required stoichiometrically to tie-up the sulphur are required.

Table 3 shows the effect of current density on the hardness and stress of deposits from the Watts, conventional sulphamate, and NI-Speed solutions. At the lower current densities, the differences in hardness values are what might be expected, consideri the different solution types. However, at the higher current densities the hardness values are quite similar, probably due to the increasing influence of the saccharin sodium present in the solutions. For the particular concentrations of saccharin sodium and manganese ion used in the solutions, the deposit stress in all three solutions remains compressive up to 10.8 A/dm². As expected, the deposit stress in the sulphamate solutions is more compressive than that in the sulphate solution. At higher current densities the stress in the sulphamate solutions rapidly changes in t tensile direction, whereas that in the sulphate solution remains compressive. This might be expected to be due to a higher manganese incorporation, but surprisingly, as seen from Table 2, at such current densities more manganese is incorporated from the Watts solution. The control of stress in electroforming solutions by variation in organic additive concentration, solution composition, and operating variables is well known. In the presence of manganese ions in the solution, the stress is similarly affected by such variations. The values of stress presented in Table 3 may therefore be considered as being representative of the particular conditions

under which they were recorded, and not typical of manganese-containing Watts type and sulphamate solutions. For example, if less compressive stresses were required, these could be obtained by lowering the saccharin sodium concentration in the solution, by lowering the solution temperature or by increasing the current density.

Deposit Properties - Elevated Temperature

To examine the effect of heat treatment on the mechanical properties of sulphur-containing nickel-manganese electrodeposits, a number of samples of varying manganese content were prepared from Watts and conventional sulphamate solutions, Table 4. An additional control sample was prepared from the conventional sulphamate solution containing saccharin sodium, without the addition of manganese ions. Tables 5 and 6 show the hardness and ductility values measured at room temperature, after heat treatment for 4 hours and 22 hours, at temperatures between 200°C and 500°C.

Above 200°C the deposits softened appreciably, the biggest decrease in hardness occurring after heat treatment at 300°C. This type of behaviour is similar to that observed previously for nickel and nickel-cobalt alloy electrodeposits[13,14]. At temperatures in excess of 300°C, all the deposits were softened, little difference being observed between deposits from the Watts and sulphamate solutions, or between the 4 hour and 22 hour heat treatments. At 300°C, the time of heat treatment has a marked effect on hardness, the latter generally being much lower for the longer heat treatment times. However, at 200°C, an increase in hardness was found to occur after the 4 hour heat treatment, little difference being noted after the 22 hour heat treatment.

This effect was particularly noticeable in deposits containing more than 0.1% manganese. For example, a nickel-0.18% manganese deposit from the sulphamate solution had a hardness of 428 HV as plated, 483 HV after 4 hours at 200°C, and 165 HV after 4 hours at 300°C, Table 6. This increase in hardness is surprising and has not been observed previously during the heat treatment of nickel and nickel-cobalt alloy deposits[13,14]. The effect may be due to the formation of discrete grain boundary particles of manganese sulphide (see later Section) whilst at higher temperatures the softening of the matrix is the determining factor. The non-manganese containing nickel deposit from the sulphamate solution, Table 6, also showed an increase in hardness after the 4 hour heat treatment at 200°C, but, unlike the manganese-containing deposits, it softened after the 22 hour heat treatment. The transitory behaviour of hardness in this deposit suggests that the more permanent hardening effect in the manganese-containing deposits may be due to the dispersion and size characteristics of the manganese sulphide particles, compared with the nickel sulphide grain boundary film.

Tables 5 and 6 show that the as-plated ductility decreases with increasing manganese content, although the decrease is small above 0.1% manganese. The ductility after heat treatment is dependent on the manganese content of the deposit and the heat treatment temperature. The time of heat treatment has little effect on ductility, except at lower levels of manganese, less than 0.1%. The non-manganese containing deposit from the sulphamate solution, Table 6, containing 0.032% sulphur is as expected, brittle after heat treatment at all temperatures.

The results show that even at very low concentrations of manganese, 0.02% and 0.04%, in deposits from the Watts and sulphamate solutions, respectively, embrittlement does not occur after heat treatment at 200°C and 300°C. However, at 300°C, the ductility is adversely affected by increased time of heat treatment, and embrittlement occurs after heat treatment for 4 hours at 400°C and 500°C. To prevent embrittlement at temperatures higher than 300°C, a manganese content in excess of nominally 0.1% is required in deposits containing nominally 0.03% sulphur, supporting previous results[10]. However, at these higher temperatures, if maximum ductility is required, it is necessary to co-deposit at least 0.2% manganese. For example, in Table 6, deposits containing 0.12% manganese record 4 bends to failure after 22 hours at 500°C, whereas deposits containing 0.23% manganese record 11 bends to failure after a similar heat treatment. Deposits from the Watts solution containing 0.27% manganese, and from the sulphamate solution containing 0.18% and 0.23% manganese, show an increase in ductility after heat treatment at 400°C and 500°C. This is probably due to softening of the matrix, as shown by the corresponding hardness measurements, although the increased mobility of the manganese may make some contribution. However, the increased ductility with increasing manganese content, particularly at higher temperatures, is more likely due to a greater proportion of sulphur being tied up as manganese sulphide, preventing the formation of brittle grain boundary films of nickel sulphide.

Metallographic Examination of Heat Treated Deposits

The retention of ductility after heat treatment of sulphur-containing nickel-manganese electrodeposits is assumed to be due to manganese preferentially combining with sulphur, and preventing the formation of brittle grain boundary films of nickel sulphide. In wrought nickel alloys containing higher percentages of manganese and sulphur, it is possible to see manganese sulphide inclusions using optical metallography[3]. However, electrodeposits are characterised by a very fine grain size, and due to the low percentages of manganese and sulphur present, no identification of manganese sulphide inclusions can be made using low power metallography[9]. Furthermore, attempts to identify a second phase using transmission electron microscopy and electron diffraction techniques were unsuccessful, perhaps due to removal of the particles during the electropolishing stage[9]. An attempt was therefore made to locate and identify particles, using the scanning electron microscope, with energy dispersive X-ray analysis (EDX).

A nickel foil, 100 microns thick, containing 0.03% sulphur and 0.15% manganese, was electrodeposited from a Watts solution containing 0.25 g/l saccharin sodium and 20 g/l manganese ions. The foil was heat treated in a dry argon atmosphere for 24 hours at 600°C, to form a large grain size to facilitate metallographic examination. After polishing to 1 micron, the foil was etched in a 1:1:2 mixture of nitric acid:acetic acid:acetone and sputtered with silver to give improved surface conductivity.

Figure 1 shows the presence of a second phase occurring as spherical particles at grain boundaries, and Figure 2, a typical EDX analysis of such particles. The latter indicates the presence of manganese associated with sulphur in the particles, the nickel signal being due to background, and penetration of the beam through the particles. It is probable that such particles are manganese sulphide.

DISCUSSION

The embrittlement of electrodeposited nickel has been the subject of a number of investigations[9,15,16,17]. Harris and Braddick[15] postulated that during annealing at temperatures in excess of 600°C, carbon monoxide containing gas bubbles formed at the grain boundaries, and caused embrittlement during subsequent room temperature testing of deposits plated at 0.2 A/dm². Deposits plated at 2.7 A/dm² and 5.4 A/dm² remained ductile up to 1000°C. Further investigation[16] involving elevated temperature tensile testing showed embrittlement in deposits plated at 5.4 A/dm², at temperatures in excess of 400°C. This embrittlement was again shown to be associated with voids at the grain boundaries. The difference in ductility between testing at room temperature and elevated temperatures is explained by the formation of excess voids on straining during tensile testing at the elevated temperatures. In general, a lower strain rate results in a slightly lower ductility.

On the other hand, Dini et al.[9] suggested that the reduction in ductility at testing temperatures above 400°C is a result of the high rate of sulphur diffusion along the grain boundaries, where the low melting point, nickel-nickel sulphide

eutectic is formed, thus destroying the co-hesion between the grains. Co-deposition of 0.02% manganese eliminated the high temperature embrittling effect. The nickel electrodeposit contained 0.001% sulphur, suggesting that a manganese:sulphur ratio of 20:1 was necessary to tie up all the sulphur as manganese sulphide. Further work[17] showed the importance of stra rate on the reduction in ductility, although unfortunately no results were given for manganese-containing deposits, tested under similar conditions.

Many metals and alloys suffer from a reduction in ductility at elevated temperatures, and fail by intergranular cracking, the onset of which can be promoted by grain boundary impurities. Thus, in the case of electrodeposited nickel, although sulphur may play an important role, other impurities may also contribute to the overall failure mechanism. Nevertheless, the evidence for a reduction in ductility at temperatures greater than 400°C has been conclusively shown, and as such, any results which help to define the operating or service conditions to be avoided are of value.

Although intergranular in nature, the above embrittlement must not be confused with that described in the present paper. Most electroplaters understand sulphur embrittlement as the catastrophic failure which occurs when electrodeposited nickel containing greater than nominally 0.01% sulphur, incorporated from organic addition agents, is heat treated at temperatures in excess of 200°C[2]. The mode of failure is intergranular, caused by the formation of brittle grain boundary films of nickel sulphide. The nickel deposits investigated by Harris and Dini contained nominally 0.001% sulphur, and,as their results demonstrated, showed no loss in ductility below 400°C. There is a clear

distinction, therefore, between low temperature sulphur embrittlement in nickel containing more than 0.01% sulphur, and elevated temperature embrittlement in nickel containing as little as 0.001% sulphur. It would appear that manganese is effective in reducing both types of embrittlement, Dini suggesting a ratio of manganese:sulphur of 20:1, whereas in the present work a ratio of less than 10:1 is shown to be effective.

Electroforming Applications

Earlier work[10] suggested that a minimum manganese incorporation of 0.1% was necessary to prevent embrittlement on heat treatment in deposits containing 0.03% sulphur, requiring current densities greater than 8.6 A/dm^2. Although this is satisfactory for many electroformed foil and mesh products, such as screen printing cylinders which are generally electroformed with uniform current density in excess of 8.6 A/dm^2, there are obvious problems associated with shaped articles, such as moulds and dies, where the current density may be 3-4 A/dm^2. However, the present results show that manganese contents less than 0.1% are effective in preventing embrittlement at 200°C, the upper operating temperature for many plastic moulds. Thus the process may be suitable for electroforming heat resistant moulds for plastics, with hardness values greater than those presently attainable using the nickel-cobalt alloy process, but which can still be backed using casting or metal spraying techniques[18,19]. Further solution development is necessary before the process can be used for electroforming articles which are subject to service temperatures in excess of 200°C, but which are plated at low current densities, such as zinc die casting dies.

CONCLUSIONS

Electrodeposited nickel containing in excess of nominally 0.01% sulphur becomes embrittled when heated. Such sulphur-embrittlement can be prevented by co-depositing sufficient manganese to combine preferentially with the sulphur, and so prevent the formation of brittle grain-boundary films of nickel sulphide. The amount of manganese to prevent embrittlement is dependent on the heat treatment temperature, the ratio of manganese to sulphur to tie up the sulphur varying between nominally 1:1 for heat treatment at 200°C, to 5:1 for heat treatment at 500°C. The internal stress in sulphur-containing nickel-manganese deposits can be controlled to enable the process to be used for electroforming applications. It will be particularly valuable where service temperatures exceed 200°C, and cause embrittlement problems when ordinary sulphur-hardened nickel deposits are used.

ACKNOWLEDGEMENT

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REFERENCES

1. R.J.Kendrick, Trans. I.M.F., Proc. 6th International Met. Fin. Conf. 1964, 42, 235.

2. W.H.Safranek, Plating, 1966, 53, 1211.

3. P.D.Merica and R.G.Waltenberg, Trans A.I.M.E., 1925, 71, 709.

4. K.M.Olsen, C.F.Larkin and P.H.Schmitt, Jr., Trans. A.S.M. 1961, 53, 349.

5. A.M.Hall, Trans. A.I.M.E., 1943, 152, 278.

6. T.S.Vanaja and T.L.Rama Char, Metal Finishing, 1971, 69, 59.

7. W.A. Bell, Trans. Inst. Met. Fin., 1954, 31, 466.

8. W.M.Stephenson Jr., Plating, 1966, 53, 183.

9. J.W.Dini, H.R.Johnson and L.A.West, Plating and Surface Finishing, 1978, 65, 36.

10. W.R.Wearmouth and K.C.Belt, Metalloberfläche, 1978, 8, 338.

11. U.K. Patent Specification 1 524 748.

12. F.Henke, Giessereipraxis, 1970, 18, 281.

13. K.C.Belt, J.A.Crossley and S.A.Watson, Trans. I.M.F., 1970, 48, 132.

14. W.R.Wearmouth, Plastics and Rubber: Processing, December 1977, 131.

15. D.M.Braddick and S.J.Harris, Trans. I.M.F., 1972, 50, 46.

16. S.J.Harris and D.M.Braddick, Trans. I.M.F., 1973, 51, 165.

17. H.R.Johnson, J.W.Dini and R.E.Stoltz, 65th A.E.S. Conference. Washington D.C., June 1978.

18. A.V.Dean and W.R. Wearmouth, Electroplating and Metal Finishing, 1975, 28.

19. A.V.Dean, Metallurgia, 1978, 45, 243.

TABLE 1

SOLUTION COMPOSITIONS

Solution Type	Concentration, g/l				
	Nickel Sulphate	Nickel Sulphamate	Nickel Chloride	Manganese*	Boric Acid
Watts	285	-	26	15	38
Conventional Sulphamate	-	280	5	13	33
NI-Speed	-	560	8	14	33

* Manganese added as manganese sulphate.

TABLE 2

EFFECT OF CURRENT DENSITY ON DEPOSIT COMPOSITION

Current Density A/dm^2	Solution Type					
	Watts		Conventional Sulphamate		NI-Speed	
	% Mn	% S	% Mn	% S	% Mn	% S
4.3	0.03	0.024	0.02	0.040	0.03	0.018
6.5	0.05	0.030	0.06	0.037	0.06	0.022
8.6	0.16	0.033	0.10	0.040	0.10	0.023
10.8	0.20	0.034	0.12	0.033	0.11	0.023
12.9	0.22	0.035	0.18	0.031	0.17	0.026

TABLE 3

EFFECT OF CURRENT DENSITY ON DEPOSIT PROPERTIES

Current Density A/dm^2	Solution Type †					
	Watts		Conventional Sulphamate		NI-Speed	
	HV1 *	S ▲	HV1 *	S ▲	HV1 *	S ▲
4.3	240	-43	295	-95	398	-86
6.5	274	-62	333	-98	405	-80
8.6	408	-59	378	-100	405	-91
10.8	418	-56	420	-94	410	-62
12.9	437	-53	420	+17	443	+36

† All containing Mn as indicated in Table 1.

* Vickers hardness, 1 kg. load.

▲ Stress, N/mm^2.

Negative value denotes compressive stress. Positive value denotes tensile stress.

TABLE 4

SAMPLE PREPARATION

Solution Type	Current Density A/dm^2	Sulphur Concentration Deposit, % by wt.	Manganese Concentration	
			Solution, g/l*	Deposit, % by wt.
Watts	6.5	0.026	5	0.02
"	12.9	0.031	5	0.10
"	10.8	0.033	20	0.20
"	12.9	0.036	20	0.27
Conventional Sulphamate	5.4	0.024	5	0.04
"	10.8	0.025	5	0.12
"	12.9	0.027	5	0.18
"	7.5	0.032	20	0.23
"	10.8	0.032	Nil	<0.01

* Manganese added as manganese sulphate

TABLE 5

EFFECT OF HEAT TREATMENT ON HARDNESS AND DUCTILITY OF DEPOSITS FROM WATTS SOLUTION

Deposit % Mn	As Plated	200°C	300°C	400°C	500°C
	Hardness HV1. 4h (22h)				
0.02	287	301 (298)	283 (214)	165 (129)	127 (143)
0.10	405	428 (445)	205 (178)	186 (168)	178 (178)
0.20	405	454 (445)	245 (156)	159 (138)	145 (150)
0.27	420	445 (463)	368 (153)	168 (143)	129 (140)
	Ductility* 4h (22h)				
0.02	8	7 (6)	8 (5)	<1 (<1)	<1 (<1)
0.10	4	2 (3)	3 (3)	<1 (1)	1 (1)
0.20	3	3 (3)	3 (3)	2 (3)	3 (4)
0.27	3	2 (2)	2 (7)	6 (6)	9 (9)

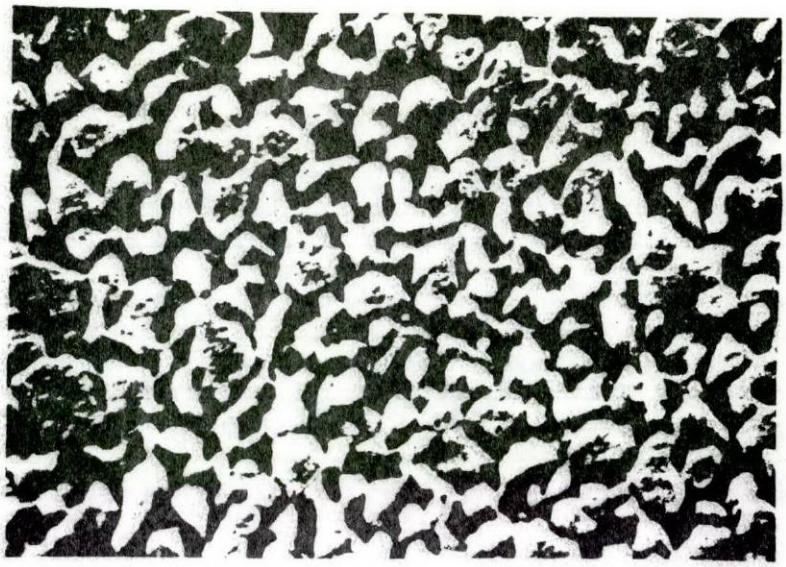
* Number of reverse bends through 90° before fracture

TABLE 6

EFFECT OF HEAT TREATMENT ON HARDNESS AND DUCTILITY OF DEPOSITS FROM CONVENTIONAL SULPHAMATE SOLUTION

Deposit % Mn	As Plated	200°C	300°C	400°C	500°C
	Hardness HV1 4h (22h)				
0.04	338	338 (333)	210 (165)	153 (145)	143 (143)
0.12	390	428 (420)	175 (165)	168 (175)	175 (165)
0.18	428	483 (483)	165 (172)	150 (182)	159 (165)
0.23	445	493 (493)	378 (131)	148 (156)	148 (131)
<0.01	445	483 (320)	239 (251)	165 (159)	140 (159)
	Ductility * 4h (22h)				
0.04	5	4 (5)	5 (3)	<1 (<1)	<1 (<1)
0.12	4	3 (3)	4 (4)	2 (3)	3 (4)
0.18	3	2 (2)	3 (4)	3 (4)	8 (9)
0.23	3	3 (2)	3 (5)	5 (5)	9 (11)
<0.01	2	<1	<1	<1	<1

* Number of reverse bends through 90° before fracture



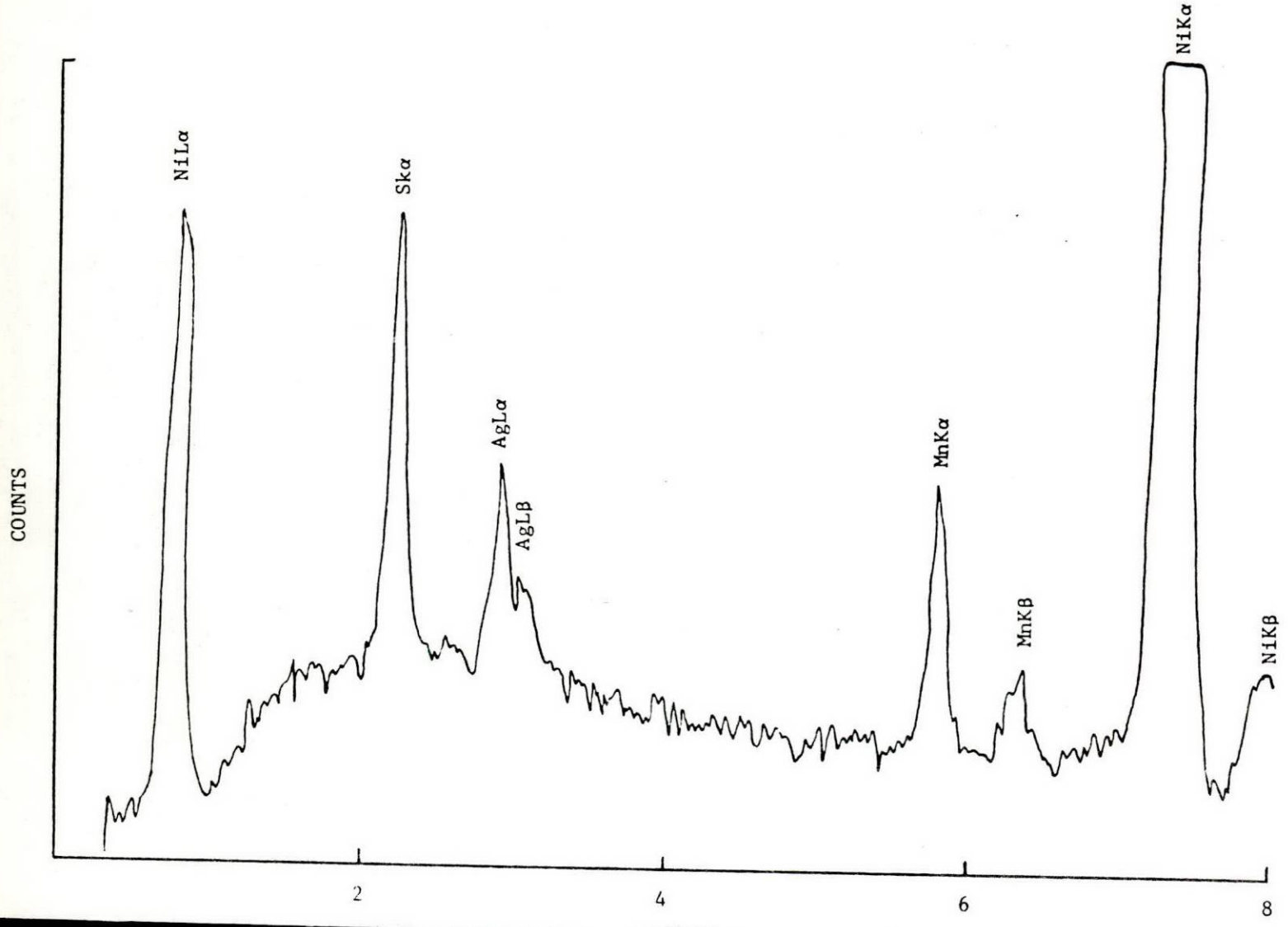
x 3500 1105.06



x 12,500 1105.05

FIGURE 1 Manganese-Containing Nickel Electrodeposit
Nitric Acid/Acetic Acid/Acetone Etch

FIGURE 2 Typical EDX Analysis of Particles at Grain Boundaries in Manganese-Containing Nickel Electrodeposit



E-3

Electroforming I
Session E

Composition Control and Microstructure Of Electrodeposited Nickel-Cobalt Alloys

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COMPOSITION CONTROL AND MICROSTRUCTURE OF ELECTRODEPOSITED NICKEL-COBALT ALLOYS

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ABSTRACT

The variables determining the Ni/Co ratio in an approximately EDNi-50Co alloy produced from a sulfamate electrolyte were studied. It was found that the influence of current density and agitation on the Ni/Co ratio was due to concentration polarization of the Co^{++} ion, which is about 10 times less concentrated than Ni^{++}. Cathode polarization measurements indicate Tafel slopes are identical for Ni and Ni-50Co deposition confirming the independence of current density on Ni/Co ratio. The recrystallization temperature of EDNi-50Co is about 1200 F. The recrystallized microstructure contains voids; the density of which is determined by the cobalt content. Electron transmission microscopy indicates that the voids are produced by coalescence of micropores during recrystallization.

INTRODUCTION

Electrodeposited nickel-cobalt (EDNi-Co) alloys are attractive because of their high ambient temperature tensile properties. Codeposition of nickel-cobalt alloys has evolved from very hard, brittle deposits produced in Watts type nickel-cobalt sulfate and chloride electrolytes to ductile deposits produced in nickel-cobalt sulfamate electrolytes (Ref. 1-3). The tensile properties of EDNi-Co are determined by the Ni-Co composition, which in turn is controlled by the electrodeposition variables.

Endicott and Knapp (Ref. 4) performed a comprehensive investigation of the electrodeposition variables associated with codeposition of nickel-cobalt in sulfamate electrolytes. They showed that the alloy content was determined by the relative concentration of nickel-cobalt in the electrolyte and the deposit current density. The cobalt content decreased with increasing current density. Agitation is also an important variable controlling the nickel-cobalt ratio of the deposit. Dini, Johnson, and Helms (Ref. 5) observed for a sulfamate nickel-cobalt electrolyte ($Ni^{++}/Co^{++} \sim 10$) and 25 asf current density, that cobalt content was 28.5 percent with no agitation, 50 percent with moderate agitation, and 53.5 percent with vigorous agitation.

There have, however, been no investigations performed in which both agitation and current density were independently varied to determine any interrelationship or synergistic effects between current density, agitation, and cobalt

content. For example, the influence of current density on deposit composition may be due to increasing concentration polarization with increasing current density and could, therefore, be prevented by adequate electrolyte agitation.

This paper reports the results of experiments performed to measure the current density and agitation synergistic effects for the prupose of obtaining controlled EDNi-Co compositions. Also included in this paper is metallography of EDNi-Co as a function of electrodeposition variables and heat treatment.

PROCEDURE

A nickel-cobalt sulfamate electrolyte containing boric acid buffer and a wetting agent was used for these studies. Most of the experiments were performed at about 68 g/ℓ Ni and 7 g/ℓ Co for an approximate Ni/Co ratio of 10. The anodes were titanium baskets filled with cobalt chips and titanium baskets filled with sulfur depolarized nickel chips and controlled by separate rectifiers for the nickel and cobalt anodes.

The electrolyte flow nozzle arrangement consisted of a pair of capped 1/2-inch diameter pipes on each side of the test panel. A multitude of holes were drilled in the caps to distribute electrolyte flow across the panel. The electrolyte flow was varied by the number of tank inlet lines opened.

The cathode potential was monitored by means of a dual compartment saturated KCl calomel electrode. The outer compartment was filled with the nickel-cobalt sulfamate plating solution, so there was no KCl contamination in the electrolyte. Figure 1 shows the electrode mounted in a hole through the top of the shield and with the electrode outer permeable membrane in contact with the EDNi-Co cathode. A special electrode housing was constructed to isolate the electrode from the electrolyte potential field.

RESULTS AND DISCUSSION

DEPOSIT COMPOSITION

To quantitatively measure the influence of electrolyte flow and current density on EDNi-Co composition, an EDNi-Co panel was produced during which these variables were changed in steps, and the composition across the panel determined by electron microprobe X-ray spectrometry. The results are shown in Fig. 2. The cobalt concentration in the deposit increased with increasing electrolyte flow and decreasing current density. The flowrate needed to obtain the maximum cobalt content (65%) at 5 and 10 asf was 0.5 gpm. At 40 asf, 4.0 gpm flow was needed to obtain essentially the same (63%) cobalt concentration. The 20 and 30 asf measurements were not conducted at sufficiently high flowrates to achieve this apparent maximum cobalt content. These measurements,

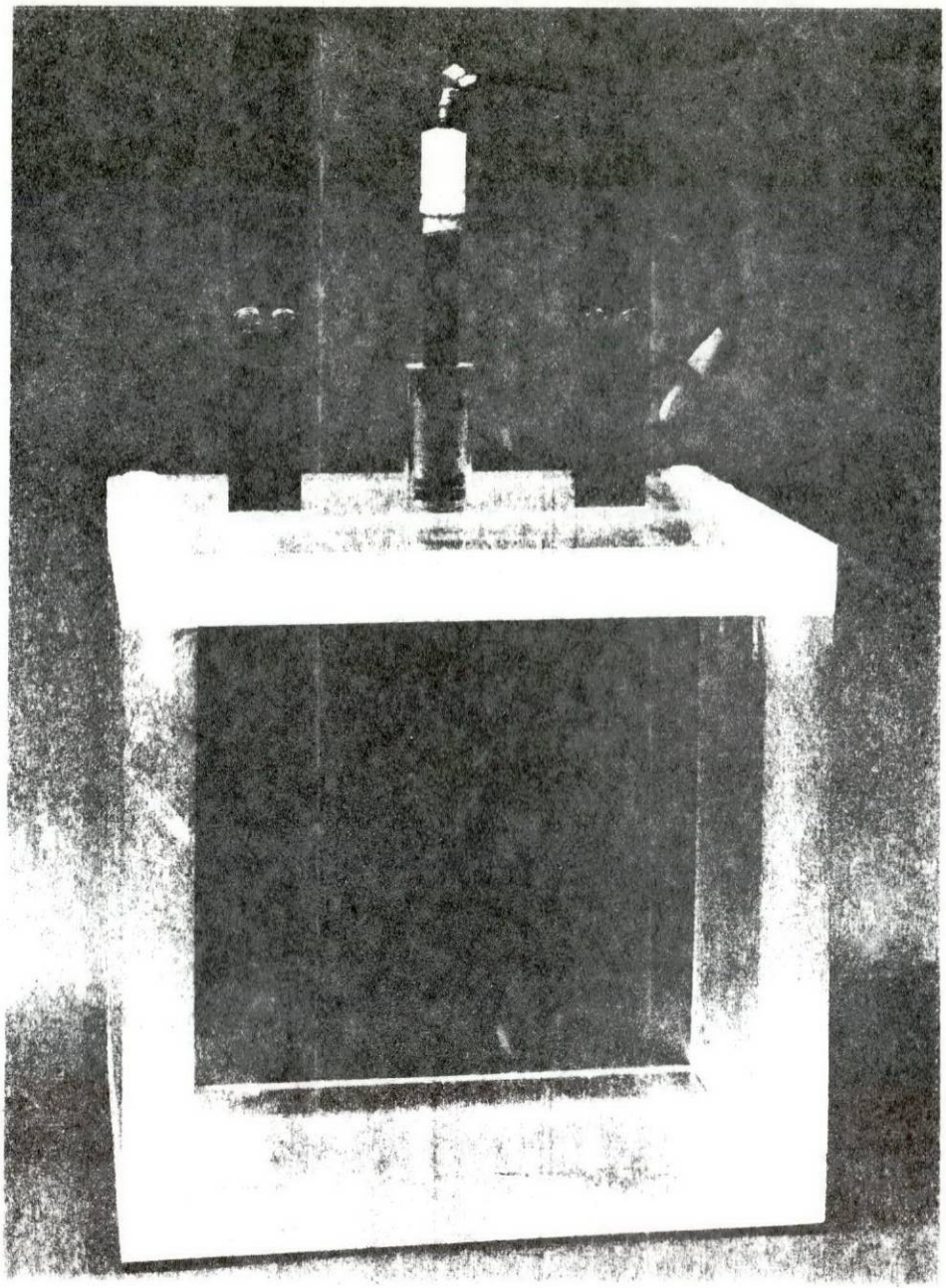


Figure 1. Shielded Panel With Standard Electrode Adjacent to Panel

therefore, indicate that the deposit composition is independent of current density providing the electrolyte flow is above that needed to prevent concentration polarization of Co^{++}, which was 10 times less than the Ni^{++} concentration.

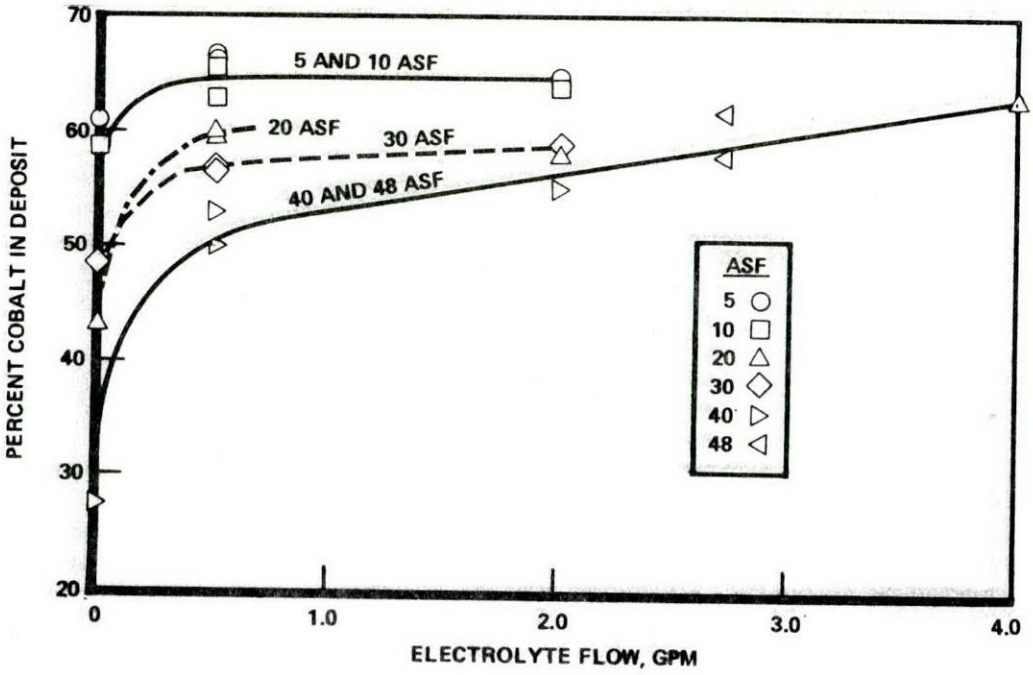


Figure 2. Influence of Current Density and Electrolyte Flowrate on the Composition of EDNi-Co (Electrolyte: Ni/Co = 10)

Since the total deposition current equals the sum of the individual deposition currents, independence of alloy composition with current density infers that the $Ni^{++} + 2e \rightarrow Ni$ and $Co^{++} + 2e \rightarrow Co$ Tafel slopes (ε vs log I) are equal. This follows because the deposition currents (or deposition composition) is determined by the cathode potential. Cathode polarization measurements were determined for EDNi and EDNi ~ 50 Co deposition (Fig. 3). The nickel electrolyte was the same as the nickel-cobalt electrolyte except for the absence of cobalt. It is seen that the Tafel slopes are identical, confirming the independence of current density on the Ni-Co deposit content. The tail-off of the Ni deposition current at high current density was due to concentration polarization as there was no electrolyte impingement during the measurements performed in the Ni^{++} electrolyte. There was, on the other hand, adequate electrolyte impingement to prevent concentration polarization for the measurements conducted in the Ni-Co electrolyte.

Since the deposition Tafel slopes of nickel and cobalt are the same, the main variable affecting deposition composition is the relative concentration of nickel and cobalt in the electrolyte. Ni^{++} and Co^{++} concentration changes will shift the Tafel lines but will not change their slopes. Figure 4 is a plot of cobalt content in the deposit as a function of Ni/Co ratio in the sulfamate electrolyte for 40 asf current density. Comparison with Endicott and Knapp's (Ref. 4) 40 asf data indicates 17 to 25 percent higher cobalt content in our deposits than obtained by Endicott and Knapp. Presumably,

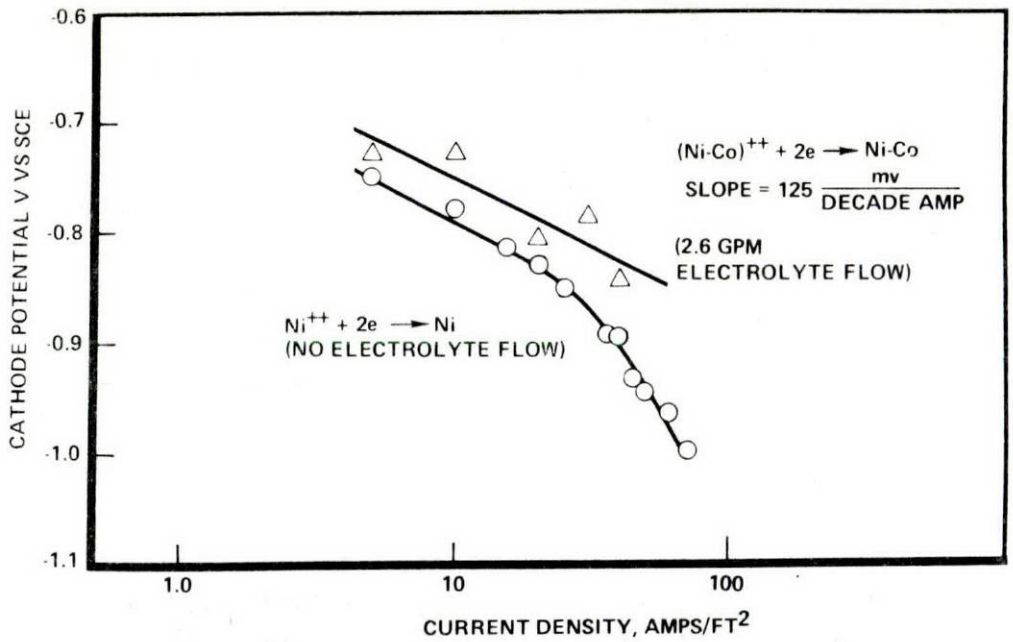


Figure 3. Polarization Data for Deposition of EDNi and EDNi-Co in Sulfamate Electrolyte

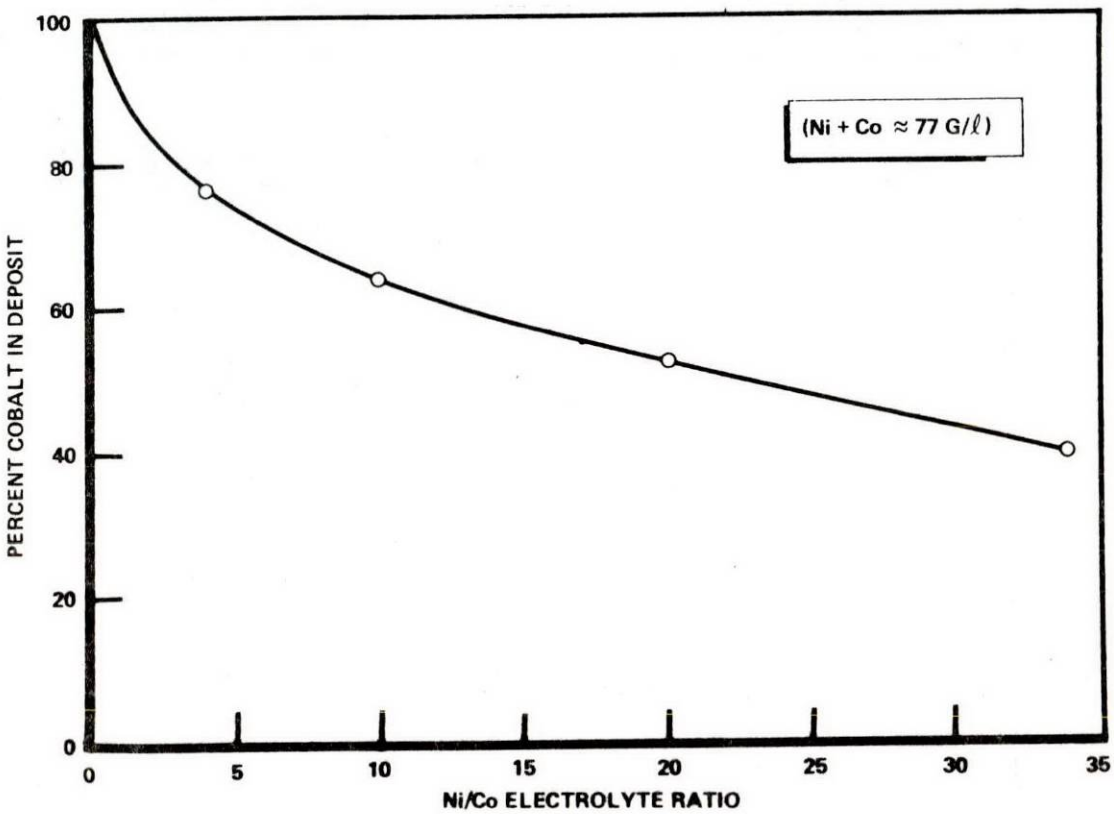


Figure 4. Deposit Composition vs Ni/Co Electrolyte Ratio

this difference was caused by differences in electrolyte flow impingement. The Ni-Co deposits were produced with sufficient electrolyte flow to eliminate concentration polarization as a significant variable. On the other hand, Endicott and Knapp showed decreasing cobalt content with increasing current density indicating insufficient electrolyte flow to prevent Co^{++} concentration polarization.

METALLOGRAPHY

Metallography of as-deposited EDNi-Co is shown in Fig. 5. The as-deposited microstructure appears to be composed of an almost unlimited number of layers as indicated in the optical (100x) and electron (10,000x) micrographs. The most likely explanation for these striations is that they represent composition gradients, but microprobe analysis showed only minor chemistry variation between adjacent areas in the deposit. It is, however, possible that even these small compositional variations can produce a striated microstructure. Transmission electron microscopy indicates the grain size to be about 0.07 to 0.1 micron requiring 20,000 to 40,000 magnification to resolve.

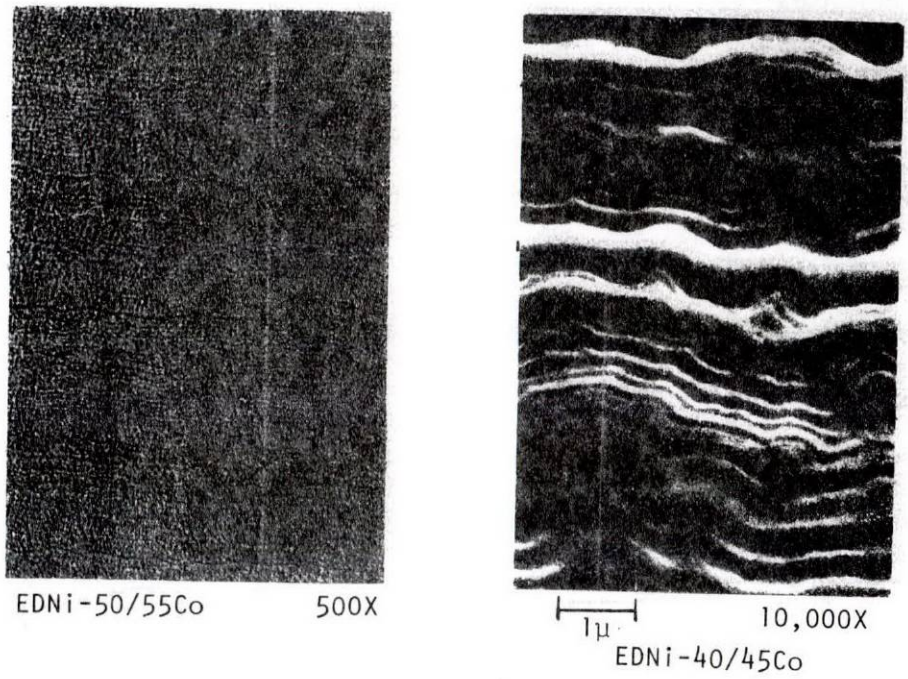
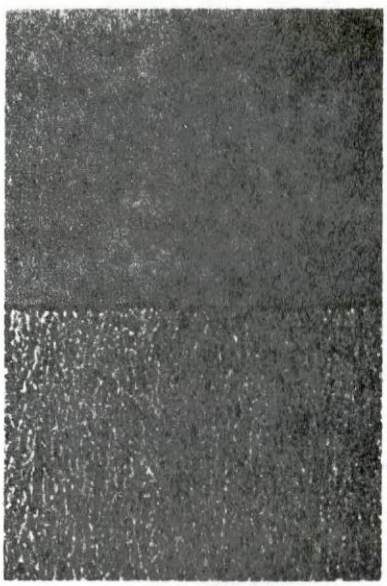


Figure 5. Metallography of As-Deposited EDNi-Co (Etchant: 7-1/2 HF, 2-1/2 HNO_3, 100 CH_3OH)

Figure 6 shows the microstructure of an EDNi-50/55Co panel in various heat treatment conditions, and for comparison, the photomicrographs include the EDNi strike. Heat treating 100 hours at 400 F did not affect the microstructure of either EDNi or EDNi-Co. EDNi recrystallization initiated during the 4-hour, 700 F heat treatment, but this heat treatment had no

discernible affect on the EDNi-Co microstructure. The 4-hour, 1200 F heat treatment initiated recrystallization in EDNi-Co, and produced a totally equax microstructure in EDNi. The EDNi-Co grains were, however, very small and were not truly resolved by 500x magnification.



124 HOURS AT 400 F



4 HOURS AT 700 F



4 HOURS AT 1200 F



1 HOUR AT 1800 F

Figure 6. Microstructure of EDNi-50/55Co (Top) and EDNi (Bottom) in Various Heat Treatment Conditions at 500X (Etchant: 7-1/2HF, 2-1/2HNO_3, 100CH_3OH)

Complete recrystallization and grain growth of EDNi and EDNi-Co occur by heat treating 1 hour at 1800 F. A main feature of the recrystallized EDNi-Co microstructure is the presence of microvoids. The actual void volume, however, was less than indicated in the photomicrograph because of void enlargement produced by etching. Figure 7 is a scanning electron micrograph of the voids in this EDNi-50/55Co specimen. An interesting aspect of the voids is that they are similar to Kirkendall voids, which we have observed by scanning electron microscopy of EDCu-EDNi diffusion couples. Kirkendall voids form as a result of vacancy precipitation resulting from lattice depletion of the diffusing element. As indicated earlier, microprobe analysis showed very little short range inhomogeniety of the Ni-Co concentration, therefore, it is unlikely that the voids are produced by preferential migration of Ni or Co atoms.

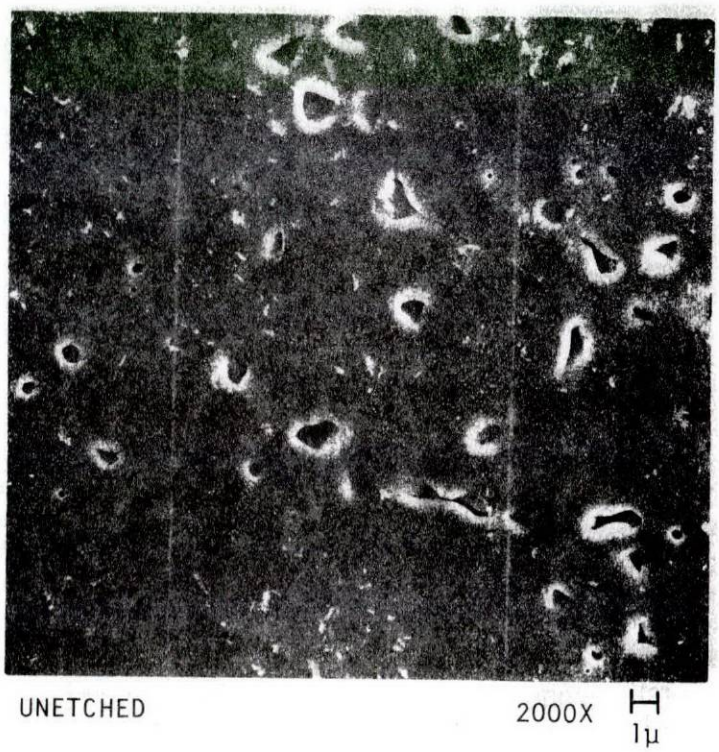
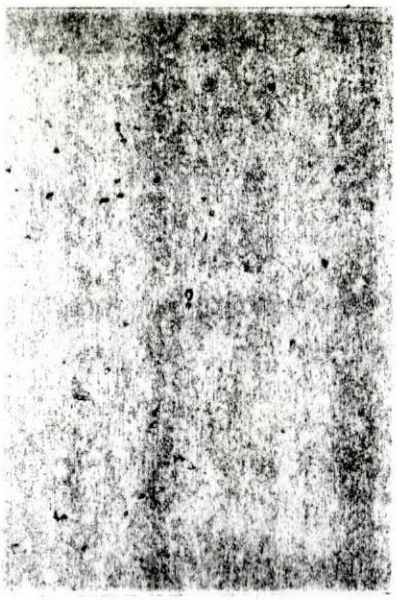


Figure 7. Scanning Electron Micrograph of EDNi-50/55Co Heat Treated 1 hour at 1800 F in Argon

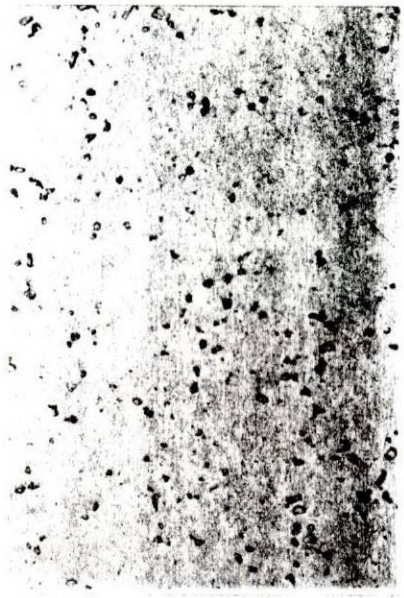
The void density in recrystallized EDNi-Co varied with the cobalt concentration of the deposit. The panel produced at various electrolyte flowrates and current densities contained a wide range of void densities corresponding to the various electrolyte flow and current density combinations. The voids increased with increasing electrolyte flow and decreasing current density as did the cobalt content of the deposit. As is seen in Fig. 8, the void density was not strictly a function of cobalt content, but for equal cobalt content, was greater in deposits produced at the lower electrolyte flowrates.



40 ASF, 1 GPM, 50% Co



40 ASF, 2 GPM, 55% Co



40 ASF, 4 GPM, 63% Co



10 ASF, 1 GPM, 63% Co

Figure 8. Photomicrographs, Unetched at 100X, of Recrystallized EDNi-Co Deposited at Various Current Densities and Electrolyte Flowrates

Various void densities can also be produced by changing the cobalt concentration in the electrolyte which also controls the deposit composition. Figure 9 shows photomicrographs of a specimen which has a relatively large range of cobalt contents and corresponding void densities. The cobalt content of this deposit increased from about 40 to 53% Co during deposition, which was caused by a corresponding increase of cobalt content in the electrolyte from 2.2 to 3.8 g/ℓ. The void density in the deposit increased with increasing cobalt content, and was about the same as shown in Fig. 8 for similar EDNi-Co compositions.



INITIAL DEPOSIT EDNi-40/43Co



MIDDLE DEPOSIT EDNi-44/47Co



FINAL DEPOSIT EDNi-50/53Co

Figure 9. Photomicrographs at 500X of Panel No. 129, EDNi-40/53Co (Etchant: 7-1/2HF, 2-1/2HNO_3, 100CH_3OH)

Figure 10 contains photomicrographs of an EDNi-75/80Co panel. The as-deposited microstructure is banded which is characteristic of EDNi-Co, but there is also an indication of columnar like grains. Columnar, as-deposited microstructure is characterististoc of EDNi but was not observed in EDNi-45/60Co deposits even at very high (500 to 2000x) magnifications. The re-crystallized microstructure of EDNi-75/80Co contains a larger void density then in EDNi-40/53Co. In fact, the void density was so great as to mask the recrystallized grain boundaries.

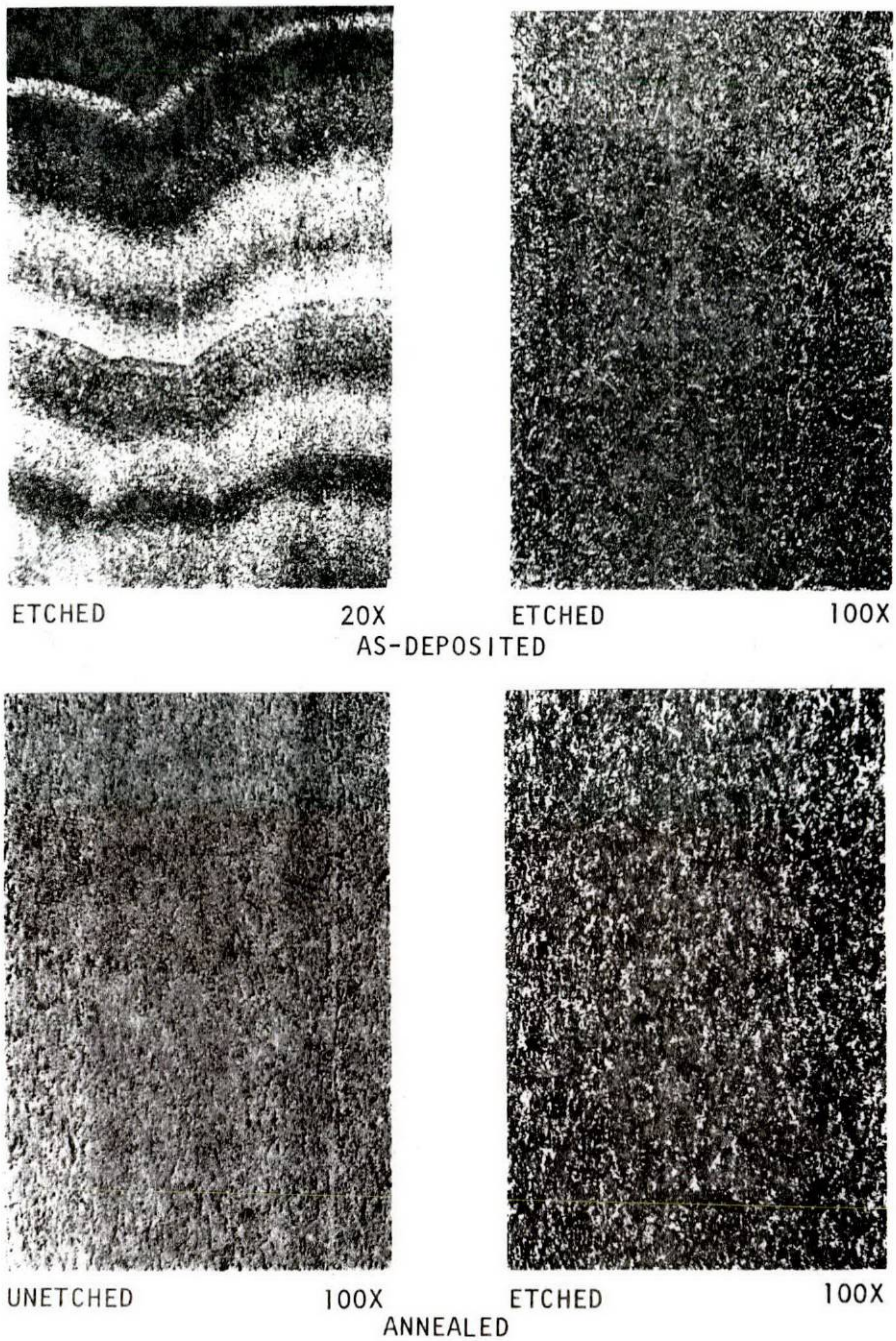


Figure 10. Photomicrographs of EDNi-75/80Co (Etchant: 7-1/2HF, 2-1/2HNO_3, 100CH_3OH)

To determine whether swelling develops during annealing of EDNi-Co, specimens containing 46, 56, 58, and 77% Co and 5 to 63 ppm hydrogen were annealed in argon at 1800 F for 1 hour and their densities measured before and after heat treating. The results are tabulated in Table 1. There was a volume increase of 0.34 to 5.72% during recrystallization and the amount of swelling was roughly proportional to the hydrogen cobalt content of the deposit. The high cobalt alloy, EDNi-75/80Co, contained the highest as-deposited hydrogen content, greatest swelling and void density.

Table 1. Influence of Heat Treatment* on the Density of EDNi-Co

PANEL NO.	AVERAGE COBALT CONTENT %	AS-DEPOSITED HYDROGEN CONTENT PPM	DENSITY		PERCENT DENSITY CHANGE DURING HEAT TREATMENT
			BEFORE HEAT TREATMENT	AFTER HEAT TREATMENT	
129	46	13	8.86	8.83	-0.34
203	56	5	8.88	8.80	-0.90
201	58	15	8.89	8.74	-1.69
128	77	63	8.83	8.32	-5.72

*HEAT TREATMENT: 90 MINUTES AT 1800 F IN ARGON

Electron transmission microscopy was performed (Ref. 6) to determine whether the microstructural voids were produced from microporosity in as-deposited EDNi-Co. The examination revealed the presence of angstrom size pores in the as-deposited microstructure. Only large microvoids were observed in the recrystallized microstructure indicating pore coalescence and/or enlargement during recrystallization. There were no impurities or second phase particles identified as associated with either the micropores or microstructural voids although the most probable impurities, hydrogen, oxygen, and carbon have too low a molecular weight to be identified by microprobe analysis. Oxides and carbides, however, would have been observed and identified by their diffraction pattern.

Farrell and Houston (Ref. 7) showed that microstructural voids develop during annealing electrodeposited nickel containing 1940 to 2700 atomic ppm (33 to 46 wt. ppm) hydrogen. Transmission electron microscopy examination did not reveal the presence of micropores in as-deposited nickel. The initial presence of pores occurred after annealing for 24 hours at 500 C (932 F). At this stage, the pores were only 70 Å in diameter. Swelling was produced during annealing between 600 and 1000 C (1112 and 1832 F). Maximum swelling (~6%) developed when recrystallization was complete. There was a direct relationship between microstructural void size and the amount of swelling of the electrodeposit.

The void formation and swelling of EDNi and EDNi-Co therefore correlate reasonably well. One possible exception is the apparent absence of micropores in as-deposited EDNi and the observation of micropores in as-deposited EDNi-Co.

Void formation and swelling of EDNi and EDNi-Co appear to be produced by the hydrogen absorbed during electrodeposition. The cobalt content of the deposit, however, must also have an important role in the void formation. For example, EDNi panels produced at Rocketdyne contain 10 to 30 ppm hydrogen, and are virtually free of microstructural voids although the recrystallized microstructure of EDNi~50 Co contain a relatively large void density. Thus, higher hydrogen concentration is required to produce microstructural voids in EDNi than in EDNi-Co. Secondly, the void density in EDNi-Co appears to be a function of cobalt content whether the cobalt content and void density were obtained by varying the current density and agitation or by adjusting the cobalt content of the electrolyte. On the other hand, hydrogen absorption would be predicted to be greatest at high current density and low electrolyte flow which produces concentration polarization of the metal ions being deposited.

Thus, although void formation and swelling are probably produced by the absorbed hydrogen, the cobalt content per se must also have a role. A mechanism suggested by G. Thomas (Ref. 8), which may be operating, is that point defects and absorbed hydrogen are swept to grain boundaries or twin boundaries during recrystallization. The cancellation of point defects by combining with opposite point defects requires dislocation climb which is difficult in metals with low stacking fault energy. Also, dislocation climb promotes dislocation entanglement, which decreases the effective hydrogen sweeping distance. The stacking fault energy of nickel-cobalt alloys decreases with increasing cobalt content which is consistent with increasing cobalt content.

CONCLUSIONS

1. The influence of current density and agitation on the Ni/Co deposit composition is due to concentration polarization of the Co^{++} ion.

2. The recrystallization temperature is about 1200 F for EDNi-Co and about 700 F for EDNi.

3. The recrystallized microstructure of EDNi-Co contains a large density of microvoids, the density of which is determined by the cobalt content. These voids are most likely produced by the hydrogen absorbed during electrodeposition.

ACKNOWLEDGEMENTS

The electron microprobe analysis was performed by R. T. Kessler and L. J. Havemann. The transmission electron microscopy examination was performed by Cecil Rhodes of the Rockwell International Science Center. Appreciation is extended to W. T. McFarlen and A. W. Lakin, who initiated the nickel-cobalt investigation and for their technical assistance throughout the program.

REFERENCES

1. Schuler, F. T., "Properties of Electrodeposited Nickel-Cobalt Alloys," presented at the International Conference on Metallic Coatings, 5-8 April 1976.

2. McFarlen, W. T., "Electroformed Nickel-Cobalt Alloy Deposits: An Evaluation," Plating, January 1966.

3. Thompson, A. W. and H. Saxton, "Structure, Strength, and Fracture of Electrodeposited Nickel and Ni-Co Alloys," Met. Trans., Vol. 4, June 1973, pp 1599.

4. D. Endicott and J. R. Knapp, Jr., "Electrodeposits of Nickel Cobalt Alloys: Operating Variables and Physical Properties of the Deposits," Plating, January 1966.

5. Dini, J. W., H. R. Johnson, and J. R. Helms, High Strength Nickel-Cobalt Deposits for Electroforming Applications, SCL-DR-720090, Sandia Laboratories, March 1973.

6. Communication with C. Rhodes, Rockwell Science Center, Thousand Oaks, California, November 1978.

7. Kenneth Farrell and John H. Houston, "Thermal Rejection and Growth of Gas Bubbles in Electrodeposited Nickel," Met. Trans., Vol. 1, July 1970, pp 1979.

8. Communication with Gareth Thomes, University of California at Berkeley, 15 December 1977.

E-4

Electroforming I
Session E

Electroforming Accelerated By Forced Solution Flow

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Paper not available at time of printing of proceedings.

E-5

Electroforming I
Session E

Chemical Vapor Deposition of Nickel Molds

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CHEMICAL VAPOR DEPOSITION OF NICKEL MOLDS

A way of making nickel molds is by the chemical vapor deposition of nickel or the "Vaporforming" process. The raw material used, nickel tetracarbonyl, is a compound of nickel powder and carbon monoxide. It is stored as a liquid and used as a gas. It was first found to possess the property, that its vapors decompose at a hot surface and deposit nickel, by Ludwig Mond in 1890. The process has advanced to where today we are able to manufacture molds used in rotomolding, RIM molding, vacuum forming, injection molding and slush molding.

The Vaporforming method takes advantage of a spontaneous chemical reaction caused to occur at an elevated temperature. The particular chemical reaction in this process absorbs heat energy to breakdown into its components, nickel and carbon monoxide.

The compound, nickel tetracarbonyl, or simply nickel carbonyl, $Ni(CO)_4$, is a liquid under normal laboratory conditions its boiling point is 43°C (107°F). Liquid $Ni(CO)_4$ can be vaporized easily and used as a vapor. At a temperature of 177°C (350°F) nickel carbonyl decomposes readily into nickel and carbon monoxide gas.

When carbonyl vapor is brought into contact with a heated surface of 350°F nickel metal deposits upon the surface as if it were "plating from the vapor". Temperature is the critical factor in controlling the decomposition or plating of carbonyl and its use as a constant source of metallic nickel. Carbon monoxid a product of the reaction, escapes from the surface leaving a clean deposit of nickel.

Chemical vapor deposition is an ideal method of producing forms or shells of nickel for use in making tooling for molding plastics. Other uses of the process involve the construction of parts which are difficult to make by ordinary machining methods. The nickel deposit is found to be uniform, forms well into corners and recesses, does not build-up on projections, and reproduces the surface it is deposited upon exactly.

Much of the success of the overall forming process depends upon the care exercised in constructing the form upon which the nickel deposits. This form is referred to as the mandrel. Many of the steps encountered in the Vaporforming process involve the precise construction and preparation of the appropriate mandrel.

Our most common mandrels are constructed basically of layers of epoxy applied over a tooling aid or mold which supplies the original form. Epoxy

resins are chosen for the mandrel because of their properties of remaining strong and hard at high temperatures. Aluminum granules are added to the epoxy layers in building up the mandrel. This aids in the heat transfer process necessary to achieve even plating. The mandrel is separated from the tooling aid and used in the vapor deposition step as the surface upon which the nickel shell is formed.

The plating mandrels are brought up to temperature of 350°F in the plating chamber. A heat transfer fluid is used to bring the mandrel up to temperature for plating and to maintain it. On some applications, infrared heat lamps, hot plates, or strip heaters, are used. The plating temperature is monitored and controlled by thermocouples and non-contact pyrometers.

The nickel carbonyl vapors are passed into the chamber and distributed through a series of manifolds, tubes and troughs. As the carbonyl vapors come in contact with the heated mandrel surface, decomposition takes place and metallic nickel deposits. The nickel builds on the mandrel surface atom by atom forming a hard nickel layer.

Carbon monoxide is used as the carrier gas for nickel carbonyl. The carbon monoxide flow rate is chosen so that it constitutes 10% of the vapor

volume entering the chamber. The actual flow rates of carbonyl and carbon monoxide are monitored with a series of flowmeters. During the operation in the plating chamber only 40% of the nickel carbonyl supplied to the chamber is consumed, so that 60% of the carbonyl vapors pass out of the chamber as exhaust. This exhaust is recycled.

Plating thickness and rate is controlled by raising or lowering temperature By placing more heat at a given area of the mandrel, it will plate faster than the surrounding points. By controlling "Hot Spots" a plating can be made thicker in selected locations.

The major advantages of this process are:

1. Deposits or plating of 99.9% pure nickel.
2. Almost any material can be coated or reproduced provided it can stand a maximum of 400°F without decomposition, and can transfer Heat. Surface to be plated can be metals, i.e. aluminum, brass, steel or aluminum filled epoxy.
3. Uniformity of coating regardless of configuration.
4. Weldability
5. Useful hard surface of 100 Rb scale with 45 - 50 Rc obtainable.

6. No build-up at projections, plus ability to fill internal corners and recesses.

7. No direction limitations such as line of sight plating or the directional blast. Freedom from bad nodular growths and treeing.

8. Process is controllable, giving a uniform thin or thick nickel mold.

9. Exact duplication obtained from the model, i.e. leather grain, stitching, decorative figures, engravings and etchings.

10. C.V.D. nickel is deposited at a rate of .010" per hour.

11. Nickel, as deposited, is not porous.

12. Plating thickness can be varied from a few thousands to over 3/4 inch.

Disadvantages of Vaporforming.

1. Cost - roughly $1\frac{1}{2}$ to 2 times electro deposition.

2. Toxicity of gas.

3. Plated surface must withstand $400^{\circ}F$ and not give off gases while at heat.

4. Plated surface must be free of cracks and porosity.

Physical Properties of C.V.D. Nickel

Typical physical properties are those listed in TABLE I. The tensile specimens for these tests were flat bars 1/16" thick and 1/2" wide at the gauge area and were machined on all surfaces and from bulk nickel deposited in masses .080" thick or heavier.

TABLE I

	Yield	Tensile	Elongation in 2"	Hardness
A	79,200	101,000	17%	95 Rb
B	70,000	92,500	19%	100 Rb
C	87,400	118,333	15.6%	91.3 Rb

Bulk nickel deposits that have these properties are fully dense with a specific gravity of 8.92.

Effect of Annealing on Physical Properties.

The temperature at which recrystallization of C.V.D. bulk nickel begins is below 600°F. It has not been determined at what temperature this is complete. Extensive investigations on pure nickel indicate that recrystallization is complete at around 700°F. Presence of trace elements will raise this, but except for carbon, such elements are never encountered in C.V.D. nickel. .03% carbon will raise the recrystallization temperature approximately 50°C.

The data below show the response of deposited nickel to various annealing temperatures. The nickel tested was in the form of strips cut from a thin walled tube 48" long x 3.1" diameter, with .010" wall thickness. Most of the effect occurs within one (1) hour, very little change occurring beyond this.

TABLE II

Condition	Sample	Tensile Strength psi	Elongation (% in 2")	Test Gage Length
As deposited, average of several values		96,000	15%	2"
1 Hour @ 600°F,	A	76,500	18%	2"
1 Hour @ 600°F,	B	77,100	18%	2"
1 Hour @ 700°F,	A	77,400	25%	2"
1 Hour @ 700°F,	B	72,900	25.5%	2"
1 Hour @ 800°F		67,100	29%	2"

Chemical Analysis of the above deposit: Carbon: .015% - .020%
Sulfur: .012%

An unusual by-product of annealing at 700°F is that the nickel form retains the position held during anneal. For example, a shape slightly out of flat can be clamped against a flat plate during the anneal. When released after the anneal, it is as flat as the plate used.

If a set of nickel shells intended to match and form a mold do not fit perfectly, they can be clamped together, annealed, and on release are found to match perfectly.

Properties of Vaporformed High-Yield Nickel Alloy

Vaporformed nickel can be alloyed by making a proprietary addition during the chemical vapor deposition. The amount of this alloying ingredient in the final alloy is only a maximum of .05%, and can be controlled to produce a full range of yield strengths from 80,000 psi to over 200,000 psi, with hardness ranging from 100 B to 57 Rc. A hardness value of 40-45 Rc produces material with yield strengths of 175,000 psi minimum.

The alloy has a residual tensile stress as produced. After heat treatment to develop a uniform metallurgical structure and higher elongation (around 10%), residual stress is zero. Residual compressive stresses can be achieved by blasting with beads or shot.

As deposited, elongation is 1 - 2%, so the anneal is required to create useful properties. Hardness drops 2 - 4 points Rc during the anneal.

After one hour anneal at 700°F, properties of this alloy fall in the following range.

Elongation (2 inch gage length)	6 - 12%
Tensile Strength, psi	198,000-211,000
Yield Strength, psi	178,000-190,000
Hardness	38 - 47
Density	theoretical

In thick platings (over 1/8), high yield nickel is deposited .04 to .06-in. with softer nickel added for additional thickness.

C.V.D. nickel offers a high strength alloy that can be produced in limitless configurations, providing unique mechanical properties resulting in uniform high quality molds, coatings and parts.

Information about Carbonyl

Nickel carbonyl, along with other carbonyls, has been known since the year 1890. It is a compound readily formed by passing carbon monoxide gas over fine nickel powder. At 25°C (77°F) and one atmosphere pressure, nickel carbonyl is a colorless, flamable liquid. The compound has a boiling point of 43°C (107°F) and a melting point of -25°C (-13°F). Liquid carbonyl is 1.32 times more dense than water. It does not mix with water, nor does it react chemically with it.

The compound has a very characteristic odor described to be like the smell of a "musty basement". The odor is mild and non-irritating. Many individuals can detect concentrations of the compound in the air as low as 0.03 to 0.04 ppm. However, it is a suspect carcinogenic. OSHA allowable limit is 1 ppB.

F-1

Light Metals Finishing II
Session F

Pre-Paint Treatment Of Metals Today and Tomorrow

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PRE-PAINT TREATMENT OF METALS TODAY AND TOMORROW

The organic coating is a remarkable material.

The organic coating whose applied dry film thickness is measured in mils (thousands of an inch) performs a function out of proportion to its meager size.

This thin organic film not only converts a drab, dull metal object into an eye-pleasing finished product, it also protects the product by forming a physical barrier that excludes the corrosive elements of the environment from the metal surface.

As remarkable as this organic coating is, it cannot perform the protection function by itself, because moisture and oxygen can permeate the coating with the result that the bases metal may still corrode. It needs help.

The surface onto which the organic coating is applied must be properly conditioned. The metal surface must be chemically treated to insulate the anodic and cathodic areas. No anodes, no cathodes, no galvanic corrosion.

Out of this need came the chemical pre-paint treatments: namely iron phosphates, zinc phosphates and chromate conversion coatings.

They joined with organic coatings and together they produced a synergistic effect. The total protection produced by this union is greater than the sum of each acting alone.

This union...this marriage...has been in existence for many decades, protecting and decorating. But, as we all know, something is happening in our industrial society. That something is the concern over pollution.

In many places, chemical solutions are being looked at closely for their pollution properties. The happy marriage between chemical coatings and organic coatings is being put to the test. The industry of which I am a member does not intend to see this marriage go down the drain. As a result, we have developed products that will eliminate the pollution problem without a sacrifice in performance.

Before discussing the solution to the pollution problem, let's first take a closer look at the problem.

A chemical conversion coating is produced by converting the surface of the metal into an oxide, salt or other chemical compound of extremely low solubility.

This is accomplished by exposing the metal to a specific chemical solution. Along with the formation of extremely low solubility compounds, unfortunately, compounds of higher solubility also form, the reaction by-products.

These higher solubility compounds must be removed, otherwise they will cause paint failure. These undesirable compounds are removed by water rinsing. And wince these compounds have greater solubility in acid solutions, a water rinse is often followed by an acidified rinse. The premium type of acidified rinse, of course, is a chromic acid solution. This solution not only removes the undesirable salts, it also leave a residual chromate film on the surface which increases greatly the corrosion resistance of the finish.

A chromic acid rinse often made the difference between poor paint performance and excellent paint performance. Unfortunately, because of environmental considerations, the chromic acid rinse is rapidly becoming extinct.

These rinse stages must be continuously overflowed or periodically dumped to prevent a build-up of soluble salts in the rinses. These salts will redeposit on the metal surface causing a decrease in corrosion resistance and an increased tendency to blister.

The soluble compounds that must be removed by rinsing before painting consist of heavy metal salts, fluorides, mitrates, chromates, phosphates and in some systems, complex cyanide compounds. They are the cause of the pollution problem. They go down the drain with the rinse water.

This pollution problem can be solved by one of two methods. One method is to treat the rinse to remove the toxic materials. This could be costly. The second method is to remove the need for a rinse. By eliminating the formation of objectionable soluble compounds, the need for a rinse is removed.

After many years of religiously preaching the need for good rinsing and now harboring ideas of eliminating them, such a person sounds like a guy gone loco. We have been conditioned over the years to do something a certain way. It is difficult to believe that a change can be made. That is human nature at work.

The change has been made not because it's an unsurmountable problem. It has not been made up until now because there was no need for a change. Necessity was not there to mother an invention. It is now.

Actually, a no-rinse pre-paint treatment has been around for many years... about 30 years. It consisted of chromates, phosphates and a resin in a non-aqueous solution. It was not generally recognized that this product was a conversion coating. It is. It reacts with the metal surface to form a conversion coating. A deposition coating also forms. Many of you are familiar with this product. It is known as a vinyl wash primer: WP-1.

This product, however, cannot be used in equipment used to produce today's conventional conversion coatings. It is applied as a paint, using paint spraying equipment. For that reason it has been looked upon as a paint and its conversion coating feature has often been forgotten.

Another form of a chemical no-rinse treatment that has been used for many years and is still being used is a passivation treatment for galvanized steel. Its function is to prevent the formation of wet storage stains on the zinc coating. This product is also a chromate based material. As we all know, it is not a prepaint treatment. And as we all know it must be removed before a conversion coating can be applied. And as we all know it is removed with difficulty.

As one of the prime suppliers of passivation chemicals to the galvanizing industry, we and other have been asked many years ago by this industry if we could develop a chemical treatment for galvanizing that will not only protect the metal during storage and transit but also serve as a pre-paint treatment and if their customers still choose to apply a conventional conversion coating this new passivation chemical could easily be removed in the pre-paint line.

If such a product could be developed it would cure some big headaches. A customer ordering non-passivated galvanize and receiving passivated galvanize in error would not have his production put out of whack trying to remove the passivation. Another headache avoided would be the receipt of specified non-passivated galvanize with white rust because of inadequate protection against the elements in storage and transit.

After many years of research work, on-line evaluation by some continuous hot dip galvanizers and evaluation by several paint producers and paint consumers, a product by the name of Okemcoat 2000 was developed.

This new pre-paint treatment does not form the troublesome soluble compounds. Therefore, rinsing is not required. No rinsing, no pollution.

It is a pre-paint treatment for steel, zinc galvanize, electro-zinc and aluminum.

Exposure time of the metal to the solution is not a factor.

The solution is used at ambient temperatures although it can be heated to facilitate drying.

The treatment requires no on the job chemical balancing such as the adjustment of Free Acid, Total Acid, Accelerator Content, pH or Fluoride level.

It requires no special equipment for its application. Existing equipment in good working order is used to apply the material.

It contains no component that will settle out.

Sludge is not formed.

Finally, the treatment can be electronically automated to maintain proper solution strength.

We have evaluated this product vs. standard pre-paint treatments under a large variety of paints such as acrylics, polyesters, siliconized polyester, powder coating, waterborne coatings, vinyls, alkyds, epoxies. Two-coat systems and one coat systems were tested, too. The treatment was tested over aluminum, steel, zinc galvanize and electro-zinc. We compared salt spray exposures, distilled water immersion, humidity, boiling water, impact (both wet and dry), T bends, conical bends, crosshatch adhesion.

Based on the results of the evaluation, our company, a very conservative company, made the decision to make the product available.

We understand that it is very difficult for a person responsible for the pre-paint treatment to stick his neck out to try something new. In a like situation I would feel the same. I would not risk my livelihood to try something new unless I had very good reasons to do so. Like the man who ate the first raw oyster. He must have had a very good reason to swallow that slimy mass. He most likely was mighty hungry to become a pioneer. A good reason.

Soon many of us will have very good reasons to try a new concept. In California, where this product is now being used, the good reasons have arrived.

To test a new pre-paint treatment in production often requires considerable preparation such as dumping the existing treatment, cleaning out the system, charging with the new material, adjusting the new material and if it fails, repeating the process. Going back to the original material.

If the existing process is operating without problems there is little motivation to go through the hassle of dumping and redumping.

Fortunately, this new no-rinse treatment can be tested on the production line without the need of dumping any existing chemical solutions. The solution is prepared in the rinse tank. The existing conversion stage is shut down during processing, not dumped. After the trial it's a simple matter to restore the line to its previous condition.

This material is applied to clean, water break-free surfaces. Application is either by immersion, flow-on or spray. It is applied at a concentration of 5 to 10% bv with water. The coating weights range between 10 and 20 mg per square foot. It's a three-stage operation consisting of: clean, rinse, and chemical treat.

Now the bottom line. What will this new method cost? Compared with zinc phosphates, the cost will be approximately 1/3. About 30 cents per 1000 square feet of surface. That includes cleaning costs.

Once there was a sign in a local tavern stating in bold letter, "Free Beer Tomorrow." Going back the next day for my free beer, I saw the same sign, "Free Beer Tomorrow."

Today we see a sign reading, "Pollution Control Tomorrow." Unlike the tavern sign, tomorrow the sign will read, "Pollution Control Today."

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Light Metals Finishing II
Session F

Electroless Nickel Plating On Aluminum Alloys

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AUTOCATALYTIC (ELECTROLESS) NICKEL PLATING ON ALUMINUM

By Donald W. Baudrand

The use of aluminum is rapidly growing because of its light weight, strength, ease of fabrication and certain other desirable characteristics. The high affinity of aluminum for oxygen results in a natural, thin oxide film that protects the aluminum from further corrosion in a mild environment. However, for many applications the environment is too severe, and additional protection is required. Thus, methods for increased protection have been developed, such as chromate conversion coatings, anodizing, paint systems, electroplating and autocatalytic (electroless*) nickel alloy plating. Each of these processes or finishes are suitable for different kinds of applications.

In particular, autocatalytic nickel alloy coatings on aluminum exhibit good corrosion protection, increased resistance to abrasion and wear, high hardness, solderability, electrical conductivity and decorative appeal. It is because of one or more of these properties, that autocatalytic nickel-plated aluminum has increased in use as a replacement for steel, stainless steel, cast iron, etc. in many applications.

There are several problems in preparing aluminum surfaces for autocatalytic nickel plating and several methods have been developed. This investigator has tested the majority of these methods and found successes and failures. Probably, the zincate immersion method is the most widely used and is described in some detail in this paper. The purpose of this paper is to call attention to the need for an improved method (or methods) of surface preparation and processes, and, hopefully, to encourage further investigation into this area. A bibliography is provided at the end of this paper.

OBSTACLES TO OVERCOME

There are many obstacles in the way of successful nickel deposition on aluminum. Additional problems are encountered when the deposit is from an autocatalytic nickel solution. Some of these problems are discussed in the following sections.

Natural Oxide Removal

The natural oxide film on aluminum must be removed before plating. For most processes, the aluminum must remain oxide-free to ensure adequate adhesion of the coating. Important characteristics of the natural oxide film are that it is very thin, on the order of 5 nm (2×10^{-7} inches); it reforms very rapidly after removal, often faster than practical rinsing and transfer operations can take place; and it is amphoteric (soluble in both acid and alkali) making removal, control or replacement more complicated.

Anodizing procedures which remove the natural oxide and replace it with a controlled oxide film have been proposed and used (see bibliography) as a means of overcoming the natural oxide obstacle.[1] Other methods, such as the immersion zincate[2] process, involve the simultaneous removal of the natural oxide, and its replacement with a zinc deposit.

*AES and ASTM have recommended that the term "autocatalytic" be used in place of the term "electroless", as being more definitive.

Chemical Displacement

Aluminum is an extremely active metal, chemically. It forms displacement reactions with different metal ions in solution. Displacement deposits usually tend to be non-adherent. Simply immersing aluminum into most plating solutions will result in a non-adherent immersion deposit before electroplating can start. Under special controlled conditions, it is possible to achieve a good degree of adhesion with some displacement reaction ions. Zincate immersion and stannate immersion are examples of fairly adherent displacement processes.

Galvanic Corrosion

Since aluminum is active (aluminum and its alloys are high in the electromotive series) it tends to protect most of the common metals from corrosion (except zinc and cadmium). In a corrosive environment, galvanic action can occur between any exposed aluminum and the plated coating resulting in very rapid corrosion of the aluminum. Plated coatings on aluminum must be continuous (free from any pits or other discontinuities) and of sufficient thickness to assure good protection.

Thermal Expansion

Aluminum and its alloys are soft, somewhat malleable, and expand on heating more than autocatalytic nickel alloy deposits. The difference in coefficient of thermal expansion gives rise to extreme stresses at the plate / aluminum interface which can result in adhesion failure, or apparent adhesion failure if the fracture occurs in the aluminum and not exactly at the interface. Deforming plated aluminum parts produces extreme stresses at the interface since the aluminum deforms much more easily than does the deposit. Cracking and apparent or actual adhesion failure can occur.

Alloying Constituents

Aluminum as used in industry is not pure aluminum, but consists of a large variety of alloys. Numerous alloying constituents are commonly used to give specific properties to the aluminum alloy making it suitable for a wide variety of applications. Table I shows some common alloys and the alloying constituents.

Table I. Composition Of Some Commonly Plated Aluminum Alloys

Aluminum Alloy	Composition, Percent					
	Cu	Mn	Mg	Cr	Si	Zn
1100	—	—	—	—	—	—
3003	—	1.2	—	—	—	—
2024	4.5	0.6	1.5	—	—	—
5052	—	—	2.5	0.25	—	—
6061	0.25	—	1.0	0.25	0.6	—
7075	1.6	—	2.5	0.3	—	5.6
319	3.5	—	—	—	6.0	—
355	1.3	—	0.5	—	5.0	—
350	3.5	—	—	—	8.0	—

The alloying materials are not always soluble in the aluminum nor are they always uniformly dispersed throughout the body of the aluminum.[2] Particles of metals or other alloying materials at the surface can result in a corrosion cell which would accelerate the corrosion rate of the surrounding aluminum. Sometimes these alloying constituents are difficult to remove in the preparation for plating steps. For example, silicon-containing alloys are best prepared in steps using fluorides, and copper-containing alloys can be prepared in nitric acid.

METHODS OF SURFACE PREPARATION

Numerous methods have been proposed and used commercially for preparing aluminum alloys for autocatalytic nickel deposition. It is the author's observation that because of the variety of aluminum alloys, the high affinity of aluminum for oxygen, the chemical activity of aluminum, and numerous other variables, there is no single simple preparation method suitable for preparing all aluminum alloys for autocatalytic nickel plating.

Zincate Method

The zincate process[3] is described in more detail than the others. Since, as with all other methods, it has shortcomings, some variations are presented.

1. Solvent clean. This step is done only when necessary to remove heavy oils and grease. It should be omitted if colloidal metal particles or other solids of small particle size are part of the soil to be removed since these particles or colloids may adhere more tightly to the aluminum surface after solvent cleaning and interfere with subsequent steps.
2. Etch-clean in a very mild acid cleaner. Proprietary phosphoric acid-based cleaners are used which are capable of maintaining the RMS finish of polished or machined surfaces and close tolerance of machined parts.
3. Rinse.
4. Deoxidize in a non-chromated system which removes no metal.
5. Rinse.
6. Alkaline zincate. Typical formulation is:
   NaOH – 500 g/L, ZnO – 100 g/L, $FeCl_2$ – 1 g/L, Rochelle salt – 10 g/L
   2024 Alloy: Immerse in the zincate solution for 120 sec. at 20°C (70°F).
   6061 Alloy: Immerse in the zincate solution for 30 sec. at 15°C (60°F).
   7075 Alloy: Immerse in the zincate solution for 60 sec. at 20°C (70°F).
7. Rinse thoroughly.
8. Strip zincate in 50% by volume nitric acid.
9. Rinse.
10. Immerse in the zincate solution for 30 sec. at 20°C (70°F).
11. Rinse thoroughly.
12. Rinse thoroughly.
13. Immerse in a mild acid, such as 0.25% H_2SO_4 or 7.5 g/L sulfamic acid, for 10-15 sec. at room temperature. This step removes the tightly adherent strongly alkaline film from the zinc surface without stripping the immersion zinc. A strongly alkaline surface

can be harmful to an autocatalytic nickel solution, and can interfere with adhesion of the deposit.

14. Rinse.
15. Autocatalytic nickel plate.

The great advantage of this zincate process is that very good adhesion is obtained on a wide variety of aluminum alloys. Furthermore, coupled with a properly selected autocatalytic nickel solution, this process produces excellent corrosion resistance. The disadvantages are: (1) many steps in the process, (2) the steps are critical with little room for variation of time, temperature, solution composition, etc. and (3) for scribed panels, creep corrosion attributed to the zinc film has been reported.[4]

Other Methods

Kampert of Alcoa[5] suggests a zincate process as above, followed by a special nickel strike consisting of 375 g/L nickel sulfate, 45 g/L boric acid, pH of 3.6-4.5, an anti-pit agent, and operated at 35-40°C, approximately 4 volts to produce about 2 amps/dm^2 for about 2 minutes. Note the absence of chloride ion in this formulation. The nickel-coated aluminum alloy is transfered without rinsing to a semibright nickel solution for buildup of nickel plate, or to an autocatalytic nickel solution for buildup of nickel alloy.

Missel[6] proposed an acetate-buffered nickel glycolate strike plating solution for use after zincate.

Petit, R. Wright, C. Wright and Kwasnoski[7] report a method which eliminates the zincate process. The steps are:

1. Degrease.
2. Etch (considered the most important step). Consists of 350-360 g/L $NiCl_2 \cdot 6H_2O$ and 500 ml/L (16N) concentrated nitric acid. Another etch suitable for a wider variety of alloys consists of 640 g/L $NiCl_2 \cdot 6H_2O$ and 100 ml of 85% lactic acid/L.
3. Nitric acid dip (2-5 ml of 48% HF per litre of 8N HNO_3). Immerse for 2-3 minutes. For 380 casting alloy, HF is increased to 80-100 ml/L.
4. Activate. Consists of immersion in a solution containing 25 g/L sodium hypophosphite and 25 ml/L of concentrated ammonium hydroxide, followed by an activation strike in a solution containing 25 g/L of sodium hypophosphite, 25 g/L of nickel sulfate hexahydrate, 50 g/L of ammonium citrate, pH 9-9.5 adjusted with ammonium hydroxide, and operated at 85-90°C.
5. Without rinsing, the aluminum is plated in a conventional autocatalytic nickel alloy solution.

Anodizing aluminum as a pretreatment for electroplating on aluminum has been proposed which may find application for autocatalytic nickel deposits. ([8], [9], [10], [11]).

Schwartz and Newkirk[12] report a method which utilized AC current with a brass plating solution to replace zincate immersion.

Miller[13] advocates preparation (after cleaning) in an ammonium bifluoride-dimethylamine borane dip followed by a dimethylamine borane-reduced nickel solution.

Bellis[14] claims a hydrofluoric acid-metal salt which is catalytic to deposition followed by an amine borane reduced autocatalytic nickel.

Winkström, Osmo and Nils of the Axel Johnson Institute, Sweden,[15] developed a method of preparing aluminum for plating consisting of (1) a degreasing step, (2) rinse, (3) pretreatment which consists of mixed acids and a metal salt (nickel, chromium, cobalt, manganese, magnesium or zinc), room temperature, 20 seconds to 1 minute depending on the alloy, (4) rinse, and (5) electroplate, preferably nickel or autocatalytic nickel plate.

IMPORTANCE OF AUTOCATALYTIC NICKEL SOLUTION CONSTITUENTS

The influence of bath composition in plating on aluminum is profound. The selection of complexing agents for nickel is important. It is important also to completely complex the nickel ions (not necessary for plating on steel). One reason for this may be that nickel is displaced from ionic solutions by aluminum. Secondary complexors are useful in the baths designed for plating on aluminum. These materials should be capable of complexing on aluminum. Under certain circumstances, aluminum hydroxide could form. This precipitated basic oxide can lead to instability by stripping the bath stabilizers, and by forming nuclei for "plating out" causing roughness or spontaneous decomposition of the bath.

The selection of stabilizers is important. Usually two or more different types are used, and in quantities somewhat larger than for plating on ferrous alloys.

The bath must have a tolerance for zinc contamination if the zincate pretreatment is used. This is accomplished by certain patented additives.[16] Furthermore, it has been found that low chloride, or no chloride at all, in the bath is beneficial in promoting good adhesion. Numerous other factors affect adhesion as previously mentioned.

CONCLUSIONS

Autocatalytic nickel plating on aluminum is practiced extensively even though there are numerous problems in preparing aluminum alloys, and in proper selection of the plating solution. After extensive testing and investigation it is concluded that the zincate immersion method offers the best opportunity to produce good plating results on the largest number of aluminum alloys. A better, easier, more reliable method is still being sought.

REFERENCES

1. G. A. Miller, U.S. Patent 3,667,991 (1972).
2. ASTM Standards, B253-68
3. G. O. Mallory, Ninth Annual Connector Symposium, Electrical Connector Study Group, pp 179-192 (1976).
4. G. DeBari, Plating and Surface Finishing, 64 (5), 68-74 (1977).
5. W. P. Kampert, U.S. Patent 3,515,564 (1970).
6. L. Missel, Plating and Surface Finishing, 64 (7), 32-35 (1977).
7. G. S. Petit, R. R. Wright, C. C. Wright, and T. Kwasnoski, Plating, 59 (6), 567-570 (1972).
7. R. R. Wright, G. S. Petit, C. C. Wright, U.S. Patent 3,666,529 (1972).
8. K. S. Indira, R. Subramanian and B. A. Shenoi, Met. Fin., 69 (4), 53-58 (1971).
9. R. C. Spooner and D. P. Seraphim, Trans. Inst. Met. Fin., 31, 29 (1954).
10. W. H. Wiltrock, Proc. Am. Electropl. Soc., 48, 52 (1961).
11. E. Lytal, Aluminum, 19 (6), 381 (1937).
12. B. C. Schwartz and J. B. Newkirk, Plating, 59 (5), 431-436 (1972).
13. G. A. Miller, U.S. Patent 3,767,582 (1973).
14. H. E. Bellis, U.S. Patent 3,672,964 (June 27).
15. British Patent 1,445,553 (March 21, 1975).

APPENDIX

APPLICATIONS – AUTOCATALYTIC NICKEL ON ALUMINUM

Heat sinks – (solderability and corrosion protection)
Candle molds – (good release properties)
Electroforming mandrels (scratch resistance)
Small engine blocks – (lubricity)
Aircraft pistons
Aluminum gas gauge housings
Food equipment – aluminum baking pans
Connectors, including glass-sealed
Marine hardware
Mixer beater blades
Precision fit of mating parts
Servo valves
Piston heads
Alternator heat sinks
Pistons for anti-skid devices (wear resistance)
Pistons for disc brakes (wear resistance, lubricity)
Air conditioning tubing (hardness)
Electronic packages, modular
Mass course adjustor
Signal selector (high frequency)
Wave guides
Carburetor components
Hydraulic cylinders
Lock nuts
Shafts
Slide tube assembly
Slide valve plates
Threaded fittings

BIBLIOGRAPHY

Activating Treatments For Plating On Aluminum

S. Wernick and R. Pinner, Surface Treatment and Finishing of Aluminum and its Alloys, Robert Draper, Teddington, Middlesex, England, pp. 581-679 (1964).

R. H. Keller, Met. Finish., 48, 12, 56 (1950).

E. Herrmann, Galvanotechnik, 51, 219, 336 (1960).

J. T. N. Atkinson, Plating, 47, 509 (1960).

G. Fitzgerald-Lee, Prod. Finish., (London), 13, 74, 84 (1960).

C. L. Faust, G. R. Schaer, and D. E. Semones, Plating, 48, 605 (1961).

F. L. Church, Mod. Met, 23 (5), 65 (1967).

R. V. Vanden Berg, Aluminum, Vol. III, American Society for Metals, Metals Park, Ohio Chap. 20, (1967).

H. Richaud, Rev. D'Aluminum, 45 (377), 896 (1969).

D. J. Bailey, Electroplat. Met. Finish., 23 (5), 42 (1970).

K. A. Holbrook and P. J. Twist, Plating, 56, 523 (1969).

A. Brenner and G. Riddell, J. Res. Nat. Bur. St., 37, 31, (1946); ibid., 39, 385 (1947).

J. W. Tharp, Plating, 58, 328 (1971).

J. W. Tharp, Prod. Finish., 34 (5), 64 (1970).

D. I. Garland and R. S. Gray Jr., U.S. Patent 2,575,214 (Nov. 13, 1951).

R. R. Reschan and A. Krieg, U.S. Patent 2,694,017 (Nov. 9, 1954).

Reynolds, U.S. Patent 2,958,601 (1958).

H. Bardsorf and K. Muller, Aluminum, 35 (1959).

Pechiney, Brit. Patent 870,060 (1961).

H. O. Hansson, U.S. Patent 3,867,265 (Feb. 18, 1975).

W. E. Cooke and J. Hodgson, U.S. Patent 4,097,342 (June 27, 1978).

R. A. Tremmel, W. J. Wieczerniak, and R. J. Clauss, U.S. Patent 3,915,811 (Oct. 28, 1975).

K. F. Dockus, U.S. Patent 4,028,200 (June 7, 1977).

D. G. McBride and G. P. Vlasak, J. Electrochem. Soc., 118 (12), 2055 (1971).

J. W. Tharp, Prod. Fin., 37, 82 (1972).

G. S. Petit, R. R. Wright, C. C. Wright and T. Kwasnoski, Plating, 59, 567 (1972).

G. A. Miller, U.S. Patent 3,667,991 (June 6).

H. E. Bellis, U.S. Patent 3,672,964 (June 27).

R. R. Wright, G. S. Petit and C. C. Wright, U.S. Patent 3,666,529 (1972).

G. A. Miller, U.S. Patent 3,767,582 (Oct. 23).

J. W. Dini and H. R. Johnson, Met. Finish., 72, 44 (Aug.).

B. L. Berdan and B. M. Luce, U.S. Patent 3,969,199 (July 13).

Zincate

ASTM Standards, B253-68.

J. Korpiun, U.S. Patent 2,142,564 (1939).

Zincate (Continued)

R. A. Ehrhardt and J. M. Guthrie, Mon. Rev. Am. Electroplat. Soc., 34, 421 (1947).

W. G. Zelley, J. Electrochem. Soc., 100, 320 (1953).

E. Armstrong, Met. Treat., 6, 153 (1940).

E. H. Hewitson, U.S. Patent 1,627,900 (1927).

B. K. Braund and H. Sutton, Trans. Faraday Soc., 31, 1595 (1935).

G. Elssner, Aluminum, 17, 376 (1935).

V. I. Lainer and S. I. Orlova, Legk. Metall., 5 (2), 22 (1933); Chem. Abstr., 30, 7047 (1936).

L. Perner, U.S. Patent, 2,297,241 (1942).

J. Bengston, Trans. Electrochem. Soc., 88, 307 (1945).

W. R. Meyer, Mon. Rev. Am. Electroplat. Soc., 33, 269 (1946).

W. Bullough and G. E. Gardam, J. Electrodepositors' Tech. Soc., 22, 169 (1947).

S. Heiman, J. Electrochem. Soc., 95, 205 (1949).

F. Keller and W. G. Zelley, Proc. Am. Electroplat. Soc., 36, 149 (1949).

W. R. Meyer and S. H. Brown, Proc. Am. Electroplat. Soc., 36, 163 (1949).

F. Keller and W. G. Zelley, J. Electrochem. Soc., 96, 143 (1950).

G. L. J. Bailey, J. Electrodepositors' Tech. Soc., 27, 233 (1951).

W. G. Zelley, U.S. Patent 2,650,886 (1953).

J. W. Tharp, Miami Branch News, Plating, 51, 73 (1964).

E. Herrmann, Galvanotechnik, 51, 219, 336 (1960).

C. L. Faust, G. R. Schaer and D. E. Semones, Plating, 48, 605 (1961).

R. Leloup, U.S. Patent 3,284,323 (1966).

H. Richaud, French Patent 1,496,255 (1967).

A. M. Howard, U.S. Patent 3,982,055 (Sept. 21, 1976).

W. P. Kampert, U.S. Patent 3,989,606 (1976).

G. A. Laitinen, Plating (Nov. 1977).

Anodizing

W. J. Traverse, U.S. Patent 1,971,761 (1934).

J. Fischer, U.S. Patent 2,036,962 (1936).

H. J. Wittrock, Proc. Am. Electroplat. Soc., 48, 52, (1961).

NASA SP-5025 (1966).

J. C. McConnell, U.S. Patent 3,468,765 (1969).

A. E. Weber, U.S. Patent 3,493,474 (1970).

T. Asada, U.S. Patent 3,515,650 (1970).

A. L. Peach, U.S. Patent 3,531,379 (1970).

K. S. Indira, R. Subramanian and B. A. Shenoi, Met. Finish., 69 (4), 52 (1971).

A. Akiyama, K. Uasuhara, K. Tanaka and T. Saji, Plating, 58, 504 (1971).

W. H. Wiltrock, Proc. Am. Electroplat. Soc., 48, 52 (1951).

Anodizing (Continued)

J. W. Tharp, Midwest Florida Branch News, Plating, 53, 1378 (1966).

J. W. Tharp and J. J. Tyminski, Plating, 55, 580 (1968).

J. W. Tharp, Baltimore-Washington Branch News, Plating, 57, 641 (1970).

H. J. Wittrock, U.S. Patent 3,943,039 (Mar. 9).

Tin Immersion

E. J. Seyb, J. C. Jongkind and L. P. Gowman, Proc. Am. Electroplat. Soc., 51, 133 (1964).

J. C. Jongkind and P. G. Kenedi, U.S. Patent 3,274,021 (1966).

S. J. Beyer, Plating, 56, 257 (1969).

J. C. Jongkind, Trans. Inst. Met. Fin., 45, 155 (1967).

P. G. Kenedi, U.S. Patent 3,108,006 (1963).

G. A. DiBari, Plating and Surface Finishing, 64 (5), 68-74 (1977).

Solutions For Plating On Aluminum

C. A. Boose, Trans. Inst. Met. Fin., 53 (1975).

G. O. Mallory, Plating, 61 (11), 1005-1014 (1974).

V. N. Flerov and L. V. Golovushkina, U.S.S.R. Patent 388047 (April 1971).

Kenji Iijima, Japan Patent 75160145 (June 1974).

Kosaka, Jaruo; Ohno, Kaishi, Aruminyumu Kenskyu Kaishi, 112, 18-19 (1978) (Japanese).

A. Wasserman, Prod. Finish., 42 (5), 48-50, 52 (1978).

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Light Metals Finishing II
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The Effect of Environmental Concerns And Energy Conservation Upon Cleaning and Treating of Aluminum

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Paper not available at time of printing of proceedings.

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Light Metals Finishing II
Session F

Pollution Control in Anodizing Operations

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The following essay is a comprehensive study of an aluminum anodizing pollution abatement program in actual operation. The study was performed on the abandoned City of Terrell Municipal Waste Treatment Plant. Details in modification to this system have been outlined explicitly in precise form accompanied by photographs.

INDUSTRIAL UTILIZATION OF A DOMESTIC WASTE TREATMENT FACILITY

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In many instances, municipal growth and stringently changing discharge parameters dictate renovation of existing domestic waste treatment plants or construction of a modern facility that meets the present or future needs of the municipal growth factors. In many cases, the latter alternative is chosen considering the economic feasibilities involved.

If, in fact, this does occur, construction of a new plant can create the need for relocation and the existing treatment facilities, as a result, being abandoned.

These facilities are an excellent means by which industry can process their own waste water and if accomplished properly, discharge to a public waterway.

Depending on the qualitative and quantitative properties of the waste to be treated, alteration to the system are imperative before proper treatment is to occur.

Howmet Aluminum Corporation's Texas Extrusions Division discharged all waste water from our anodizing facility to the municipal treatment plant prior to January 1978. Previous to this date, we were striving to renovate the old abandoned municipal treatment plant to enable us to treat our waste water so the effluent would

meet or surpass the E.P.A. and Texas Department of Water Resources discharge parameters.

Our primary effort was to achieve pH control to the extent that there would be a variation of no more than a $\pm$.6 pH value. This necessitated the fabrication of a four chambered vessel with adequate mixing of raw influent in order to achieve pH stabilization. The first chamber is for primary mixing of raw influent and initiates pH adjustment. The second chamber contains an on-off course pH adjustment reagent feed system that corrects the pH if it is less than 4.0 or greater than 10.0. Number three chamber is the fine pH adjustment chamber which has a reagent feed system regulated by demand type air actuated valves that are proportionally controlled by a pH monitoring controller. This stage makes the final pH adjustment and records the value on a strip chart recorder for future reference. The final stage is for mixing and tertiary pH stabilization.

Problems existed with the monitoring probes becoming scaled and reporting the wrong values. But an ultrasonic cleaning device has proven to be a remedy. Otherwise, the system has proven to be quite efficient for our needs with minimum maintenance required.

After proper pH control has been sufficied, renovation and modification of the prospective industrial waste treatment facility has to be considered, keeping in mind all possible future needs.

The domestic waste treatment plant that we are utilizing consisted of three aerators, six small clarifiers, one large clarifier, a digestor, and sludge drying via drying beds.

Primary alteration consisted of deletion of all treatment processes except primary clarification (the one large clarifier), final clarification, the digestor, and the addition of a rotary vacuum filter.

The digestor serves as a holding tank for sludge resulting from solids separation occurring in the primary clarifier. Solids separation is accomplished through addition of a polyelectrolyte to the influent as it enters the clarifier. The type clarifier most municipal waste plants utilize, as in our case, has a divider approximately two feet from the wall extending from above water level to approximately two feet above the bottom of the clarifier. As the electrolyte is added; 1) flocculation occurs, 2) the solids drop to the bottom of the sludge divider, and 3) primary sludge compaction begins. The sludge rake then moves the sludge toward the center of the clarifier where continuous solids concentration evolves. This type of clarifier suffices if the sludge drying device is sized enough to handle all solids that are produced at a maximum rate. But difficulties can arise from the lack of retention time resulting from the inferior mode of operation from this type of clarifier.

Sludge from the clarifier is pumped into a digestor which, for our purposes, is a holding tank with the approximately same volume as the clarifier. It seems that anerobic bacterial action in the digestor induces further concentration abilities, again, depending on retention time and ambient temperature. Transference of sludge from the primary clarifier to the digestor thence to our rotary

vacuum filter results in the "flocced" solids particles to be sheared. This shearing effect henders an efficient drying operation. Improvements in sludge condition could be achieved in the vacuum filter sludge container if we bypassed the digestor and pumped off of the clarifier directly to the filter. But considering the inefficient type of clarifier we have to utilize, the digestor is needed for storage capacity or else we would have to operate the vacuum filter continuously. Also, intermittent pumping from the primary clarifier to the digestor for not more than ten minutes at a time and then waiting one hour or more before pumping again helps to decrease the shearing of sludge particles. Another problem existed with the ten minute pumping procedure in that if the ten minute period is increased the sludge blanket starts to cavitate and clear water is mixed with the sludge which decreased the solids concentration.

The drying bed method of drying sludge was used in the past and is still being used by many municipal treatment plants today. A drying bed consists of a large area contained by a concrete dyke on all sides and having two layers of filtering material. The top layer being six inches of sand and below it three feet of washed rock. This enables the operator to dry sludge from the digestor by filling the bed with wet sludge and the water filtering through the sand and rock layers into a series of drainage pipes with resulting dried sludge within two to three days. The dried sludge then has to be removed by shoveling it out manually. This method of sludge drying is quite inefficient and expensive. It is

inefficient from the standpoint that the operation can be haulted or slowed down from such interferences as bad weather, lack of manpower, or equipment malfunction. The expense can be quite high considering the sand has to be replaced each time it is cleaned out, cost of three employees and equipment cost. Also, wet weather is an operational deterrent that ceases the drying process completely. In all, the drying beds are not the most efficient method of solids drying.

The drying method we chose was a rotary vacuum filter, but the drying beds are still available for emergency use. We purchased a used Filtration Engineering rotary vacuum filter and made necessary modifications and renovations for proper operation. The filter size is 10' x 16' and is capable of drying 40,000 gallons of wet sludge per day resulting in 60 yards of dried sludge, again, depending on quality of sludge.

Our filter is relatively maintenance free as far as major malfunctions are concerned. It is constructed from 316 stainless steel on the components that are exposed to sludge. This is necessary in regard that the compositional hydroxide salts and the continuous moisture exposure from the sludge is extremely conducive to corrosion.

Our sludge drying operation begins with solids being pumped from the digestor to the vacuum filter. The filter then dries the sludge from 5% to 15% solids and is conveyed to a dump truck. It is then transported to our privately owned on-site industrial landfill designated solely for disposition of all sludge produced from our

treatment plant.

An advantage of treating your own waste, as in our case, is the possibility of discharging treated effluent to a creek or river. This, in turn, can create a savings from omission of the municipal sewage treatment cost. But consequently, it poses a liability for the company to discharge effluent that meets the parameters designated by the Texas Department of Water Resources.

In order to discharge to a public waterway in the state of Texas, one must first obtain a permit from the Texas Department of Water Resources. This agency closely monitors our effluent which made it necessary for Howmet to install a water quality testing laboratory. The facilities are in the same building with the vacuum filter and all analysis and plant operations are conducted by one person in an eight hour shift.

Our effluent has never exceeded the parameters set by the TDWR. This achievement, obviously, compliments the proficiency you can achieve by proper utilization of a converted domestic waste treatment plant. The following is an example of our effluent and an average monthly discharge value.

Parameters	Average Lbs./Day Permitted	Actual Average Lbs./Day Reported
pH	6.0-9.5	8.4
TSS	130.0	10.27
Oil & Grease	43.00	8.41
SO4	6000.0	5494.9
Fe	16.600	.0267
Ni	.4300	.1922
Al	4.300	1.310
Flow	510,000 gal/day	319,995 gal/day

These figures are common for a monthly discharge from our Aluminum Finishing facility assuming an average production rate of 35,000 lbs/day. The 35,000 lbs. of production per day yields approximately 30,000 gallons of wet sludge. This is entirely dependent on our clarifier efficiency. As observed from the previous figures, flow rates averaged 319,995 gal/day. Sludge concentration as a result of treatment, originally comprised of 9% of the total volume. This volume is further reduced to a concentrated solid content via rotary vacuum filter by another 3% which creates a sludge with a consistency somewhat thicker than mayonnaise. The cost of operation is approximately $500.00 per month not including the salary of an operator. Conversion cost at this time has been $125,000.00. This figure can vary depending on factors such as purchase of new or used process eqiupment, the degree of sophistication of equipment that is chosen, and amount of fabrication of equipment required.

Since our treatment plant does have all the existing aerators and clarifiers that are not being used for our chosen process, they still can serve as a back-up system for temporary treatment. The influent flow can be re-routed through the six small clarifiers, the polyelectrolyte added to the influent, and the solids settle to the bottom of the clarifiers. The clear effluent would follow a path to the three aerators and thence to the creek. This backup system can maintain solids accumulation without need of sludge disposition for six days. In addition, the drying beds serve as a

back-up system for the vacuum filter.

At the present time, improvements of our facilities would be to install a high rate reaction type clarifier. This would extend our retention time and in turn improve our sludge characteristics. An alarm system is also being installed that will sound a warning when abnormal solids content in our effluent is present. The system will consist of a conductivity meter that constantly monitors the clear effluent. When solids content of the effluent increases above an established maximum limit, an alarm is activated and transferred through our telephone system which rings a phone in the supervisor's office at the anodizing plant. This alarm is necessary since our pollution control plant is a distance of one mile from the anodizing plant and is operated for eight hours a day. During the remaining sixteen hours there is no employee on duty fulltime. The process lab technicians at the anodizing plant make routine inspections of water quality every two hours. Nevertheless, an emergency situation can occur between these inspections. So the alarm system will ensure that discharge quality is being maintained at legal limits when no operator is on duty.

So, in all, a properly utilized municipal sewage plant is an ideal facility to treat industrial waste water considering the available equipment and the cost of renovation vs. the cost of fabrication of a new facility with the most basic equipment and no back-up systems.

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Light Metals Finishing II
Session F

Air and Water Pollution Control for Anodizing

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Paper not available at time of printing of proceedings.

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Light Metals Finishing II
Session F

Pre-Paint Treatment Of Metals Today and Tomorrow

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PRE-PAINT TREATMENT OF METALS TODAY AND TOMORROW

The organic coating is a remarkable material.

The organic coating whose applied dry film thickness is measured in mils (thousands of an inch) performs a function out of proportion to its meager size.

This thin organic film not only converts a drab, dull metal object into an eye-pleasing finished product, it also protects the product by forming a physical barrier that excludes the corrosive elements of the environment from the metal surface.

As remarkable as this organic coating is, it cannot perform the protection function by itself, because moisture and oxygen can permeate the coating with the result that the bases metal may still corrode. It needs help.

The surface onto which the organic coating is applied must be properly conditioned. The metal surface must be chemically treated to insulate the anodic and cathodic areas. No anodes, no cathodes, no galvanic corrosion.

Out of this need came the chemical pre-paint treatments: namely iron phosphates, zinc phosphates and chromate conversion coatings.

They joined with organic coatings and together they produced a synergistic effect. The total protection produced by this union is greater than the sum of each acting alone.

This union...this marriage...has been in existence for many decades, protecting and decorating. But, as we all know, something is happening in our industrial society. That something is the concern over pollution.

In many places, chemical solutions are being looked at closely for their pollution properties. The happy marriage between chemical coatings and organic coatings is being put to the test. The industry of which I am a member does not intend to see this marriage go down the drain. As a result, we have developed products that will eliminate the pollution problem without a sacrifice in performance.

Before discussing the solution to the pollution problem, let's first take a closer look at the problem.

A chemical conversion coating is produced by converting the surface of the metal into an oxide, salt or other chemical compound of extremely low solubility.

This is accomplished by exposing the metal to a specific chemical solution. Along with the formation of extremely low solubility compounds, unfortunately, compounds of higher solubility also form, the reaction by-products.

These higher solubility compounds must be removed, otherwise they will cause paint failure. These undesirable compounds are removed by water rinsing. And wince these compounds have greater solubility in acid solutions, a water rinse is often followed by an acidified rinse. The premium type of acidified rinse, of course, is a chromic acid solution. This solution not only removes the undesirable salts, it also leave a residual chromate film on the surface which increases greatly the corrosion resistance of the finish.

A chromic acid rinse often made the difference between poor paint performance and excellent paint performance. Unfortunately, because of environmental considerations, the chromic acid rinse is rapidly becoming extinct.

These rinse stages must be continuously overflowed or periodically dumped to prevent a build-up of soluble salts in the rinses. These salts will redeposit on the metal surface causing a decrease in corrosion resistance and an increased tendency to blister.

The soluble compounds that must be removed by rinsing before painting consist of heavy metal salts, fluorides, mitrates, chromates, phosphates and in some systems, complex cyanide compounds. They are the cause of the pollution problem. They go down the drain with the rinse water.

This pollution problem can be solved by one of two methods. One method is to treat the rinse to remove the toxic materials. This could be costly. The second method is to remove the need for a rinse. By eliminating the formation of objectionable soluble compounds, the need for a rinse is removed.

After many years of religiously preaching the need for good rinsing and now harboring ideas of eliminating them, such a person sounds like a guy gone loco. We have been conditioned over the years to do something a certain way. It is difficult to believe that a change can be made. That is human nature at work.

The change has been made not because it's an unsurmountable problem. It has not been made up until now because there was no need for a change. Necessity was not there to mother an invention. It is now.

Actually, a no-rinse pre-paint treatment has been around for many years... about 30 years. It consisted of chromates, phosphates and a resin in a non-aqueous solution. It was not generally recognized that this product was a conversion coating. It is. It reacts with the metal surface to form a conversion coating. A deposition coating also forms. Many of you are familiar with this product. It is known as a vinyl wash primer: WP-1.

This product, however, cannot be used in equipment used to produce today's conventional conversion coatings. It is applied as a paint, using paint spraying equipment. For that reason it has been looked upon as a paint and its conversion coating feature has often been forgotten.

Another form of a chemical no-rinse treatment that has been used for many years and is still being used is a passivation treatment for galvanized steel. Its function is to prevent the formation of wet storage stains on the zinc coating. This product is also a chromate based material. As we all know, it is not a prepaint treatment. And as we all know it must be removed before a conversion coating can be applied. And as we all know it is removed with difficulty.

As one of the prime suppliers of passivation chemicals to the galvanizing industry, we and other have been asked many years ago by this industry if we could develop a chemical treatment for galvanizing that will not only protect the metal during storage and transit but also serve as a pre-paint treatment and if their customers still choose to apply a conventional conversion coating this new passivation chemical could easily be removed in the pre-paint line.

If such a product could be developed it would cure some big headaches. A customer ordering non-passivated galvanize and receiving passivated galvanize in error would not have his production put out of whack trying to remove the passivation. Another headache avoided would be the receipt of specified non-passivated galvanize with white rust because of inadequate protection against the elements in storage and transit.

After many years of research work, on-line evaluation by some continuous hot dip galvanizers and evaluation by several paint producers and paint consumers, a product by the name of Okemcoat 2000 was developed.

This new pre-paint treatment does not form the troublesome soluble compounds. Therefore, rinsing is not required. No rinsing, no pollution.

It is a pre-paint treatment for steel, zinc galvanize, electro-zinc and aluminum.

Exposure time of the metal to the solution is not a factor.

The solution is used at ambient temperatures although it can be heated to facilitate drying.

The treatment requires no on the job chemical balancing such as the adjustment of Free Acid, Total Acid, Accelerator Content, pH or Fluoride level.

It requires no special equipment for its application. Existing equipment in good working order is used to apply the material.

It contains no component that will settle out.

Sludge is not formed.

Finally, the treatment can be electronically automated to maintain proper solution strength.

We have evaluated this product vs. standard pre-paint treatments under a large variety of paints such as acrylics, polyesters, siliconized polyester, powder coating, waterborne coatings, vinyls, alkyds, epoxies. Two-coat systems and one coat systems were tested, too. The treatment was tested over aluminum, steel, zinc galvanize and electro-zinc. We compared salt spray exposures, distilled water immersion, humidity, boiling water, impact (both wet and dry), T bends, conical bends, crosshatch adhesion.

Based on the results of the evaluation, our company, a very conservative company, made the decision to make the product available.

We understand that it is very difficult for a person responsible for the pre-paint treatment to stick his neck out to try something new. In a like situation I would feel the same. I would not risk my livelihood to try something new unless I had very good reasons to do so. Like the man who ate the first raw oyster. He must have had a very good reason to swallow that slimy mass. He most likely was mighty hungry to become a pioneer. A good reason.

Soon many of us will have very good reasons to try a new concept. In California, where this product is now being used, the good reasons have arrived.

To test a new pre-paint treatment in production often requires considerable preparation such as dumping the existing treatment, cleaning out the system, charging with the new material, adjusting the new material and if it fails, repeating the process. Going back to the original material.

If the existing process is operating without problems there is little motivation to go through the hassle of dumping and redumping.

Fortunately, this new no-rinse treatment can be tested on the production line without the need of dumping any existing chemical solutions. The solution is prepared in the rinse tank. The existing conversion stage is shut down during processing, not dumped. After the trial it's a simple matter to restore the line to its previous condition.

This material is applied to clean, water break-free surfaces. Application is either by immersion, flow-on or spray. It is applied at a concentration of 5 to 10% bv with water. The coating weights range between 10 and 20 mg per square foot. It's a three-stage operation consisting of: clean, rinse, and chemical treat.

Now the bottom line. What will this new method cost? Compared with zinc phosphates, the cost will be approximately 1/3. About 30 cents per 1000 square feet of surface. That includes cleaning costs.

Once there was a sign in a local tavern stating in bold letter, "Free Beer Tomorrow." Going back the next day for my free beer, I saw the same sign, "Free Beer Tomorrow."

Today we see a sign reading, "Pollution Control Tomorrow." Unlike the tavern sign, tomorrow the sign will read, "Pollution Control Today."

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Light Metals Finishing II
Session F

Electroless Nickel Plating On Aluminum Alloys

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AUTOCATALYTIC (ELECTROLESS) NICKEL PLATING ON ALUMINUM

By Donald W. Baudrand

The use of aluminum is rapidly growing because of its light weight, strength, ease of fabrication and certain other desirable characteristics. The high affinity of aluminum for oxygen results in a natural, thin oxide film that protects the aluminum from further corrosion in a mild environment. However, for many applications the environment is too severe, and additional protection is required. Thus, methods for increased protection have been developed, such as chromate conversion coatings, anodizing, paint systems, electroplating and autocatalytic (electroless*) nickel alloy plating. Each of these processes or finishes are suitable for different kinds of applications.

In particular, autocatalytic nickel alloy coatings on aluminum exhibit good corrosion protection, increased resistance to abrasion and wear, high hardness, solderability, electrical conductivity and decorative appeal. It is because of one or more of these properties, that autocatalytic nickel-plated aluminum has increased in use as a replacement for steel, stainless steel, cast iron, etc. in many applications.

There are several problems in preparing aluminum surfaces for autocatalytic nickel plating and several methods have been developed. This investigator has tested the majority of these methods and found successes and failures. Probably, the zincate immersion method is the most widely used and is described in some detail in this paper. The purpose of this paper is to call attention to the need for an improved method (or methods) of surface preparation and processes, and, hopefully, to encourage further investigation into this area. A bibliography is provided at the end of this paper.

OBSTACLES TO OVERCOME

There are many obstacles in the way of successful nickel deposition on aluminum. Additional problems are encountered when the deposit is from an autocatalytic nickel solution. Some of these problems are discussed in the following sections.

Natural Oxide Removal

The natural oxide film on aluminum must be removed before plating. For most processes, the aluminum must remain oxide-free to ensure adequate adhesion of the coating. Important characteristics of the natural oxide film are that it is very thin, on the order of 5 nm (2×10^{-7} inches); it reforms very rapidly after removal, often faster than practical rinsing and transfer operations can take place; and it is amphoteric (soluble in both acid and alkali) making removal, control or replacement more complicated.

Anodizing procedures which remove the natural oxide and replace it with a controlled oxide film have been proposed and used (see bibliography) as a means of overcoming the natural oxide obstacle.[1] Other methods, such as the immersion zincate[2] process, involve the simultaneous removal of the natural oxide, and its replacement with a zinc deposit.

*AES and ASTM have recommended that the term "autocatalytic" be used in place of the term "electroless", as being more definitive.

Chemical Displacement

Aluminum is an extremely active metal, chemically. It forms displacement reactions with different metal ions in solution. Displacement deposits usually tend to be non-adherent. Simply immersing aluminum into most plating solutions will result in a non-adherent immersion deposit before electroplating can start. Under special controlled conditions, it is possible to achieve a good degree of adhesion with some displacement reaction ions. Zincate immersion and stannate immersion are examples of fairly adherent displacement processes.

Galvanic Corrosion

Since aluminum is active (aluminum and its alloys are high in the electromotive series) it tends to protect most of the common metals from corrosion (except zinc and cadmium). In a corrosive environment, galvanic action can occur between any exposed aluminum and the plated coating resulting in very rapid corrosion of the aluminum. Plated coatings on aluminum must be continuous (free from any pits or other discontinuities) and of sufficient thickness to assure good protection.

Thermal Expansion

Aluminum and its alloys are soft, somewhat malleable, and expand on heating more than autocatalytic nickel alloy deposits. The difference in coefficient of thermal expansion gives rise to extreme stresses at the plate / aluminum interface which can result in adhesion failure, or apparent adhesion failure if the fracture occurs in the aluminum and not exactly at the interface. Deforming plated aluminum parts produces extreme stresses at the interface since the aluminum deforms much more easily than does the deposit. Cracking and apparent or actual adhesion failure can occur.

Alloying Constituents

Aluminum as used in industry is not pure aluminum, but consists of a large variety of alloys. Numerous alloying constituents are commonly used to give specific properties to the aluminum alloy making it suitable for a wide variety of applications. Table I shows some common alloys and the alloying constituents.

Table I. Composition Of Some Commonly Plated Aluminum Alloys

Aluminum Alloy	Composition, Percent					
	Cu	Mn	Mg	Cr	Si	Zn
1100	—	—	—	—	—	—
3003	—	1.2	—	—	—	—
2024	4.5	0.6	1.5	—	—	—
5052	—	—	2.5	0.25	—	—
6061	0.25	—	1.0	0.25	0.6	—
7075	1.6	—	2.5	0.3	—	5.6
319	3.5	—	—	—	6.0	—
355	1.3	—	0.5	—	5.0	—
350	3.5	—	—	—	8.0	—

The alloying materials are not always soluble in the aluminum nor are they always uniformly dispersed throughout the body of the aluminum.[2] Particles of metals or other alloying materials at the surface can result in a corrosion cell which would accelerate the corrosion rate of the surrounding aluminum. Sometimes these alloying constituents are difficult to remove in the preparation for plating steps. For example, silicon-containing alloys are best prepared in steps using fluorides, and copper-containing alloys can be prepared in nitric acid.

METHODS OF SURFACE PREPARATION

Numerous methods have been proposed and used commercially for preparing aluminum alloys for autocatalytic nickel deposition. It is the author's observation that because of the variety of aluminum alloys, the high affinity of aluminum for oxygen, the chemical activity of aluminum, and numerous other variables, there is no single simple preparation method suitable for preparing all aluminum alloys for autocatalytic nickel plating.

Zincate Method

The zincate process[3] is described in more detail than the others. Since, as with all other methods, it has shortcomings, some variations are presented.

1. Solvent clean. This step is done only when necessary to remove heavy oils and grease. It should be omitted if colloidal metal particles or other solids of small particle size are part of the soil to be removed since these particles or colloids may adhere more tightly to the aluminum surface after solvent cleaning and interfere with subsequent steps.
2. Etch-clean in a very mild acid cleaner. Proprietary phosphoric acid-based cleaners are used which are capable of maintaining the RMS finish of polished or machined surfaces and close tolerance of machined parts.
3. Rinse.
4. Deoxidize in a non-chromated system which removes no metal.
5. Rinse.
6. Alkaline zincate. Typical formulation is:
   NaOH – 500 g/L, ZnO – 100 g/L, $FeCl_2$ – 1 g/L, Rochelle salt – 10 g/L
   2024 Alloy: Immerse in the zincate solution for 120 sec. at 20°C (70°F).
   6061 Alloy: Immerse in the zincate solution for 30 sec. at 15°C (60°F).
   7075 Alloy: Immerse in the zincate solution for 60 sec. at 20°C (70°F).
7. Rinse thoroughly.
8. Strip zincate in 50% by volume nitric acid.
9. Rinse.
10. Immerse in the zincate solution for 30 sec. at 20°C (70°F).
11. Rinse thoroughly.
12. Rinse thoroughly.
13. Immerse in a mild acid, such as 0.25% H_2SO_4 or 7.5 g/L sulfamic acid, for 10-15 sec. at room temperature. This step removes the tightly adherent strongly alkaline film from the zinc surface without stripping the immersion zinc. A strongly alkaline surface

can be harmful to an autocatalytic nickel solution, and can interfere with adhesion of the deposit.

14. Rinse.
15. Autocatalytic nickel plate.

The great advantage of this zincate process is that very good adhesion is obtained on a wide variety of aluminum alloys. Furthermore, coupled with a properly selected autocatalytic nickel solution, this process produces excellent corrosion resistance. The disadvantages are: (1) many steps in the process, (2) the steps are critical with little room for variation of time, temperature, solution composition, etc. and (3) for scribed panels, creep corrosion attributed to the zinc film has been reported.[4]

Other Methods

Kampert of Alcoa[5] suggests a zincate process as above, followed by a special nickel strike consisting of 375 g/L nickel sulfate, 45 g/L boric acid, pH of 3.6-4.5, an anti-pit agent, and operated at 35-40°C, approximately 4 volts to produce about 2 amps/dm^2 for about 2 minutes. Note the absence of chloride ion in this formulation. The nickel-coated aluminum alloy is transfered without rinsing to a semibright nickel solution for buildup of nickel plate, or to an autocatalytic nickel solution for buildup of nickel alloy.

Missel[6] proposed an acetate-buffered nickel glycolate strike plating solution for use after zincate.

Petit, R. Wright, C. Wright and Kwasnoski[7] report a method which eliminates the zincate process. The steps are:

1. Degrease.
2. Etch (considered the most important step). Consists of 350-360 g/L $NiCl_2 \cdot 6H_2O$ and 500 ml/L (16N) concentrated nitric acid. Another etch suitable for a wider variety of alloys consists of 640 g/L $NiCl_2 \cdot 6H_2O$ and 100 ml of 85% lactic acid/L.
3. Nitric acid dip (2-5 ml of 48% HF per litre of 8N HNO_3). Immerse for 2-3 minutes. For 380 casting alloy, HF is increased to 80-100 ml/L.
4. Activate. Consists of immersion in a solution containing 25 g/L sodium hypophosphite and 25 ml/L of concentrated ammonium hydroxide, followed by an activation strike in a solution containing 25 g/L of sodium hypophosphite, 25 g/L of nickel sulfate hexahydrate, 50 g/L of ammonium citrate, pH 9-9.5 adjusted with ammonium hydroxide, and operated at 85-90°C.
5. Without rinsing, the aluminum is plated in a conventional autocatalytic nickel alloy solution.

Anodizing aluminum as a pretreatment for electroplating on aluminum has been proposed which may find application for autocatalytic nickel deposits. ([8, 9, 10, 11]).

Schwartz and Newkirk[12] report a method which utilized AC current with a brass plating solution to replace zincate immersion.

Miller[13] advocates preparation (after cleaning) in an ammonium bifluoride-dimethylamine borane dip followed by a dimethylamine borane-reduced nickel solution.

Bellis[14] claims a hydrofluoric acid-metal salt which is catalytic to deposition followed by an amine borane reduced autocatalytic nickel.

Winkström, Osmo and Nils of the Axel Johnson Institute, Sweden,[15] developed a method of preparing aluminum for plating consisting of (1) a degreasing step, (2) rinse, (3) pretreatment which consists of mixed acids and a metal salt (nickel, chromium, cobalt, manganese, magnesium or zinc), room temperature, 20 seconds to 1 minute depending on the alloy, (4) rinse, and (5) electroplate, preferably nickel or autocatalytic nickel plate.

IMPORTANCE OF AUTOCATALYTIC NICKEL SOLUTION CONSTITUENTS

The influence of bath composition in plating on aluminum is profound. The selection of complexing agents for nickel is important. It is important also to completely complex the nickel ions (not necessary for plating on steel). One reason for this may be that nickel is displaced from ionic solutions by aluminum. Secondary complexors are useful in the baths designed for plating on aluminum. These materials should be capable of complexing on aluminum. Under certain circumstances, aluminum hydroxide could form. This precipitated basic oxide can lead to instability by stripping the bath stabilizers, and by forming nuclei for "plating out" causing roughness or spontaneous decomposition of the bath.

The selection of stabilizers is important. Usually two or more different types are used, and in quantities somewhat larger than for plating on ferrous alloys.

The bath must have a tolerance for zinc contamination if the zincate pretreatment is used. This is accomplished by certain patented additives.[16] Furthermore, it has been found that low chloride, or no chloride at all, in the bath is beneficial in promoting good adhesion. Numerous other factors affect adhesion as previously mentioned.

CONCLUSIONS

Autocatalytic nickel plating on aluminum is practiced extensively even though there are numerous problems in preparing aluminum alloys, and in proper selection of the plating solution. After extensive testing and investigation it is concluded that the zincate immersion method offers the best opportunity to produce good plating results on the largest number of aluminum alloys. A better, easier, more reliable method is still being sought.

REFERENCES

1. G. A. Miller, U.S. Patent 3,667,991 (1972).
2. ASTM Standards, B253-68
3. G. O. Mallory, Ninth Annual Connector Symposium, Electrical Connector Study Group, pp 179-192 (1976).
4. G. DeBari, Plating and Surface Finishing, 64 (5), 68-74 (1977).
5. W. P. Kampert, U.S. Patent 3,515,564 (1970).
6. L. Missel, Plating and Surface Finishing, 64 (7), 32-35 (1977).
7. G. S. Petit, R. R. Wright, C. C. Wright, and T. Kwasnoski, Plating, 59 (6), 567-570 (1972).
7. R. R. Wright, G. S. Petit, C. C. Wright, U.S. Patent 3,666,529 (1972).
8. K. S. Indira, R. Subramanian and B. A. Shenoi, Met. Fin., 69 (4), 53-58 (1971).
9. R. C. Spooner and D. P. Seraphim, Trans. Inst. Met. Fin., 31, 29 (1954).
10. W. H. Wiltrock, Proc. Am. Electropl. Soc., 48, 52 (1961).
11. E. Lytal, Aluminum, 19 (6), 381 (1937).
12. B. C. Schwartz and J. B. Newkirk, Plating, 59 (5), 431-436 (1972).
13. G. A. Miller, U.S. Patent 3,767,582 (1973).
14. H. E. Bellis, U.S. Patent 3,672,964 (June 27).
15. British Patent 1,445,553 (March 21, 1975).

APPENDIX

APPLICATIONS – AUTOCATALYTIC NICKEL ON ALUMINUM

Heat sinks – (solderability and corrosion protection)
Candle molds – (good release properties)
Electroforming mandrels (scratch resistance)
Small engine blocks – (lubricity)
Aircraft pistons
Aluminum gas gauge housings
Food equipment – aluminum baking pans
Connectors, including glass-sealed
Marine hardware
Mixer beater blades
Precision fit of mating parts
Servo valves
Piston heads
Alternator heat sinks
Pistons for anti-skid devices (wear resistance)
Pistons for disc brakes (wear resistance, lubricity)
Air conditioning tubing (hardness)
Electronic packages, modular
Mass course adjustor
Signal selector (high frequency)
Wave guides
Carburetor components
Hydraulic cylinders
Lock nuts
Shafts
Slide tube assembly
Slide valve plates
Threaded fittings

BIBLIOGRAPHY

Activating Treatments For Plating On Aluminum

S. Wernick and R. Pinner, Surface Treatment and Finishing of Aluminum and its Alloys, Robert Draper, Teddington, Middlesex, England, pp. 581-679 (1964).

R. H. Keller, Met. Finish., 48, 12, 56 (1950).

E. Herrmann, Galvanotechnik, 51, 219, 336 (1960).

J. T. N. Atkinson, Plating, 47, 509 (1960).

G. Fitzgerald-Lee, Prod. Finish., (London), 13, 74, 84 (1960).

C. L. Faust, G. R. Schaer, and D. E. Semones, Plating, 48, 605 (1961).

F. L. Church, Mod. Met, 23 (5), 65 (1967).

R. V. Vanden Berg, Aluminum, Vol. III, American Society for Metals, Metals Park, Ohio Chap. 20, (1967).

H. Richaud, Rev. D'Aluminum, 45 (377), 896 (1969).

D. J. Bailey, Electroplat. Met. Finish., 23 (5), 42 (1970).

K. A. Holbrook and P. J. Twist, Plating, 56, 523 (1969).

A. Brenner and G. Riddell, J. Res. Nat. Bur. St., 37, 31, (1946); ibid., 39, 385 (1947).

J. W. Tharp, Plating, 58, 328 (1971).

J. W. Tharp, Prod. Finish., 34 (5), 64 (1970).

D. I. Garland and R. S. Gray Jr., U.S. Patent 2,575,214 (Nov. 13, 1951).

R. R. Reschan and A. Krieg, U.S. Patent 2,694,017 (Nov. 9, 1954).

Reynolds, U.S. Patent 2,958,601 (1958).

H. Bardsorf and K. Muller, Aluminum, 35 (1959).

Pechiney, Brit. Patent 870,060 (1961).

H. O. Hansson, U.S. Patent 3,867,265 (Feb. 18, 1975).

W. E. Cooke and J. Hodgson, U.S. Patent 4,097,342 (June 27, 1978).

R. A. Tremmel, W. J. Wieczerniak, and R. J. Clauss, U.S. Patent 3,915,811 (Oct. 28, 1975).

K. F. Dockus, U.S. Patent 4,028,200 (June 7, 1977).

D. G. McBride and G. P. Vlasak, J. Electrochem. Soc., 118 (12), 2055 (1971).

J. W. Tharp, Prod. Fin., 37, 82 (1972).

G. S. Petit, R. R. Wright, C. C. Wright and T. Kwasnoski, Plating, 59, 567 (1972).

G. A. Miller, U.S. Patent 3,667,991 (June 6).

H. E. Bellis, U.S. Patent 3,672,964 (June 27).

R. R. Wright, G. S. Petit and C. C. Wright, U.S. Patent 3,666,529 (1972).

G. A. Miller, U.S. Patent 3,767,582 (Oct. 23).

J. W. Dini and H. R. Johnson, Met. Finish., 72, 44 (Aug.).

B. L. Berdan and B. M. Luce, U.S. Patent 3,969,199 (July 13).

Zincate

ASTM Standards, B253-68.

J. Korpiun, U.S. Patent 2,142,564 (1939).

Zincate (Continued)

R. A. Ehrhardt and J. M. Guthrie, Mon. Rev. Am. Electroplat. Soc., 34, 421 (1947).

W. G. Zelley, J. Electrochem. Soc., 100, 320 (1953).

E. Armstrong, Met. Treat., 6, 153 (1940).

E. H. Hewitson, U.S. Patent 1,627,900 (1927).

B. K. Braund and H. Sutton, Trans. Faraday Soc., 31, 1595 (1935).

G. Elssner, Aluminum, 17, 376 (1935).

V. I. Lainer and S. I. Orlova, Legk. Metall., 5 (2), 22 (1933); Chem. Abstr., 30, 7047 (1936).

L. Perner, U.S. Patent, 2,297,241 (1942).

J. Bengston, Trans. Electrochem. Soc., 88, 307 (1945).

W. R. Meyer, Mon. Rev. Am. Electroplat. Soc., 33, 269 (1946).

W. Bullough and G. E. Gardam, J. Electrodepositors' Tech. Soc., 22, 169 (1947).

S. Heiman, J. Electrochem. Soc., 95, 205 (1949).

F. Keller and W. G. Zelley, Proc. Am. Electroplat. Soc., 36, 149 (1949).

W. R. Meyer and S. H. Brown, Proc. Am. Electroplat. Soc., 36, 163 (1949).

F. Keller and W. G. Zelley, J. Electrochem. Soc., 96, 143 (1950).

G. L. J. Bailey, J. Electrodepositors' Tech. Soc., 27, 233 (1951).

W. G. Zelley, U.S. Patent 2,650,886 (1953).

J. W. Tharp, Miami Branch News, Plating, 51, 73 (1964).

E. Herrmann, Galvanotechnik, 51, 219, 336 (1960).

C. L. Faust, G. R. Schaer and D. E. Semones, Plating, 48, 605 (1961).

R. Leloup, U.S. Patent 3,284,323 (1966).

H. Richaud, French Patent 1,496,255 (1967).

A. M. Howard, U.S. Patent 3,982,055 (Sept. 21, 1976).

W. P. Kampert, U.S. Patent 3,989,606 (1976).

G. A. Laitinen, Plating (Nov. 1977).

Anodizing

W. J. Traverse, U.S. Patent 1,971,761 (1934).

J. Fischer, U.S. Patent 2,036,962 (1936).

H. J. Wittrock, Proc. Am. Electroplat. Soc., 48, 52, (1961).

NASA SP-5025 (1966).

J. C. McConnell, U.S. Patent 3,468,765 (1969).

A. E. Weber, U.S. Patent 3,493,474 (1970).

T. Asada, U.S. Patent 3,515,650 (1970).

A. L. Peach, U.S. Patent 3,531,379 (1970).

K. S. Indira, R. Subramanian and B. A. Shenoi, Met. Finish., 69 (4), 52 (1971).

A. Akiyama, K. Uasuhara, K. Tanaka and T. Saji, Plating, 58, 504 (1971).

W. H. Wiltrock, Proc. Am. Electroplat. Soc., 48, 52 (1951).

Anodizing (Continued)

J. W. Tharp, Midwest Florida Branch News, Plating, 53, 1378 (1966).

J. W. Tharp and J. J. Tyminski, Plating, 55, 580 (1968).

J. W. Tharp, Baltimore-Washington Branch News, Plating, 57, 641 (1970).

H. J. Wittrock, U.S. Patent 3,943,039 (Mar. 9).

Tin Immersion

E. J. Seyb, J. C. Jongkind and L. P. Gowman, Proc. Am. Electroplat. Soc., 51, 133 (1964).

J. C. Jongkind and P. G. Kenedi, U.S. Patent 3,274,021 (1966).

S. J. Beyer, Plating, 56, 257 (1969).

J. C. Jongkind, Trans. Inst. Met. Fin., 45, 155 (1967).

P. G. Kenedi, U.S. Patent 3,108,006 (1963).

G. A. DiBari, Plating and Surface Finishing, 64 (5), 68-74 (1977).

Solutions For Plating On Aluminum

C. A. Boose, Trans. Inst. Met. Fin., 53 (1975).

G. O. Mallory, Plating, 61 (11), 1005-1014 (1974).

V. N. Flerov and L. V. Golovushkina, U.S.S.R. Patent 388047 (April 1971).

Kenji Iijima, Japan Patent 75160145 (June 1974).

Kosaka, Jaruo; Ohno, Kaishi, Aruminyumu Kenskyu Kaishi, 112, 18-19 (1978) (Japanese).

A. Wasserman, Prod. Finish., 42 (5), 48-50, 52 (1978).

F-3

Light Metals Finishing II
Session F

The Effect of Environmental Concerns And Energy Conservation Upon Cleaning and Treating of Aluminum

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F-4

Light Metals Finishing II
Session F

Pollution Control in Anodizing Operations

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The following essay is a comprehensive study of an aluminum anodizing pollution abatement program in actual operation. The study was performed on the abandoned City of Terrell Municipal Waste Treatment Plant. Details in modification to this system have been outlined explicitly in precise form accompanied by photographs.

INDUSTRIAL UTILIZATION OF A DOMESTIC WASTE TREATMENT FACILITY

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In many instances, municipal growth and stringently changing discharge parameters dictate renovation of existing domestic waste treatment plants or construction of a modern facility that meets the present or future needs of the municipal growth factors. In many cases, the latter alternative is chosen considering the economic feasibilities involved.

If, in fact, this does occur, construction of a new plant can create the need for relocation and the existing treatment facilities, as a result, being abandoned.

These facilities are an excellent means by which industry can process their own waste water and if accomplished properly, discharge to a public waterway.

Depending on the qualitative and quantitative properties of the waste to be treated, alteration to the system are imperative before proper treatment is to occur.

Howmet Aluminum Corporation's Texas Extrusions Division discharged all waste water from our anodizing facility to the municipal treatment plant prior to January 1978. Previous to this date, we were striving to renovate the old abandoned municipal treatment plant to enable us to treat our waste water so the effluent would

meet or surpass the E.P.A. and Texas Department of Water Resources discharge parameters.

Our primary effort was to achieve pH control to the extent that ther would be a variation of no more than a $\pm$.6 pH value. This necessitated the fabrication of a four chambered vessel with adequate mixing of raw influent in order to achieve pH stabilization. The first chamber is for primary mixing of raw influent and initiates pH adjustment. The second chamber contains an on-off course pH adjustment reagent feed system that corrects the pH if it is less than 4.0 or greater than 10.0 Number three chamber is the fine pH adjustment chamber which has a reagent feed system regulated by demand type air actuated valves that are proportionally controlled by a pH monitoring controller. This stag makes the final pH adjustment and records the value on a strip chart recorder for future reference. The final stage is for mixing and tertiary pH stabilization.

Problems existed with the monitoring probes becoming scaled and reporting the wrong values. But an ultrasonic cleaning device has proven to be a remedy. Otherwise, the system has proven to be quite efficient for our needs with minimum maintenance required.

After proper pH control has been sufficied, renovation and modification of the prospective industrial waste treatment facility has to be considered, keeping in mind all possible future needs.

The domestic waste treatment plant that we are utilizing consisted of three aerators, six small clarifiers, one large clarifier, a digesto and sludge drying via drying beds.

Primary alteration consisted of deletion of all treatment processes except primary clarification (the one large clarifier), final clarification, the digestor, and the addition of a rotary vacuum filter.

The digestor serves as a holding tank for sludge resulting from solids separation occurring in the primary clarifier. Solids separation is accomplished through addition of a polyelectrolyte to the influent as it enters the clarifier. The type clarifier most municipal waste plants utilize, as in our case, has a divider approximately two feet from the wall extending from above water level to approximately two feet above the bottom of the clarifier. As the electrolyte is added; 1) flocculation occurs, 2) the solids drop to the bottom of the sludge divider, and 3) primary sludge compaction begins. The sludge rake then moves the sludge toward the center of the clarifier where continuous solids concentration evolves. This type of clarifier suffices if the sludge drying device is sized enough to handle all solids that are produced at a maximum rate. But difficulties can arise from the lack of retention time resulting from the inferior mode of operation from this type of clarifier.

Sludge from the clarifier is pumped into a digestor which, for our purposes, is a holding tank with the approximately same volume as the clarifier. It seems that anerobic bacterial action in the digestor induces further concentration abilities, again, depending on retention time and ambient temperature. Transference of sludge from the primary clarifier to the digestor thence to our rotary

vacuum filter results in the "flocced" solids particles to be sheared This shearing effect henders an efficient drying operation. Improvements in sludge condition could be achieved in the vacuum filter sludge container if we bypassed the digestor and pumped off of the clarifier directly to the filter. But considering the inefficient type of clarifier we have to utilize, the digestor is needed for storage capacity or else we would have to operate the vacuum filter continuously. Also, intermittent pumping from the primary clarifier to the digestor for not more than ten minutes at a time and then waiting one hour or more before pumping again helps to decrease the shearing of sludge particles. Another problem existed with the ten minute pumping procedure in that if the ten minute period is increased the sludge blanket starts to cavitate and clear water is mixed with the sludge which decreased the solids concentration.

The drying bed method of drying sludge was used in the past and is still being used by many municipal treatment plants today. A drying bed consists of a large area contained by a concrete dyke on all sides and having two layers of filtering material. The top layer being six inches of sand and below it three feet of washed rock. This enables the operator to dry sludge from the digestor by filling the bed with wet sludge and the water filtering through the sand and rock layers into a series of drainage pipes with resulting dried sludge within two to three days. The dried sludge then has to be removed by shoveling it out manually. This method of sludge drying is quite inefficient and expensive. It is

inefficient from the standpoint that the operation can be haulted or slowed down from such interferences as bad weather, lack of manpower, or equipment malfunction. The expense can be quite high considering the sand has to be replaced each time it is cleaned out, cost of three employees and equipment cost. Also, wet weather is an operational deterrent that ceases the drying process completely. In all, the drying beds are not the most efficient method of solids drying.

The drying method we chose was a rotary vacuum filter, but the drying beds are still available for emergency use. We purchased a used Filtration Engineering rotary vacuum filter and made necessary modifications and renovations for proper operation. The filter size is 10' x 16' and is capable of drying 40,000 gallons of wet sludge per day resulting in 60 yards of dried sludge, again, depending on quality of sludge.

Our filter is relatively maintenance free as far as major malfunctions are concerned. It is constructed from 316 stainless steel on the components that are exposed to sludge. This is necessary in regard that the compositional hydroxide salts and the continuous moisture exposure from the sludge is extremely conducive to corrosion.

Our sludge drying operation begins with solids being pumped from the digestor to the vacuum filter. The filter then dries the sludge from 5% to 15% solids and is conveyed to a dump truck. It is then transported to our privately owned on-site industrial landfill designated solely for disposition of all sludge produced from our

treatment plant.

An advantage of treating your own waste, as in our case, is the possibility of discharging treated effluent to a creek or river. This, in turn, can create a savings from omission of the municipal sewage treatment cost. But consequently, it poses a liability for the company to discharge effluent that meets the parameters designated by the Texas Department of Water Resources.

In order to discharge to a public waterway in the state of Texas, one must first obtain a permit from the Texas Department of Water Resources. This agency closely monitors our effluent which made it necessary for Howmet to install a water quality testing laboratory. The facilities are in the same building with the vacuum filter and all analysis and plant operations are conducted by one person in an eight hour shift.

Our effluent has never exceeded the parameters set by the TDWR. This achievement, obviously, compliments the proficiency you can achieve by proper utilization of a converted domestic waste treatment plant. The following is an example of our effluent and an average monthly discharge value.

Parameters	Average Lbs./Day Permitted	Actual Average Lbs./Day Reported
pH	6.0-9.5	8.4
TSS	130.0	10.27
Oil & Grease	43.00	8.41
SO4	6000.0	5494.9
Fe	16.600	.0267
Ni	.4300	.1922
Al	4.300	1.310
Flow	510,000 gal/day	319,995 gal/day

These figures are common for a monthly discharge from our Aluminum Finishing facility assuming an average production rate of 35,000 lbs/day. The 35,000 lbs. of production per day yields approximately 30,000 gallons of wet sludge. This is entirely dependent on our clarifier efficiency. As observed from the previous figures, flow rates averaged 319,995 gal/day. Sludge concentration as a result of treatment, originally comprised of 9% of the total volume. This volume is further reduced to a concentrated solid content via rotary vacuum filter by another 3% which creates a sludge with a consistency somewhat thicker than mayonnaise. The cost of operation is approximately $500.00 per month not including the salary of an operator. Conversion cost at this time has been $125,000.00. This figure can vary depending on factors such as purchase of new or used process eqiupment, the degree of sophistication of equipment that is chosen, and amount of fabrication of equipment required.

Since our treatment plant does have all the existing aerators and clarifiers that are not being used for our chosen process, they still can serve as a back-up system for temporary treatment. The influent flow can be re-routed through the six small clarifiers, the polyelectrolyte added to the influent, and the solids settle to the bottom of the clarifiers. The clear effluent would follow a path to the three aerators and thence to the creek. This backup system can maintain solids accumulation without need of sludge disposition for six days. In addition, the drying beds serve as a

back-up system for the vacuum filter.

At the present time, improvements of our facilities would be to install a high rate reaction type clarifier. This would extend our retention time and in turn improve our sludge characteristics. An alarm system is also being installed that will sound a warning when abnormal solids content in our effluent is present. The system will consist of a conductivity meter that constantly monitors the clear effluent. When solids content of the effluent increases above an established maximum limit, an alarm is activated and transferred through our telephone system which rings a phone in the supervisor's office at the anodizing plant. This alarm is necessary since our pollution control plant is a distance of one mile from the anodizing plant and is operated for eight hours a day. During the remaining sixteen hours there is no employee on duty fulltime. The process lab technicians at the anodizing plant make routine inspections of water quality every two hours. Nevertheless, an emergency situation can occur between these inspections. So the alarm system will ensure that discharge quality is being maintained at legal limits when no operator is on duty.

So, in all, a properly utilized municipal sewage plant is an ideal facility to treat industrial waste water considering the available equipment and the cost of renovation vs. the cost of fabrication of a new facility with the most basic equipment and no back-up systems.

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Light Metals Finishing II
Session F

Air and Water Pollution Control for Anodizing

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Light Metals Finishing II
Session F

Air and Water Pollution Control for Anodizing

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G-1

Electronics II
Session G

Pulse Plating of Hard Gold Deposits

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PULSE PLATING OF HARD GOLD ELECTRODEPOSITS

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roduction

use of pulse plating has been expanded from a laboratory hnique to investigate the mechanisms of electrodeposition cesses to a process that can improve the properties of ctrodeposited metals. Avila and Brown[1] found fine grain, h purity gold deposits of significantly lower volume istivity were obtained by pulse plating as compared to conventional soft gold deposits. Rehrig[2] compared osity in high purity gold films deposited by evaporation, plating, asymmetric ac plating, and pulse plating and cluded that pulse plated deposits are the least porous. dvay and Raub[3] have reported that pulsed plated, hard d deposits exhibit a 25 percent increase in tensile ength and a twofold decrease in elongation when compared dc deposits. Despic and Popov[4] found that pulse plating copper and zinc at high frequencies maintained surface othness through the deposition. This is contrary to dc ting, where an increase in surface roughness with deposition expected. The results of these and other investigations[5-7] icate that pulse plating can significantly affect the face finish and properties of deposits.

objective of this paper is to evaluate conventional and se plated, cobalt hardened gold deposits and determine ferences in cobalt chemical composition (Atomic Absorption ctroscopy - AA) morphology (Scanning Electron roscopy - SEM) and microstructure (Transmission Electron roscopy - TEM).

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Substrate Preparation

The base substrates were the polished face of brass panels for the SEM morphology examination and passivated stainless steel samples for the TEM analysis. With the brass panels, the maskant was removed from the polished face and any residual maskant was flushed off with acetone. The panel was placed in a plastic holder with a gasket so the edges and back face of the panels were masked, leaving an area of 1/12 ft^2 (8.7×10^{-5} m^2) to be plated. Prior to plating, these brass panels were cleaned in a mild alkaline solution, water rinsed, treated with 10-volume-percent sulfuric acid, and water rinsed. The proprietary gold plating solution with a cobalt hardening agent was operated at 46°C ±2°C and a pH of 3.5 ±0.2. Gold was plated from this solution within the limits of the recommended current density range, 3 to 12 A/ft^2 (0.32 to 1.3 A/dm^2), under direct current conditions and at the same average current density under pulsed conditions. The average current density ($\bar{i}$) is defined as:

$$\bar{i} = i_p \frac{t_{on}}{t_{on} + t_{off}} \qquad (1)$$

where

i_p = peak current density,

t_{on} = on time, and

t_{off} = off time.

The duty cycles used with pulsed conditions were 1, 33, and 50 percent. The duty cycle (D) was defined as

$$D = \frac{t_{on}}{t_{on} + t_{off}} 100. \qquad (2)$$

The on and off times for the experimental duty cycles are listed in Table 1.

Gold samples were plated to 1 ampere-minute at the extremes of the current density range to determine differences in surface morphology. Samples prepared by the 50 percent duty cycle (0.1 ms on and off) were omitted in this SEM analysis. For the remaining samples, a small part of each deposit was

le 1. Experimental Duty Cycles

y Cycle rcent)	t_{on} (ms)	t_{off} (ms)
	0.2	2
	1	2
	1	1
	0.1	0.1

d for the SEM analysis, and the remainder was used for nical analysis. For the chemical analysis, the gold osits were dissolved in aqua regia, and atomic absorption ctroscopy was used to determine the cobalt in the deposit.

the TEM analysis, gold samples were plated at 10 A/ft^2 A/dm^2) conventionally and at duty cycles of 33 and percent for 1 ms intervals and a 50 percent cycle for ms in the pulsed current mode. These gold deposits were ut 1 μm thick and were relatively easy to pull from the sivated 304 stainless steel substrates. To prepare the samples, the gold deposits were ion milled using 5 keV on ions at approximately a 150° incidence angle to less n 1000 Å (0.1 μm) in thickness. Further attempts to duce more uniform thinning by varying the incidence le, beam current, specimen cooling, thinning one side y, etc., did not yield improved results. In addition, se attempts were made to be sure that the ion thinning ration did not preferentially remove the cobalt from the d deposits. Electron diffraction patterns were obtained ascertain any preferred orientation of these gold deposits.

nical Composition

cobalt contents for the different plating conditions are vn in Table 2. The cobalt contents of the gold deposits less at 0.3 A/dm^2 than at the higher currents density n all the modes investigated. In most cases, the pulse ted deposits have a higher cobalt content than the dc osits throughout the current density range.

a current density of 0.3 A/dm^2, the cobalt content of the d deposits obtained with conventional dc and a 50 percent sed duty cycle is about the same. Although the cobalt

Table 2. Cobalt Content in Gold Deposits

Plating Conditions			
Mode	Current Density (A/dm^2)	Duty Cycle (Percent)	Cobalt (Weight Percent)
dc	0.3		0.012
pc	0.3	50	0.009
pc	0.3	33	0.017
pc	0.3	10	0.018
dc	1.2		0.24
pc	1.2	50	0.34
pc	1.2	33	0.33
pc	1.2	10	0.32

contents of the deposits obtained at this current density with 33 and 10 percent duty cycles are similar, they are greater than the other deposits obtained at 0.3 A/dm^2. The pulse plated deposit prepared with a 50 percent duty cycle at this current density is the only one observed with a cobalt content that was not significantly different from the corresponding dc deposit.

Because of the small quantity of these gold deposits and their extremely low cobalt contents, the analytical error for these cobalt analyses at 0.3 A/dm^2 may be as high as 20 percent. All of the pulsed deposits at 1.2 A/dm^2 have a greater cobalt content than the corresponding dc deposits. Because the weight percentage of cobalt in these deposits is much greater, the analytical error in the cobalt analysis is estimated to be 5 to 6 percent.

The samples used in the TEM study were similarly analyzed for cobalt content and the corresponding gold was determined gravimetrically. The results are shown in Table 3. Some of the metallic contaminants found in these gold deposits were copper, iron, nickel, and silver. However, none of these contaminants were found in excess of 0.06 weight percent. In these samples, the percentage of cobalt in the pulse plated gold deposits is greater than in the dc deposit. This data again confirm the results listed in Table 2 and reported by Raub and Knodler.[8] The cathode efficiencies of

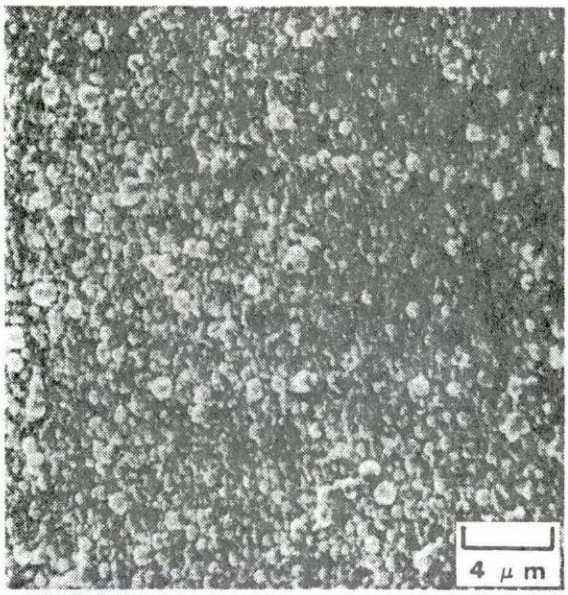
e 3. Chemical Contents of Gold Alloy Deposits for Microstructural Analysis

le ription	Gold (weight percent)	Cobalt (weight percent)
1 A/dm^2	99.48	0.33
33 percent cycle, dm^2	99.37	0.41
50 percent cycle, dm^2	99.42	0.39
50 percent cycle ms on), dm^2	99.35	0.42

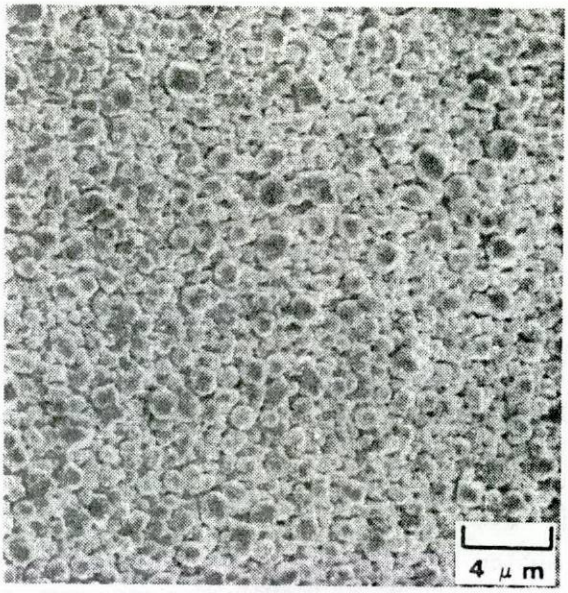
dc deposition processes increase from 13 percent at A/dm^2 to 21 percent at 1.2 A/dm^2. With pulsed duty es of 50 and 33 percent, the cathode efficiencies are oximately the same or slightly higher than the dc pro- es. As the average current density decreases in the e utilized, the cathode efficiencies of the 50 and ercent duty cycles tend to be greater than the corre- ding dc processes and approach 30 percent. At a duty e of 10 percent, the cathode efficiencies are about 40 0 percent less than the dc processes regardless of the age current density. This reduction could result because off times of the 10 percent duty cycle were not long gh to completely replenish the cathode layer when using high pulsed current density.

hology

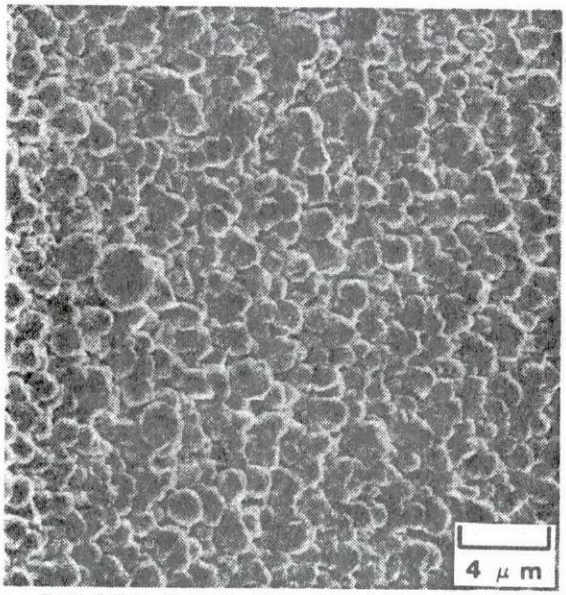
erences in the surface morphology and areal features of gold electrodeposits obtained with pulsed and direct ent were investigated using the SEM. Photomicrographs ypical deposits are shown in Figures 1 and 2. The gold y deposited with direct current at 0.3 A/dm^2 (Figure 1a) very distinct grains and grain boundries. However, the sit appears to be porous because of the relatively large



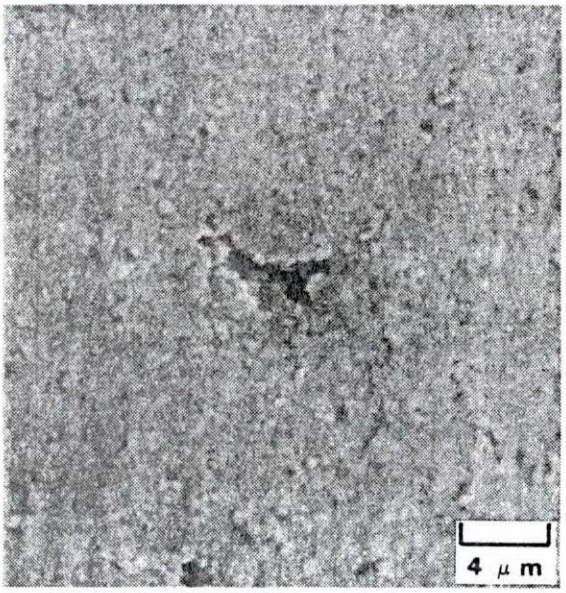
a. DIRECT CURRENT



b. PULSED CURRENT, 50% DUTY CYCLE

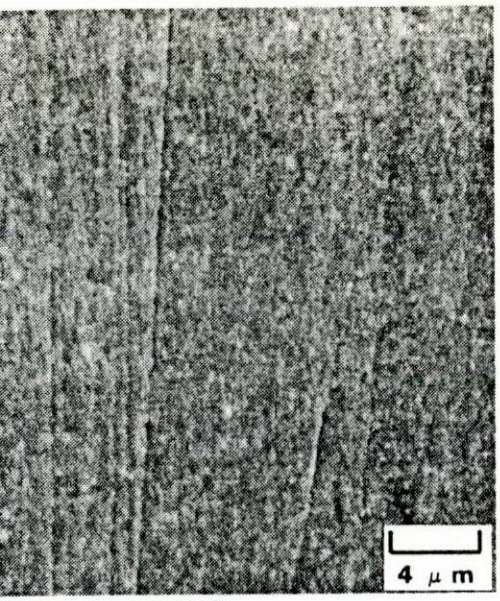


c. PULSED CURRENT, 33% DUTY CYCLE

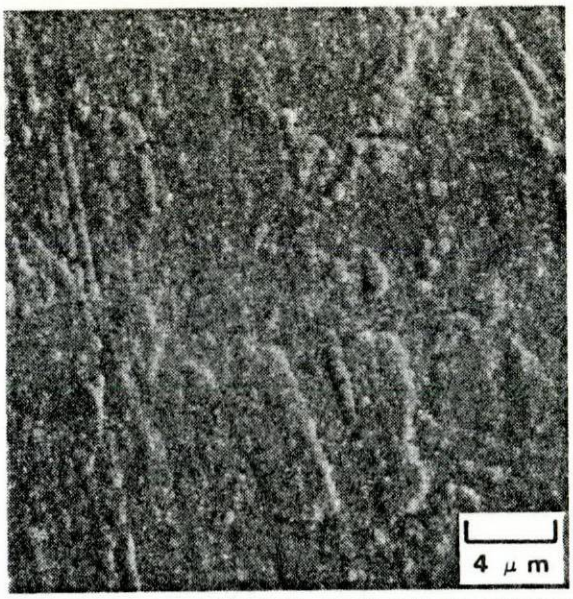


d. PULSED CURRENT, 10% DUTY CYCLE

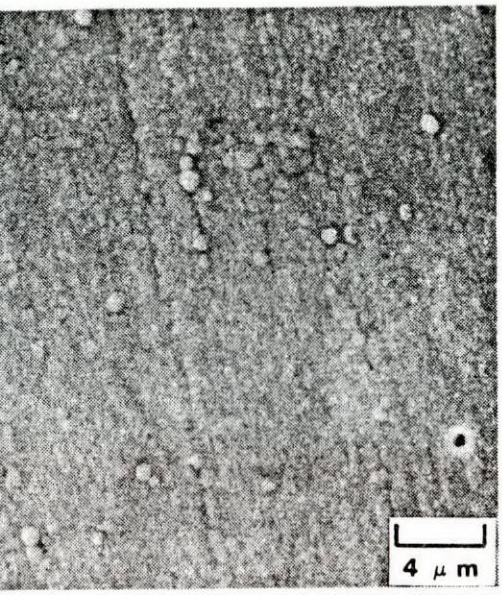
Figure 1. SEM Photomicrographs of Gold Alloy Deposits at 0.3 A/dm^2



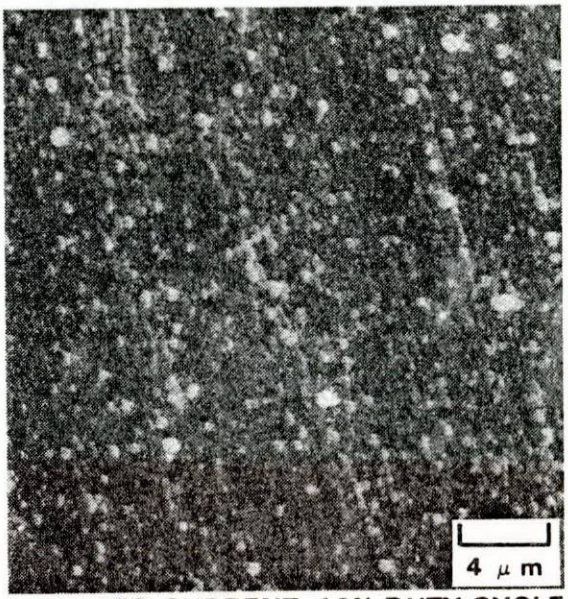
RECT CURRENT



b. PULSED CURRENT, 50% DUTY CYCLE



ULSED CURRENT, 33% DUTY CYCLE



d. PULSED CURRENT, 10% DUTY CYCLE

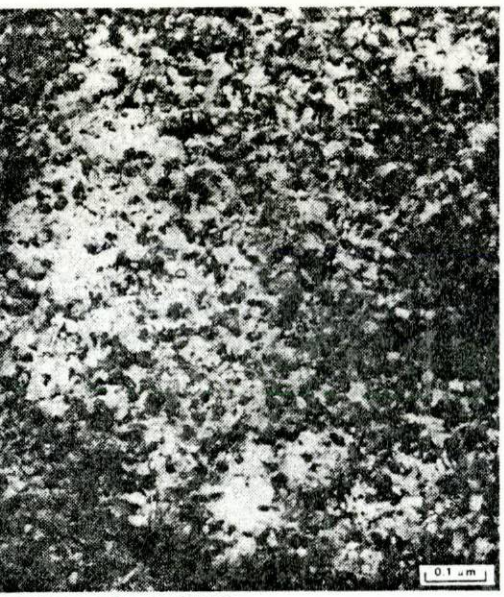
ure 2. SEM Photomicrographs of Gold Alloy Deposits at 1.2 A/dm^2

gaps evident at grain boundaries. The pulse plated deposits with duty cycles of 50 (Figure 1b) and 33 percent (Figure 1c) are very similar to this direct current deposit. When the duty cycle is lowered to 10 percent (Figure 1d), a different surface morphology is observed. This deposit appears to be compact, and the grain boundries are indistinguishable. Note the pit-shaped defect which is representative of others found for this particular deposit. The origin of this type of defect is believed to stem from either defects or foreign matter on the substrate, rather than from plating conditions. The deposits shown in Figures 1a, 1b, and 1c are matte in optical appearance, while that shown in Figure 1d has a semi-bright visual appearance. If the average current density is increased to about 0.8 A/dm^2 with the 10 percent duty cycle, the gold deposit becomes matte in appearance, and its surface appears more faceted and contains an increased number of distinct grain boundaries.

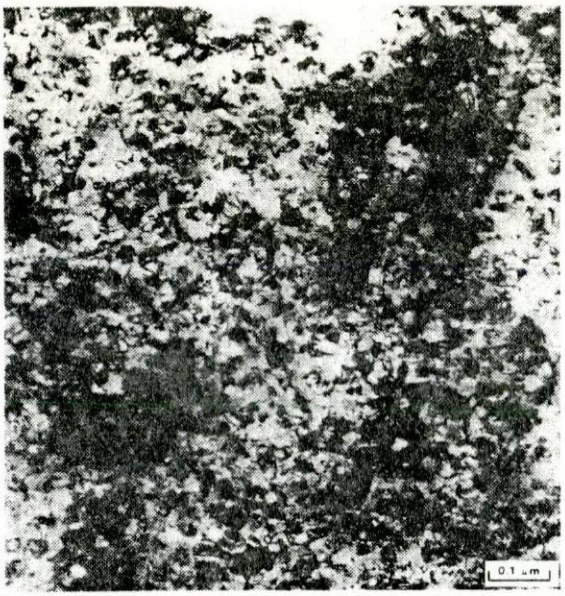
When the current density is increased to 1.2 A/dm^2, both the direct current and pulsed current gold alloy deposits are quite compact and their grain boundaries are virtually indistinguishable (Figure 2). The direct current deposit and the pulse plated deposit with a 50 percent duty cycle (Figures 2a and 2b) are very similar. However, there appears to be more leveling and less faceting in the pulse plated deposit. Both of these deposits were semi-bright in optical appearance. When the 33 and 10 percent duty cycles are used at this current density, the SEM photomicrographs (Figure 2c and 2d) show some nodular growth in these deposits. The degree of nodular growth appears the greatest for the 10 percent duty cycle. Both of these deposits are matte in optical appearance.

Microstructure

For the SEM analysis the examined gold alloy deposits were plated at the extremes of the recommended current density ranges. For the deposits analyzed with the TEM, a more nominal current density of 1.0 A/dm^2 was chosen. Representative bright field electron photomicrographs of the four samples analyzed are shown in Figure 3. It is clear that the grain size is small but somewhat variable. A moderate density of fine shaped twins is visible in all the micrographs examined. The dislocation density within these deposits was nearly impossible to establish because of their fine grain size and the diverse diffracting conditions encountered from grain to grain. Since controlled two-beam



IRECT CURRENT



b. PULSED CURRENT, 33% DUTY CYCLE



ULSED CURRENT, 50% DUTY CYCLE
ms ON



d. PULSED CURRENT, 50% DUTY CYCLE
0.1 ms ON

ure 3. Bright Field Electron Micrographs of Gold Alloy Deposits at 1.0 A/dm^2

micrographs are essential for reasonable accuracy, quantitative dislocation density measurements were not obtained. A summary of the results of the TEM analysis is given in Table 4.

The average grain sizes of the deposits from the two 50 perc duty cycles and the direct current deposit are equal. When the duty cycle is lowered to 33 percent, the average grain size is greater than the other samples. It is interesting to note that the minimum size range (120 to 190 Å) and the maximum size range (500 to 600 Å) are fairly constant from sample to sample. When these grain size ranges are compared to the average grain sizes, the distribution of grain sizes appears to be skewed towards the finer grain size. The direct current and pulse plated 33 percent duty cycle deposits have a twin density an order of magnitude greater than the pulse-plated deposits obtained with the 50 percent duty cycles. This difference in growth twins is felt to be significant, but the results of this initial investigation prohibit a definitive explanation. While it is possible that twin faults occur as random growth accidents, Hinton, Schwartz, and Cohen[9] have proposed that growth twin faults can occur if absorbed molecules have a radius greater than about twice that of the metal being deposited. This model predicts that a high concentration of twin faults is caused by a high concentration of occluded molecules. Munier[10] established that a significant concentration of occluded polymer is found in hard gold electrodeposits obtained from acid cyanide solutions. This polymer is an intrinsic contaminant produced during deposition of gold from $Au(CN)_2^-$. The difference in the twin density obtained when the 50 perce duty cycles are used would reflect less codeposition of polymer with the gold in these samples. When gold plating from a non-cyanide electrolyte where no polymer is codeposited Horkans and Romankiw[11] found the twin density of the gold deposit to be $6.5 \times 10^5/mm^2$.

Electron diffraction patterns were obtained for the four TEM samples to determine any preferred orientation in these gold alloy deposits. No tendency for preferred orientation was found, as shown in a representative pattern in Figure 4. Careful analysis of the electron diffraction patterns yielded 32 lines (rings) for all the deposits examined. Their indices were resolved by using the fcc cobalt and gold lines and all the lines but one were indexed with reasonable accuracy (±0.02 Å). Dark field images suggest the cobalt crystallites to be 50 to 100 Å in diameter. The gold-cobalt phase diagram according to Hansen[12] shows the equilibrium

ble 4. Results of TEM Analysis of Gold Alloy Deposits

mple	Plating Conditions	Microstructural Features: Grain Size (Å) Average	Grain Size (Å) Max/Min	Twin Density
	dc, 1 A/dm^2	248	530/120	3.8 x 10^9/mm^2
	pc, 33 percent duty cycle, 1 A/dm^2	333	600/190	4.3 x 10^9/mm^2
	pc, 50 percent duty cycle (1 ms on), 1 A/dm^2	250	500/150	2.5 x 10^8/mm^2
	pc, 50 percent duty cycle (0.1 ms on), 1 A/dm^2	246	510/130	2.1 x 10^8/mm^2

ubility of cobalt to be considerably lower than 0.5 ght percent at room temperature. In these gold-cobalt osits, the cobalt is present as a solid solution with d or a fine cobalt-rich phase. The quantitative distri- ion of the cobalt could not be determined. Results using rodiffraction and dark field methods to determine the alt distribution were limited; satisfactory images could be recorded because of the low intensities and the very g exposure times required. Specimen drift and contamina- n also precluded a quantitative analysis of the cobalt tribution.

mary

se plating of cobalt-hardened gold alloys increases the alt content in the alloy. At a current density of 0.3 A/dm^2 a duty cycle of 10 percent, a compact, semi-bright osit was obtained. At nominal current densities of 0.8 1.2 A/dm^2, deposits obtained with dc plating and pulse ting with a 50 percent duty cycle are compact and semi- ght. A reduction of the duty cycle at these current sities results in a rounded, nodular surface topology and

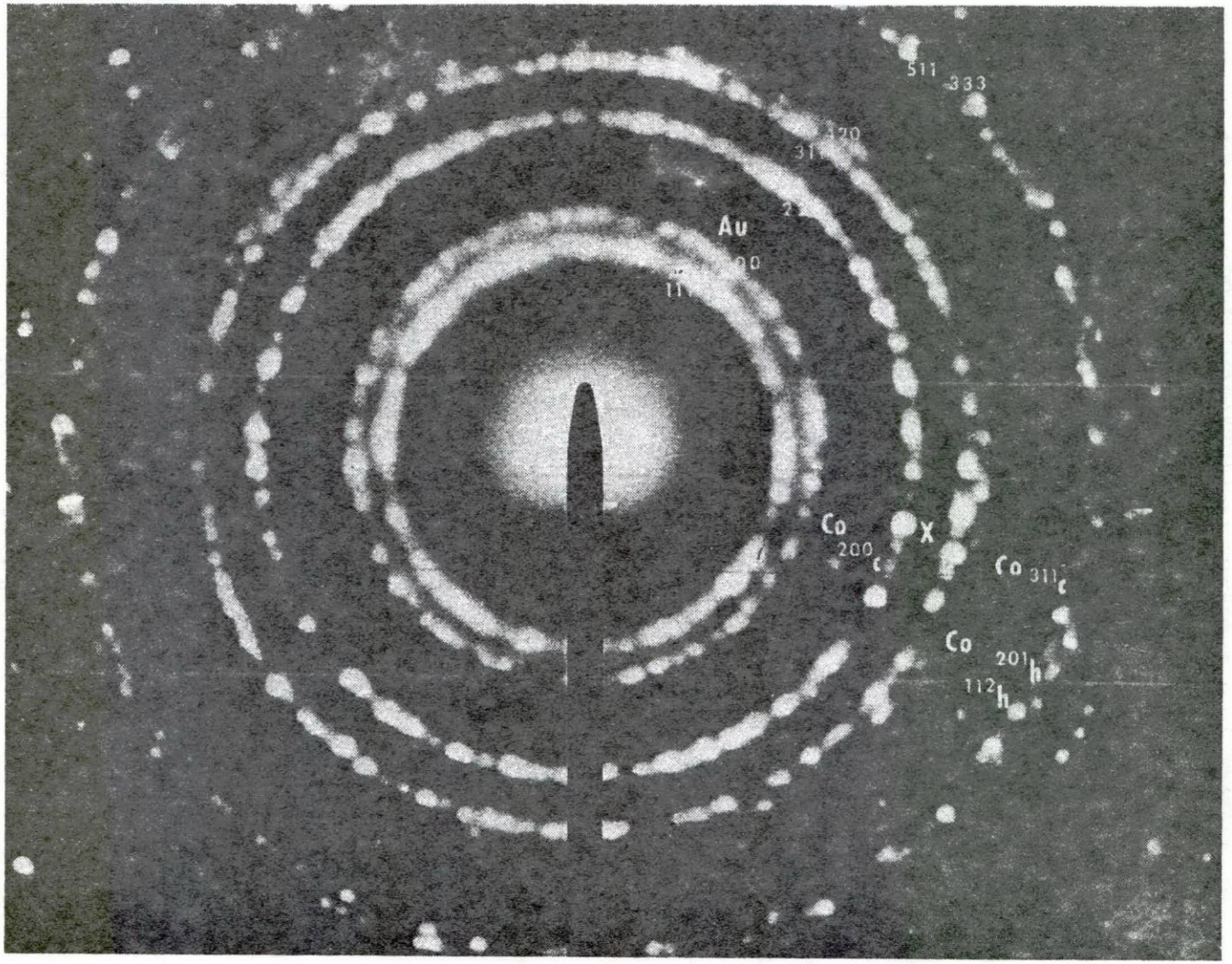


Figure 4. Electron Diffraction Pattern of Gold Alloy Deposit Obtained

ıll, matte-appearing deposit. In almost all cases, the ılt content of the pulsed current gold deposit is greater ı the corresponding dc deposit. At 1.0 A/dm^2, the cobalt tent of the gold deposit is 25 percent higher than the dc osit regardless of the duty cycle used.

TEM and electron diffraction analyses indicated no ıificant difference in microstructure between the conven- ıal and pulse plated gold alloy deposits. The grain size ge is about 120 to 600 Å for all deposits analyzed and is tributed toward the smaller grain size. There is a ference in growth twin density of the pulse plated deposits ı the 50 percent duty cycles when compared to the other ples. The significance of these twins still needs to be ertained with respect to physical, mechanical, and elec- cal properties. The electron diffraction patterns show tendency for preferred orientation. Fine 50- to 100-Å- neter cobalt-rich crystallites are distributed uniformly oughout all four samples; however, a quantitative analysis the cobalt distribution was not obtained. The indexed ctron diffraction patterns for these dc and pulsed plated ılt hardened alloys indicates a fcc crystal structure.

References

[1]A. J. Avila and M. J. Brown. Plating. 1970, 57 (11), 1105.

[2]D. L. Rehrig. Plating. 1974, 61 (1), 43.

[3]J. Lendvay and C. J. Raub. Metalloberflache. 1975, 29 (4), 165.

[4]A. R. Despic and K. I. Popov. Journal of Applied Electrochemistry. 1971, 1, 275.

[5]V. A. Lamb. Plating. 1969, 56 (8), 909.

[6]C. A. Burrus. J. Electrochem. Soc. 1971, 118 (5), 833.

[7]W. Sullivan. Plating. 1975, 62 (2), 139.

[8]C. J. Raub and A. Knodler. Gold Bulletin. 1977, 10 (2), 38

[9]R. W. Hinton, L. H. Schartz, and J. B. Cohen. J. Electrochem Soc. 1963, 110 (2), 103.

[10]G. B. Munier. Plating. 1969, 56 (10), 1151.

[11]J. Horkans and L. T. Romankiw. J. Electrochem. Soc. 1977, 124 (10), 1499.

[12]M. Hansen. Constitution of Binary Alloys. McGraw-Hill, New York, 1958, 196.

G-2

Electronics II
Session G

Electroless vs. Electrolytic Gold Barrel Plating Of Electronic Transistors

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Abstract

A practical evaluation has been made using some so-called "electroless" gold and immersion gold solutions comparing them with a standard electrolytic gold solution. The deposits were made on electronic components, essentially the TO-18 header.

The original objective was to reduce gold usage and gold cost by obtaining an autocatalytic gold solution. This solution would deposit the gold metal on all surfaces at the required thickness thereby not wasting gold that is deposited in excess on the edges of eyelets and ends of leads (high current density areas) typical of the electrolytic solutions.

Thickness distribution curves for various gold deposits, solderability as in the plated condition and after heat cycling, and some microphotographs of the gold deposits is presented.

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Introduction

Less than a decade ago the semiconductor industry was depositing 3.1 micrometers of gold onto small transistors such as the TO-18. This g thickness was required for proper eutectic die bonding. Since this t gold costs have increased from $36 per 31.1 grams to approximately $2 per 31.1 grams. Because of the gold price and the natural excessive deposition of gold on the high current areas, (the edges of eyelets a ends of leads) the semiconductor industry has always been interested an autocatalytic gold solution that could deposit up to 5.13 micromet of a eutectic die and thermal compression, wire bondable deposit whic is solderable to Military Specifications.

Improving die and wire bond techniques such as increasing the gold th ness on the die and increasing the scrubbing action and speed of die ing machines, permitted the reduction of the gold thickness while mai ing highly reliable semiconductors. Epoxy die bonding also allowed a reduced gold thickness. The gold thickness has been successfully redu to 0.25 micrometers in eutectic as well as epoxy die bonding.

A satisfactory autocatalytic gold solution is not available on the ma and the author was unsuccessful in developing such a solution, so thi reduced thickness allowed the consideration of proprietary immersion g solutions and the so-called "electroless" gold solutions. The follo describes some of the experimental data that demonstrates electrolyti gold, in the 0.25 to 0.77 micrometers thickness range, is superior fo solderability and bonding purposes without sacrificing costs.

Discussion

"Electroless" gold plating means plating without any outside current. An autocatalytic solution would give any desirable thickness without outside potential while an immersion solution displaces the metal surface cations with solution cations of a higher potential until the metal surface is no longer exposed to solution cations. Many proprietary solutions are called "electroless", but they are really immersion solutions that depend on ion displacement, such as the gold ion replacing copper, nickel, tin or iron.

Gold is deposited on nickel and other more active metals because it has a lower negative potential and displaces more active metals that have a higher negative potential and tend to form ions in solution. The displacement process continues until the surface of the nickel is completely coated with gold. At this point there is no more driving force for the reaction thus the reaction ceases. Theoretically this should occur at a molecular film thickness, however, due to porosity an additional release and acceptance of electrons occurs. Additional thicknesses are obtained until the local voids become polarized.

Table I illustrates examples and functions of chemicals in various "electroless" gold solutions.

Typical weigh-strip-weigh (WSW) differences in Tables II, III, and IV are erratic even though some solutions were new, replaced and/or replenished.

Experience has shown that an increased temperature and a lower pH giv the higher plating rates. The electroless nickel phosphorous alloy gives the better esthetic appearance.

TABLE I

POSSIBLE CHEMICAL COMPONENTS OF A PRODUCTION AND ELECTROLESS GOLD BATH

COMPONENT	PURPOSE	EXAMPLES
Gold Cations	To supply metallic gold	$KAu(CN)_2$ $Au\ Cl_2$, $HAuCl_4 \cdot 3H_2O$ AuCn
Reducing Agents	To reduce gold ions to gold via in situ generation of hydride ions (H^-)	DMAB, Glycines KBH_4 Sodium Hypophosphite Formaldehyde Hydrazine
Organic Chelating Agents	To act as a buffer and prevent rapid decomposition	Citric ions Hydroxycarboxylic acids Tartaric acid
Exaltant	To counteract the slowing effect of chelating agents	Succinic anions
Stabilizer	To inhibit solution decomposition by masking active nuclei	Thiourea, sodium ethyloxanthate KCN
pH Regulator	To adjust pH to keep pH constant during operation	H^+ ions and OH^- KOH, Citric acid
Wetting Agents	To promote wetting of the solution of parts to be plated	Sulfonate of fatty acids or Sulfated alcohols

Experimental Procedures and Data

Plating Barrel

A 5.1 X 10.2 cm horizontal plating barrel* with 0.4 cm diameter thru
was used for the "electroless" and immersion solutions. A lot size o
TO-18 devices was used. The solution volume was 2 liters.

A standard production barrel and plating lot of 20,000 TO-18 headers
with the electrolytic solution. The barrel had a solid bar and a 15.
60.76 cm cylinder. The solution volume was 378.5 liters.

Weigh - Strip-Weigh

The devices (20) were weighed before and after stripping the gold for
seconds in gold strip solution** at 60°C and a concentration of 60 gra
liter. The thickness T is determined in micrometers with the followi

$$T = \frac{W}{0.00191 \quad (A)}$$

W is the weight difference in grams as determined on a five place anal
balance*** A is the area in square centimeters and 0.00191 is the co
used for converting gold to the correct units. Each run was determine
deposit 0.51 micrometers thickness based on the information contained
manufacturers data sheet. See Tables II, III, and IV.

Beta Backscatter Thickness

Localized thickness measurements were determined on 100 units, on the
the thru lead, and the grounded lead with a beta scatter measuring ins
The leads were measured on a 0.0003 meter slotted platen and the eyele

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* A NAPCO Cylinder, National Plastics and Plating Supply Co., Terry
** Techni Strip Au, Technic Inc., Cranston, R. I.
*** A Mettler Analytical Balance, Mettler Instrument Corp., Hights To
**** A Memoderm Model MP-94, Unit Processes Assemblies Inc., Syosset,

PROPRIETARY
ELECTROLESS GOLD

RUN	WSW THICKNESS (μM)	TIME (MIN.)	TEMPERATURE (°C)	SUBSTRATE	pH	APPEARANCE AFTER SOLDER TEST AS PLATED
#2	1.23	60	60 - 65	Kovar	6.0	Voids
#3	0.10	40	55 - 60	E. NiP	6.1	Voids
#4	0.19	25	55 - 60	Kovar	5.9	Voids
#5	1.18	25	76	Kovar	6.0	Voids
#6	0.19	25	76	E. NiP	6.1	Voids
#7	0.18	10	60	E. NiP	5.9	Some Voids
#8	0.38	30	72	E. NiP	6.2	Accepted Some Voids
#9	0.09	60	66	E. NiP	6.0	No Bare Spots
#10	0.05	60	60 to 75	E. NiP	5.9	No Bare Spots

Runs #7, 8 and 9 were with ultrasonics.

MOTOROLA ELECTROLESS GOLD M[1]

RUN	THICKNESS (μM)	TIME (MIN.)	TEMPERATURE (°C)	SUBSTRATE	pH	APPEARANCE AFTER SOLDER TEST: AS PLATED	BAKE	BAKE & OXALIC*
#11	0.10	20	71 to 96	E. NiP	5.2	Acc.		
#11A	0.54	20	96			Rough	Reject Voids	Reject Voids
#12	Bare Spots	20	80 to 100	Kovar	5.4	Bare Spots		
#12A	Bare Spots	20	93 to 95			Bare Spots		
#1A	0.55	10	88 to 100	Kovar	5.3	Reject Voids & Rough	Reject Voids & Rough	Reject Voids & Rough
#2A	0.73	20	82 to 100	Kovar	5.2	Reject Voids & Rough		

*10% Oxalic acid solution was used for deoxidation prior to solder test.

PROPRIETARY
IMMERSION GOLD

RUN	THICKNESS (μM)	TIME (MIN.)	TEMPERATURE (°C)	SUBSTRATE	pH	APPEARANCE AFTER SOLDER TEST: AS PLATED	BAKE	BAKE & OXALIC
#13	1.54	12	65 to 67	Kovar	3.6	Voids	Voids	
#14	1.03	8	70 to 77	E. NiP 5 min.	3.9		Voids	Acc.
#15	1.00	6	73 to 75	E. NiP 8 min.	3.6		Voids	Acc.

Note: 1. Solution breaks down to give a yellow floculent precipitate but still plates.
2. Deposit is difficult to strip cleanly. A black oxide is apparent.

#16	1.02	4	77	E. NiP	3.5	Acc.	Voids	Acc.
#17	0.49	3	76 - 77	E. NiP 10 min.	3.6	Acc.	Voids	Acc.
#18	1.26 (Dark)	3	73 - 75	Kovar	3.6	Rough & Voids	Rough & Voids	

Note: The speed of deposition is faster on Kovar than Electroless Nickel. We will reduce temperature to 60°C.

#19	1.08	3½	61 - 62	Kovar	3.6	Rough & Voids	Rough & Voids	

measured on a 0.0012 meter circular opening platen. In both measure
the source used was PM147. See Distribution Curves in Fig. 1. It a
that the distribution on TO-18 transistors for the four solutions il
and the nominal thickness of 0.4 micrometers, are similar.

Scanning Electron Microscope (SEM)

Photomicrographs on a scanning electron beam microscope* were taken
thru lead of the TO-18 header. This is the critical surface in this
gation. The magnification utilized was 3000, 6500 and 8000 at 0° an
angles. See microphotographs in Fig. 2. There appear to be occlusi
pockets and voids in some of the "electroless" and immersion gold de
The electrolytic gold deposits appear uniform and have less imperfect

Solder Test

The solder test specification used was Mil Standard 883 without aging
was replaced by a bake test at $440^{o}C$ in air for two minutes before so
These conditions are typical of bonding thermal excursions. See Tabl
III and IV. The data was gathered from deposits utilizing a proprietar
immersion and an "electroless" solution. Also included are results f
Motorola developed "electroless" solution. There is inconsistency in
deposition rates, solution stability, and solderability. Solderabili
failures rejected the deposits from all the solutions except the elec
gold solution. For epoxy die bonding, which does not require high te
($440^{o}C$), the "electroless" and immersion gold deposits give satisfact
solderability. Solution stability, replenishment and control are sti
problems when utilizing these types of solutions.

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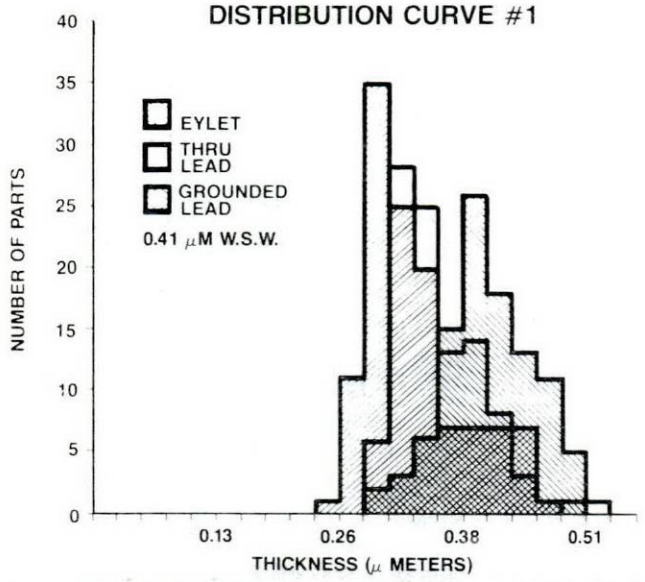
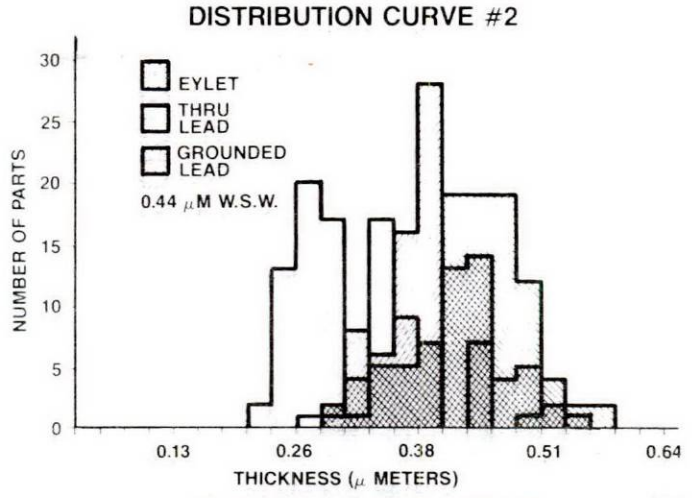
* An ETEC Autoscan, ETEC Corp., Hayward, CA.



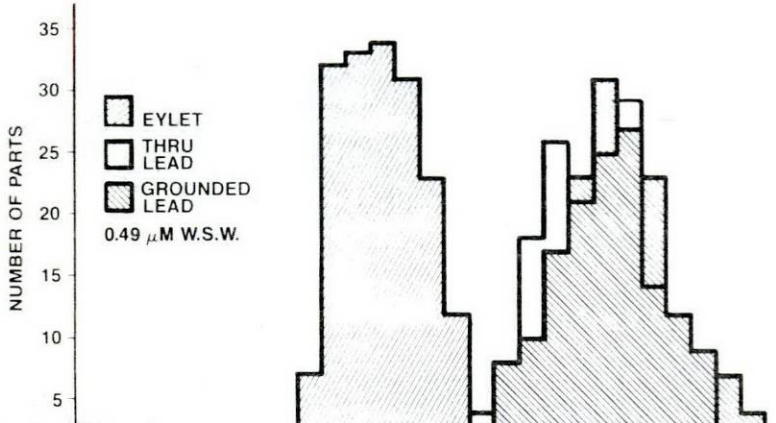
PROPRIETARY ELECTROLESS GOLD

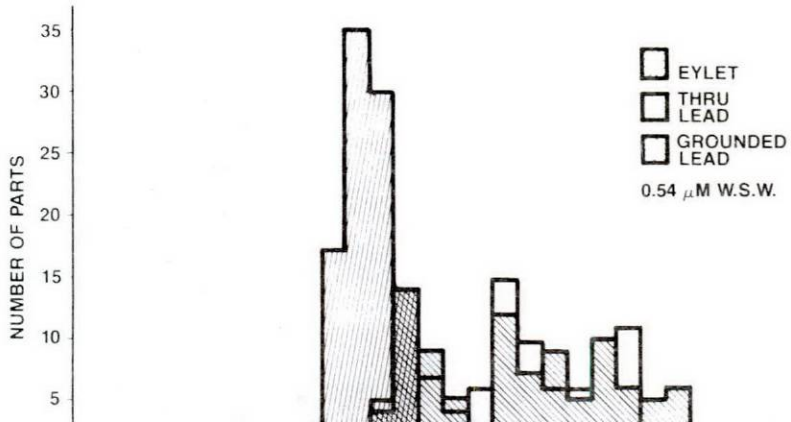
FIG. 1(a)

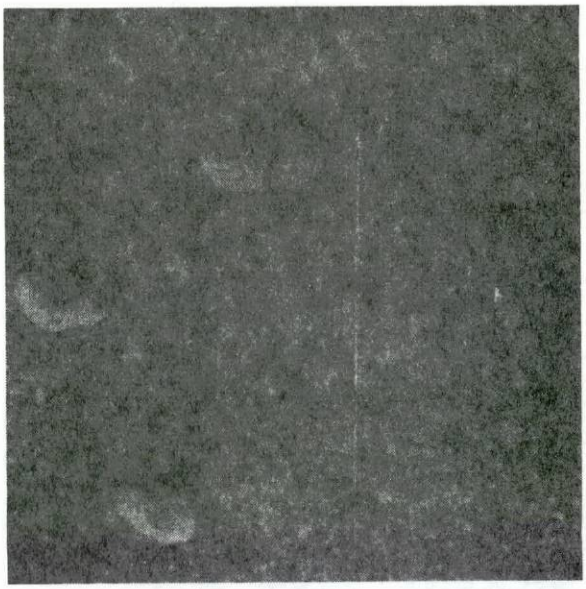


ELECTROLYTIC GOLD

FIG. 1(b)







TO-18 HEADER LEAD
6.5K X 0° 0.49 μM

ONE MICRON

FIG. 2(a)

PROPRIETARY IMMERSION GOLD



TO-18 HEADER LEAD
6.5K X 0° 0.41 μM

FIG. 2(b)

PROPRIETARY "ELECTROLE



TO-18 HEADER LEAD
6.5K X 0° 0.87 μM

ONE MICRON

FIG. 2(c)

PROPRIETARY ELECTROLYTIC GOLD

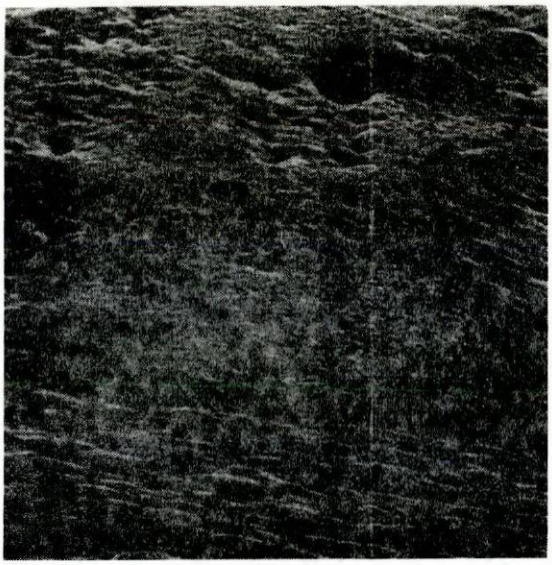


TO-18 HEADER LEAD
8K X 70° 0.51 μM

FIG. 2(d)

PROPRIETARY "ELECTRO

Fig. 2 Surface Micrographs Using the Scanning Electron Microscope

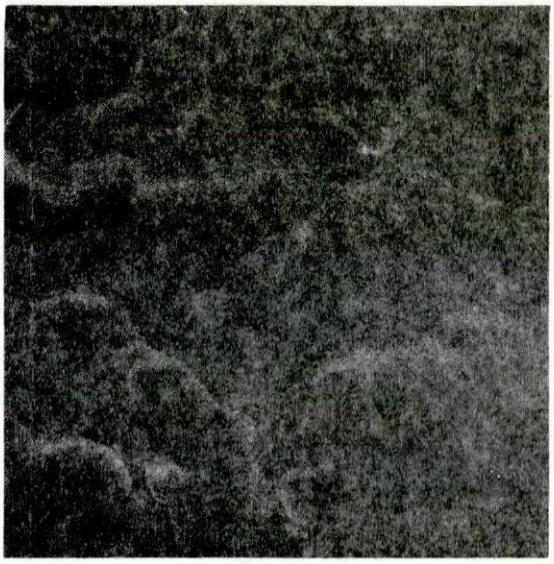


TO-18 HEADER LEAD
8K X 70° 0.56 μM

ONE MICRON

FIG. 2(e)

PROPRIETARY "ELECTROLESS" GOLD



TO-18 HEADER LEAD
3K X 0° 0.51 μM

ONE MICRON

FIG. 2(f)

PROPRIETARY "ELECTROLESS" GOLD

Fig. 2 (continued)
Surface Micrographs Using the
Scanning Electron Microscope

Ultrasonic

The TO-18 transistors were placed in the plastic cylinder and submer
in the gold solution contained in the ultrasonic cleaner* which had
frequency output of 40KHZ. Ultrasonic application has been shown to
increase the deposition rate from the "electroless" solution, howeve
this application this was not the case as seen in Run #7, 8 and 9 po
because of the damping of the plastic cylinder. More work must be d
demonstrate the economics of the system, and is beyond the scope of
paper. See Fig. 3. It is a photomicrograph of 7.61 micrometers gol
thickness acquired in an ultrasonic experiment in the Motorola "elec
Gold M solution[1] at 60°C for one hour. This particular deposit was m
a 2.5 X 2.5 X 0.3 cm Kovar panel. The panel was suspended freely in
liter glass beaker of the gold solution.

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*A Branson Ultrasonic Cleaner No. PAL 1012, Branson Instruments, Inc.
Shelton, CT.

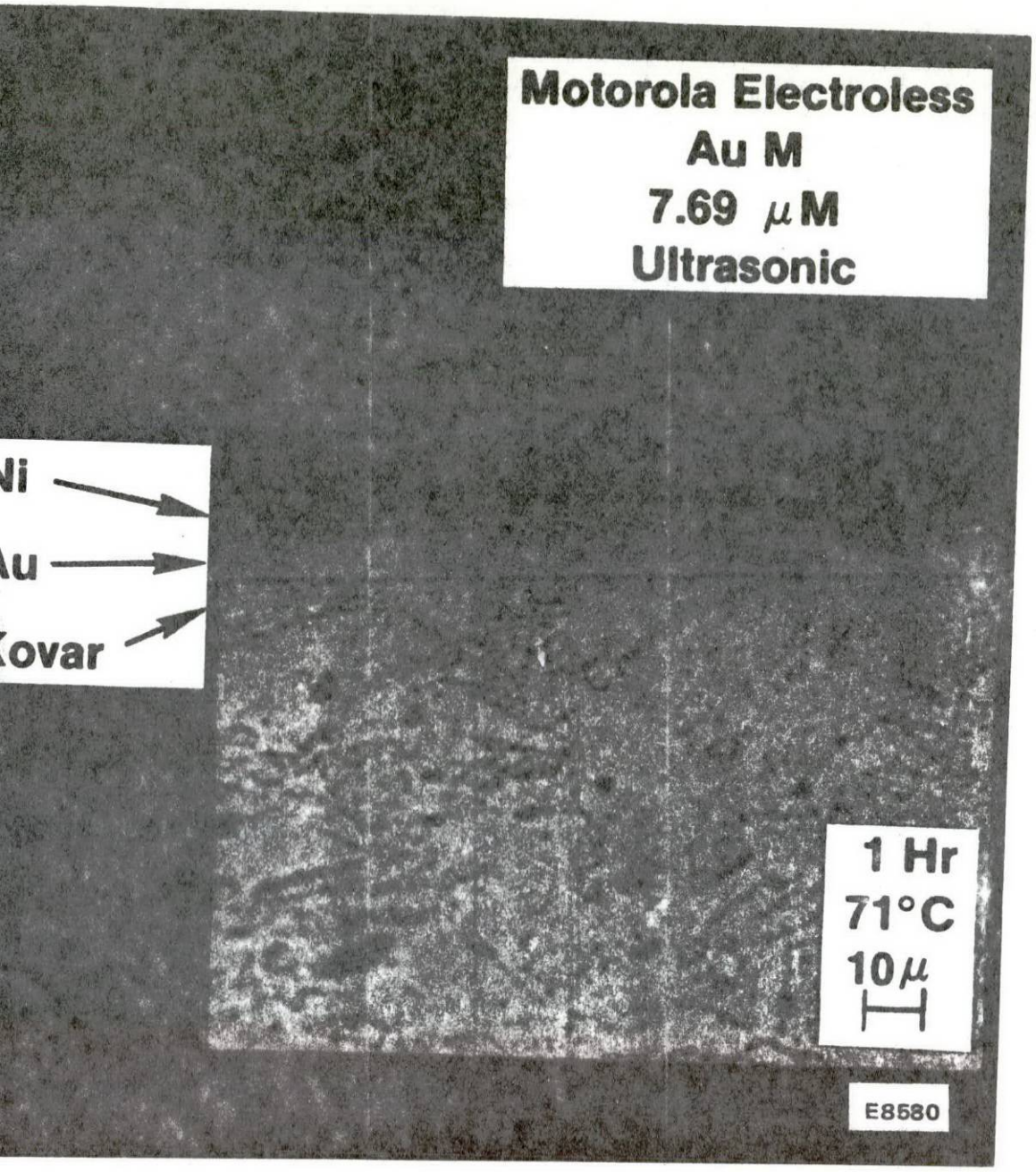

FIG. 3

Micrograph of ultrasonic deposited gold using the Motorola "Electroless" Gold M Solution. Thickness is 7.61 micrometers.

Conclusions

1. A true autocatalytic gold solution is yet to be discovered.
2. The electrolytic gold solution as deposited grain structure is m resistant to high temperature (430°C) grain boundary diffusion t the so-called "electroless" or immersion gold deposits at the 0 to 0.76 micrometer thickness range.
3. The "electroless" or immersion gold deposits perform satisfacto for epoxy die bonding and thermal compression wire bonding in th 0.26 to 0.76 micrometer thickness range due to low temperature excursions.
4. There is no appreciable cost advantage in the "electroless" ove electrolytic gold because of similar metal distribution at these thicknesses.
5. Gas voids were noticed in some "electroless" deposits.
6. It was found that tumbling eliminated bare spots on leads while p in an immersion or "electroless" solution.
7. Ultrasonics is a promising process for increasing the deposition and should be investigated, although its practicality with relati to cost is questionable.

Acknowledgments

The author expresses his thanks to D. W. Endicott and A. F. Mracek of the Electronics Material Group for their assistance and contributions, also to G. P. Thome, of the Electron Optics Laboratory for the SEM work.

References

1. Motorola Electroless Gold "M" is company confidential.

G-3

Electronics II
Session G

Effects of Prolonged Storage (up to 23 years) On the Solderability Of Electroplated Coatings

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Bell Laboratories
Murray Hill, New Jersey

Paper not available at time of printing of proceedings.

G-4

Electronics II
Session G

Thickness Measurements:
What You Are Reading—
What You Can Reasonably Expect

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Harper-Leader, Inc.
Waterbury, Connecticut

THICKNESS MEASUREMENTS, WHAT YOU ARE READING, WHAT YOU CAN REASONABLY EXPECT

Isidore Cross
Harper-Leader, Inc.

A prominent manufacturer of thickness testing ipment remarked, "...commercial considerations sometimes nt the objectivity which one expects from bulletins of a nnical nature describing the capability of a method or an trument, thus leading the prospective user, who, generally, not a specialist, to assume that his readings are correct, n if they are only approximate."(1) The purpose of this er is to try to lend more objectivity to those concerned n the testing of coating thickness and put it in a proper spective.

Writing a paper is an educational experience both the author and hopefully, his audience. In preparing this er I came away with two postulates which I cannot stress rly enough.

One, when in doubt, read the instructions for rating your equipment. The other is Murphy's Law which arently takes precedence over all other laws, natural or erwise; and in electrochemistry, that even goes for aday's Law as well. For instance, when two or more truments are checking the same part, the instrument giving lowest reading is invariably in the quality control depart- t of the ultimate user, or your customer. This is just as e as everytime your toast falls to the floor, it's always tered side down.

When some of us think of thickness measurements, often conjure up in our mind some concept of a linear suring device like a scaled ruler, a micrometer or an ical comparitor which magnifies the object to be measured a large screen and make our measurements directly. Micro- pic cross-sectioning is about the only method commonly used measure thickness directly. Micrometers are used on con- ient shapes to measure heavy deposits.

When coating thicknesses are in the vicinity of microns (.0001") microscopic cross-sectioning becomes a ter of technique and below it, of questionable accuracy, we have to rely more upon gages that do not measure thickness ectly, but rather rely upon other properties that can be nslated to thickness readings. These measurement properties be electrical, magnetic, chemical as well as the effect of

irradiating the coating-substrate combination with either be rays or x-rays.

A common characteristic of instruments for measuring coating thickness is that they must be calibrated and the reliability of a measurement is dependent upon the reliabili of the calibration standards, yet little has been written on that subject. (2)

Since a thickness gage is really measuring some property other than thickness, a calibration standard sometimes need not consist of the coating-substrate combination. A common type of calibration is a foil of known thickness of a non-magnetic material placed over a coupon of steel having the same magnetic properties of the steel substrate to be tested, thus we have a test for a non-magnetic-magnetic combination. With beta backscatter the atomic number is an all important criteria of whether that instrument can even be considered appropriate for the combination in question, a substitute like tungsten carbide for instance, may be used to standardize the instrument for a nickel-gold combination at a certain thickness because the backscatter characteristi are similar for that specific thickness combination.

Except for the electrical and magnetic gages, the coulometric, weight gain, beta ray and x-ray methods of thick ness determination have one thing in common. They measure ma per unit area, and thickness is derived from this simple equation.

$$\text{Thickness} = \frac{\text{Weight/ unit area}}{\text{Density}}\ ; \text{ or } \quad \text{Thickness in microns} = \frac{\frac{Mg}{CM2}}{\frac{Mg}{CM3}} \times$$

$$\text{Microns} = \frac{\cancel{Mg}}{\cancel{CM}^{2}} \times \frac{CM^{3}}{\cancel{Mg}} \times 10^{4}; \text{ or } CM \times 10^{4}$$

$$\text{Thickness in Microns} = CM \times 10^{4}; \text{ (Microinches} = In \times 10^{6}$$

There is of course, one "kicker" to this equation. What is the actual density of the metal we are trying to determine the thickness of? The density of gold presents one problem in particular. Those methods which actually determin mass per unit area, must be divided by density in order to obtain the thickness as shown above, and what should ordinari be a constant, is not always constant. In the case with gold there is a significant density variation due to the variables the plating process itself. The density of a gold electrodep may vary from the theoretical 19.3 down to 15.7.(4) A microscopic cross-section is not affected by density, but you may able to see that the 19.3 density gold will be more dense tha the 15.7 gold because of voids in the deposit, however the 15 gold will show just as wide a band as the 19.3 gold, and that whats reported, the width of the band. If your beta backscat

calibrated against the 19.3 density gold, the 15.7 will
ad considerably thinner. This problem will also exist with
e coulometric and x-ray fluorescent thickness determinations
or any method that converts mass per unit area to thickness.

I would like to digress briefly to discuss deposit
nsity so that the discussion of the various instruments using
ss per unit area is better understood.

G. B. Munier's[5] work on polymer codeposits with gold
a classic paper. It brought to our attention a reason for
ne of the anomalies encountered in determing electrodeposited
ld thicknesses. Munier showed why we can no longer assume
at the density of gold is always 19.3. She showed that poly-
rs codeposited with all hard golds, and in lesser quantities,
th the purer golds in the acid-cyanide systems. Polymers in
n-cyanide gold systems could not be detected. Metallic
rdeners like cobalt and nickel among others, increase the
ount of polymers. With softer golds,the polymer content is
creased with a reduced cathode efficiency. This is reason-
le, because hard golds are much less efficient than the soft,
re golds. When the soft, pure golds lose their efficiency,
obably through a buildup of metallic contamination among other
ings, polymerization does indeed take place in those baths,
wever to a lesser degree.

Antler[6] later showed that materials of a lower atomic
mber are deposited in discrete pockets within the plate. This,
rticularly in the case of thickness testing by beta backscatter
d x-ray will affect the results because the beta rays and x-rays
ll "see" the lower atomic numbered elements as well as the
gher ones.

Holt, Ellis and Stanyer[7] demonstrated that carbon is
sociated with the codepositing metals and the amount of carbon
at is deposited is a function of all of the bath variables.
the use of Carbon-14, they showed that the carbon inclusions
iginated from the cyanide of the gold complex and the amount
posited was influenced by the codepositing brightening metal.
Munier discovered, Holt, et al confirmed that a drop in current
ficiency is nearly always associated with a rise in the con-
ntration of the codeposited metal. More importantly they showed
at current density, plating temperature and other bath variables
alter the density of the gold deposited. We will later see
at solution composition can affect the electrical properties
a zinc deposit as well as the magnetic properties of nickel.

Perhaps just as every item of prepared food has an
emized account of the ingredients on the label, would it be in
der to suggest that each bottle of prepared gold be labeled with

the hardness range one could expect to get from plating unde properly prescribed conditions?

All indirect means of thickness determination requ standards in order to compare the unknown with a known -- an I have to pause a bit as I say this. There used to be an expression in this great country of ours - "as sound as the American dollar!" With inflation, how sound is the dollar, and with what I just said about density, how sound is a gold standard with a 19.3 density checking the thickness of a 17. density deposit?

This is not to say that our thickness measuring de are worthless. Far from it, they are ingenious, they are cl and they can be very accurate -- all that I'm saying is that they are not absolutely accurate.

Obtaining the density of electroplates is not the easiest thing to determine because not every plating departm lab is equipped for it. Cooley and Lemons'[8] paper confirm that in describing their work on density by using profilomet interferometry, monochromatic beams and x-ray diffraction pa This is a far cry from old Archimedes using a graduated batht which caused him to shout "Eureka!" when he discovered that a solid body, immersed in a liquid is buoyed up by a force equa to the weight of the liquid displaced -- or that when a solic heavier than water is immersed in water and weighed while in water the weight loss is equal to the weight of the liquid displaced. Thus density is equal to the weight of a solid ir air, divided by the difference of its weight in air and its weight in liquid. This is the hydrostatic method and is the standard method used with some modification. The modificatic is the use of heavy liquids like a fluorocarbon instead of water [9][4] because with the small mass of an electroplated sample, a heavier liquid will give a more accurate registry than just water.

Duva and Foulke[4] ran a series of densities on gold with interesting results. The 99.99 golds registered densiti close to the theoretical 19.3, with figures from 18.9 to 19.2 The alloy golds ranged anywhere from 15.7 to 18.9, with most the alloy golds falling in the vicinity of 17.5

It has been suggested on more than a number of occasions that platers make up their own standards from their own baths, depositing a thick enough plate for an accurate microscopic cross-section, using that for a standard for beta backscatter or x-ray. This may be all very good for the plat but knowing now what we know about why the density varies, wo the ultimate user accept it? I think not, unless the use is for decorative purposes only.

I would like to make a suggestion and incorporate the lowing into our specifications. Pure golds should be assigned acceptable density range of 18.9 to 19.3 with the gold supplier ving the density and make in house standards made from those hs. Hard gold densities falling in the range of say, not s than 17.3 be acceptable, with the gold supplier giving the sity for his process and in house standards made for those hs, too. In this way we may be better able to discipline thickness evaluations, but traceable to Bureau of Standards.

It cannot be stressed enough that every indirect ding gage for testing thickness must have a set of standards calibrate the properties that the instrument actually measures, h thickness. The thickness of the coating on the calibration ndard should be sufficiently uniform so that one cannot detect thickness variation with the instrument to be calibrated.(3) National Bureau of Standards used two techniques for measuring ir standards. The weight gain technique is used to measure thickness of the standards, and the fluorescent x-ray technique used to determine the uniformity of the thickness of the deposit.(2)

lometric

One of the neatest and a rather accurate means of suring plating thickness is the coulometric method. Very tle has been written about it, yet it is one of the most versally used machines for thickness testing and deservedly It is based on the fundamental law of electrochemistry, raday's Law. (Faraday's law is just as applicable for the ode as for the cathode, and this method is a deplating operation.) coulometic method is a weight per unit area determination, hout weighing. If a metal can be dissolved anodically at 0% current efficiency, the weight of the metal dissolved can calculated from the elapsed time, current and assumed density the metal.

This method actually is electrochemistry at its purest. plate is dissolved anodically at 100% current efficiency. The a for thickness determination is defined by the orifice in a ber gasket attached to the cell. The cell is the cathode, the cimen is the anode. A constant current is supplied, and the tage between the cell and specimen remains constant while the te is dissolving. Agitation, mechanical or air is necessary overcome any polarization that is likely to occur. When the strate is exposed after the plating is all dissolved, a sharp tage change occurs, this is the end point and this sharp voltage nge stops the test, automatically. By correlating the test rent with the area, the time read-out is numerically equal to plating thickness. This is, as I mentioned an ideal demonstra-n of Faraday's law in action. Murphy's law comes into effect

when the timer refuses to kick off when it's supposed to.

The electrolyte, and there are several different o used for different metals and substrates must not attack the plating chemically, must also permit the coating to be teste to dissolve at 100% efficiency and must not attack the subst Additive to coatings may change the electro-chemical equival for the particular metal as well as the current efficiency.

The coulometric method is unaffected by the electr and magnetic properties of both plating and substrate.

This instrument has its limitations. The exposed, deplated spot may be objectionable. The sample must be larg enough for a cell gasket to fit and seal properly - and this eliminates a great many small objects from being checked by this method. Error can crop up if the current source is not constant and applying excessive pressure to the gasket can effect the area by distortion.

The instruments are calibrated on the basis of theoretical values for densities of the various metals that can be tested. If a metal cannot be tested, then the proper electrolyte has not been developed for it.

The accuracy of this method is generally better tha ± 10% with the more accurate ranges falling between 2.5 to 4(microns, (.0001 to .0015 inches). Below a micron (.00003 in and over 50 microns (.002 in) the results are iffy, even th it is claimed that decorative chromium can be accurately determined at .075 microns (.000003 in).(10)

The instrument should be calibrated against known thickness standards daily, because we all know, in our busine anyway, what was good yesterday may not necessarily be so too

I have found this type of instrument to correlate v well with microscopic cross-sectioning, particularly in the r of 12.5 microns (.0005 in). It's always good practice to cal and check the machine at the factory at least once a year.

Drop Test

Considering the instrumentation available today, th Drop Test method for thickness testing harks back to the medi period of plating. The fact that the ASTM saw fit to review their specification for the Drop Test method (11) as late as signifies that there is still an interest in this method.

In the 1930's and the early 1940's it was one of th more popular methods of testing thickness if you couldn't aff

nicroscope. The Drop Test is, under the best of circumstances
t the most reliable method and is generally used mainly for
sting the thickness of zinc, cadmium, copper and tin. Its'
curacy is really just a ball park figure -- and a big ball park
that, ± 15% is considered very good and its reproducibility is
r greater than its accuracy, (11) which just proves that re-
oducibility doesn't always mean very much. With other instru-
nts it's supposed to be important.

The Drop Test simply consists of applying a corrosive
lution at a constant rate of 100 drops a minute to the plated
rface which is resting at a 45° degree angle for drainage
rposes. The time required to penetrate the coating and expose
e substrate, is multiplied by a factor given in a table.(11)
STM's -555-75)

The time is proportional to coating thickness.
riations in the concentration of the test solution will induce
rors and obviously, test solutions cannot be reused. Since
is is purely a chemical reaction, the temperature of the test
lutions are very important. For instance in checking cadmium,
takes 35 seconds to record a reading of 15 microns (.0006)
38C (100°F) and 45 seconds at 21C (70°F).

The end point is characterized by a change in color
d this method, like any other test method must be standardized
ainst a known thickness sample. The sample thickness can be
termined by having identical specimens checked by other methods
th a far greater degree of proven accuracy than the Drop Test.

I suppose the reason this test is still in vogue is that
gives you a rapid ball park figure when you don't want to expose
re expensive equipment to a corrosive environment.

dy Current

Eddy Current thickness testing takes advantage of the
ectrical characteristics of the substrate.

Eddy currents are produced in a coil carrying an
ternating current of a given frequency. (12,13) This coil,
ntained in a probe produces a high frequency electro magnetic
eld which induces eddy currents in the electrically conductive
rtions of any sample close to or in contact with the probe.
ese eddy currents in turn produce a reaction in the probe which
measurable and can be related to the thickness of a coating
th the use of reference coating thickness standards.

Eddy currents are affected by the frequency applied to
e coil, the conductivity of the sample, its magnetic permeability
d the heat treatment that the basis material was subjected to.

The depth of eddy current penetration varies invers with electrical conductivity. Thus the range for determining copper thickness is much less than for poorer conductors like cadmium and zinc. Differences in conductivity between coatin and a substrate, whether it's conductive or otherwise, or vic versa is what characterizes an eddy current instrument as a thickness gage. Therefore it works best when a large differe in conductivity exists between substrate and coating - like conductor and non-conductor.

Interestingly enough there is a difference in the conductivity between the low cyanide and cyanide free zincs, and zinc plated from a typically high cyanide zinc whose depo is more conductive. Thus if you are operating a non cyanide zinc installation it's important that your standard wasn't plated from a high cyanide bath. This is a specific instance where a variation in the plating process can change the instr ment response. Nickels are another example.

The instruments generally come in from the manufact with set up standards for standardizing the instrument. Erro can occur if the properties of the set up standard are differ from the raw part you are trying to check. It is best that y use the unplated basis metal as a zero point. Other sources error are curvature, surface roughness, edge effects and the pressure exerted on the probe.

Coatings tested by eddy current are non metallic coatings on non magnetic substrates like an anodized coating aluminum, paints and lacquers on non magnetic metals like aluminum, magnesium, and copper based alloys. Eddy current instruments are commonly used for non-conductor-conductor combinations whether the metal is copper, silver, non magneti stainless, zinc, aluminum, magnesium nickel and titanium.(14)

While the ASTM doesn't especially recommend the use of this instrument for conductive coatings on metal, various instrument manufacturers suggest that these combinations are measurable for copper, silver, electrolytic nickel, zinc, cadmium and tin on steel.

Magnetic Method (15)(16)

This method for thickness determination measures either the magnetic attraction between a magnet and the coatin -substrate combination, or the reluctance of a magnetic flux path passing through the coating and the basis metal, with reluctance being the magnetic resistance.

Nickel, which is magnetic can be measured on a magnetic or on a non-magnetic substrate. Non magnetic coating

turally, can only be measured on magnetic substrates. (15)

The effective measuring ranges of this instrument is to 50 microns (.002 in) for nickel on magnetic substances and microns (.001 in) for nickel on non magnetic substrates. Non gnetic coatings on magnetic basis metals have a decreasing nsitivity beyond a 25 microns (.001 in) as the thickness of e deposit increase.

Reluctance gages have a much more effective range r nickel on magnetic or non magnetic substrates and measurements to 1000 microns (.040 in) have been made. (15)

Magnetic thickness measurements are affected by riations in the magnetic properties of basis metals, but on v carbon steels these variations are minimal. It is always od practice to have your zero on the basis material that you e testing rather than the standards that come with the instrument. e gauge of the substrate is an important consideration and if is too thin, the results will vary, by how much, must be termined experimentally. If the sample is too thin, a sandwich the identical material can be made to offset this effect.

Measurements by magnetic testing, like the eddy current vices are affected by edge effect, this can be calibrated for; rvature, where this effect becomes more pronounced as the radius ereases, surface roughness and mechanical working of the basis terial are other considerations that affect the magnetic proper-es. Rotating the probe at angles of 90° will help in obtaining re consistant results.

Magnetic thickness instruments are affected by variations the magnetic properties of the nickel coating. Plating conditions, te composition and stress of the deposit will have an effect. s is particularly noted with multi nickel layers where each er of the nickel deposit has a different composition.

Since the pressure of the probe is especially sensitive consistant results, a spring loaded probe is a way around that blem because a constant pressure can be maintained.

Probe orientation is another consideration as somewhat fferent readings will be obtained if the probe is horizontal upside down due to the earth's gravity.

This instrument should not be used on very thin coatings ause of the limited sensitivity of the instrument. Vibration the test table will also affect the sensitivity of the instrument.

Effective coating-substrate combinations are copper, kel, chromium, autocatylitic nickel, zinc, cadmium, silver, , lead and solder on steel and Kovar. Nickel can be measured

on most substrates with varying results due to the permeabi variations of the coating. (14)

My experience with this instrument allows me this comment. The best that I can say for it is that it's non destructive and fast. We correlate the readings of this typ of instrument with other methods that we have more faith in, like beta backscatter, coulometric, and cross-sectioning and then use it as a go-nogo gage when we have to do 100% inspec

It should be noted that with multiple plates such copper and silver on steel, you read only the combination ra than a single metal.

The instrument at best is supposed to be accurate to a ± 10%.

Microscopic Measurements for Thickness

This is the one method commonly used where the thickness of deposit is read directly. Here you can actuall see the plated thickness, and to many people it is the ultim way to determine how much plating you have on. It really is but it certainly has a firm place in our arsenal of methods thickness determination. That it's a destructive way of tes there is no doubt, but I mention this only because at times been given two or three pieces to plate and the spec calls o for a microscopic cross section to determine the thickness.

For one thing, in multiple plates it may be the on good way to determine the thickness of the various combinati like nickel and gold, copper and tin, nickel and silver and forth, providing the thickness of the individual plates are enough to be read accurately. There are, however, severe limitations as far as reading minimum thicknesses accurately. Wilson (17) reported an error of almost 50% in viewing depos of one micron (.00004") thick.

The accuracy and reliability of this method are hig dependent upon the individual's technique and skill. Aside f the operator's ability there are other sources of error like calibration of the stage micrometer, the alignment and the fo of the mount. Ogburn found that the lines on a stage microme set at 2 mm. intervals can differ by as much as one to two mi (.00004"-.00008"). The hair line is another possible source error. Ogburn also suggests the use of green light for a sha image and a more precise measurement since the human eye has highest sensiticity to green. One of the greatest difficulti in using the microscope is that the operator often has greate confidence in his readings than he has a right to assume. (18

Albrecht (19) in reporting on his experiences in us microscopic cross sectioning found an average deviation of .2 microns (.000008-.00001 in) whether reading a sample of about 1.25 microns (.00005 in) or 3.75 microns (.00015). With the

rage deviation the same, no matter the thickness, the accuracy the higher levels has to be that much better.

Whereas microscopic cross-sectioning was once called as a referee method against alternative methods for thickness ting, ASTM (20) specifically states, "that this method shall be used as a referee method for coatings thinner than 8 microns 003").

Microscopic cross-sectioning should not be used for cknesses much below 2.5 microns (.0001), with 2 microns 0008 in) the limiting number for any degree of acceptable uracy, technicians skill notwithstanding.

The accuracy of cross-sectioning is put at ± 1 micron 0004 in); (20) even though Albrecht reports smaller deviations ng a higher magnification.

surement of Thickness by X-Ray Spectrometry

X-Ray spectrometry is quite similar to beta backscatter, without the big "hang-up" inherent in beta backscatter which the concern about the margin of difference in the atomic bers of the coating-substrate combination. However, on the er hand, the thickness range for beta backscatter far exceeds t of x-ray spectrometry.

X-ray spectrometry is applicable for determining the ckness of any metallic coating, with the maximum measurable ckness for a given coating being that thickness beyond which intensity of the characteristic secondary radiation is no ger sensitive to small changes in the thickness. (21) In other ds when the coating thickness is increased to a certain value, characteristic radiation of the substrate will disappear and coating will assume infinite thickness.

The x-ray emission method of measuring plating thickness based on irradiating a defined sample area with an intense mary beam from an x-ray tube placed close to the specimen. s stimulates from the plated material the emission of a series definitive secondary wave lengths characteristic of the ividual elements comprising the coating and the substrate.(22) measurement of the intensity of the characteristic secondary ays is expressed in counts per second by a suitable detector associated electronic circuitry. This intensity is a function the coating mass per unit area.

The primary x-ray beam is similar to in function to the ioactive sources used in beta backscatter, the secondary iation emanating from the specimen is akin to backscatter ticles. Both methods incidently, use similar basic equations measure the intensity ratio of x-ray quanta in one, and the ticle count rate in the other.

The exact relationship between the measured intens and the corresponding coating thickness must be established the use of standards having the same coating and subtrate compositions as the sample to be measured. This is one of t basic differences between beta backscatter and x-ray spectro Beta backscatter can be "fooled" by the use of so-called syn standards whose count rates are equivalent to certain coatin substrate combinations and are used because they are hard an have better wearing qualities than the real thing; x-rays c be fooled in this manner as each element reflects back its o characteristic wavelength.

Just as with beta backscatter, masks and platens a used, except that low carbon steel platens are the more suit material for x-ray rather than the anodized aluminum for bet backscatter. The larger the apertures, the more accurate th results because statistically one wants to count as much of the x-ray quanta particles for a more accurate determination

The atomic number however does have some bearing i x-ray spectrometry, but only so far as effective measuring thickness is concerned. The higher the atomic number, the thinner the limiting thickness determination for that metal. Put another way, you can efficiently measure thicker deposit of silver than you can of gold; thicker deposits of copper than you can of silver and so on down the list.

The low limit for x-ray spectrometric measurement is less than .1 micron (.000004 in); the maximum measurable thicknesses are in the order of 1 to 100 microns(.00004-.004 depending upon the coating system. (23)

Error can be caused by impurities in the deposit, or when the substrate atomic number is greater than that of the coating, like plating silver 47 on gold 79 or chromium 24, over nickel 28 or copper 29.

Like all other systems which measure mass per unit area, in converting to thickness, the known density of the coating is an important factor.

Weight Gain

This is a simple way to determine thickness, even though the results are only an average thickness for the piec It is considered a primary method for establishing working curves for secondary methods such as beta backscatter, X-Ray, and coulometric.

It's as simple as its name implies, providing your instruments have the proper sensitivity. A cathode is accura measured for area and weighed before and after plating. The weight gain is noted. The weight is divided by the density,

pefully the accurate density) to obtain thickness. This hod is not particularly accurate for thin deposits. The ained thickness is an average thickness and Ogburn (2) es a detailed account of how thickness standards are pared at the National Bureau of Standards.

a Backscatter

More articles have been written about beta backscatter n any other subject concerned with surface finishing during past 15 years. This is a most important tool for determining thickness of deposits, particularly that of gold in the area 1.25 microns (.00005 in) or less. A high degree of accuracy demanded not because the part won't function at 1.20 microns because the customer called out 1.25 microns and he doesn't t to be short changed.

While x-ray spectrometry may be considered the Rolls- ce in this field, beta backscatter is truly the Cadillac. one thing, it's much cheaper than x-ray, it's fairly versatile I have found that many of the difficulties encountered with s instrument are self-inflicted. We don't read the instructions y well and we ignore the manufacturer's requests to have what ould call perishable parts calibrated and checked. You may e senile radioactive sources that are approaching their half- e, a Geiger-Muller tube that has "tired blood" and is not y scintillating, worn platens, just to name a few items.

Instead of reading the instructions, many read into m what they feel the instrument should deliver and look for ranties that may be implied, but never specifically given. accuracy of the instrument can more than put you in the ball k. To use a baseball metaphor, it zeros in on home plate, ept that the ball and strike zones are more than a little zy. It's quite accurate, but for a number of reasons, not olutely accurate.

But what really is? Some people visualize a coating, matter how thin as if it were a continuous film of saran wrap uniform thickness, particularly those coatings in the order .12 to .25 microns (.000005-.00001 in). Yet x-ray spectrometry beta backscatter are the only practical means we have of suring so thin a deposit with any degree of accuracy. Because other considerations, like surface texture, which affects the a, the accuracy of standards in that range and the built in ree of uncertainty of the instruments, I question the degree accuracy of those readings. Melrose and Cooper reported that iations in backscatter radiation is greatest when the penetra- n is the least, and a thin coating is most affected by surface ish. (24)

Without going into any length discussing R.L.Meek's(25) ent argument contending that the scattering of electrons is

solely due to the interaction of beta particles with the nuc rather than the electrons in the ring, briefly, the princip of beta backscatter is the exposure of a specimen over a def area to a radioactive source. The radiation must be suffici strong enough to penetrate the coating and the substrate. A portion of this beta radiation will be backscattered from bo the coating and the substrate and be picked up by the detect a Geiger-Muller tube, which is integrated in a read-out unit during a fixed time period. The portion of the backscatter which is produced by the coating is used for the thickness measurement. The backscattering is proportional to the numb of atoms per unit area encountered by the beam. However, th number numerically of backscattered electrons does not have direct relationship to deposit thickness, but rather to the metal tested. The backscattered depth of penetration is dep ent on the energy of the particles from the source, and the density of the material to be tested.

What makes beta backscatter a little less than ide is that there must be a large enough difference between the atomic numbers of the substrate and the coating. This diffe in atomic numbers must be 20% larger than that of the substr The higher the atomic number of the substrate, the larger mu the difference be between substrate and coating. With subst of a high atomic number, say around 60, the difference in nu should be 12, (still your 20%). A substrate with an atomic of 40 requires a difference of 6 atomic numbers. (27) As th difference in atomic numbers between substrate and coating i so does the accuracy of the thickness determination.

Like the other methods which measure mass per unit the calibration standards should have a coating and substrat similar to the test specimen because the readings obtained a actually based on the readings produced by the calibration s Beta backscatter tests can never be better than the calibrat used to standardize the instrument.

The time of measurement is the only parameter whic be manipulated to hold the measurement uncertainty within gi acceptable limits, because everything else is fixed. While s times of 10 seconds may be adequate in some instances, longe up to 30 seconds are better and more consistant. Counts long 30 seconds do little to improve accuracy.

Platens are discs with carefully machined openings sharply define the test area. The sample is carefully placed the platen, making sure that it's not cocked, and at the same covering the opening 100% to prevent leakage of beta particle Increasing the atomic number of the platen decreases the accu of the test, thus anodized aluminum makes for a very good pla while stainless steel, steel and titanium are not. Jeweled p

ve been reported to have been used with excellent results and ey are quite expensive.(26) The largest aperture commensurate th the size and the shape of the part is what should be used. e more exposure of the sample area to the beta rays, the more urate the test.

Each radioactive source has a "best" range for a coating ckness of a particular metal. The higher the atomic number of e metal, the lower the penetrating power of the source.

A weak beta energy source like promethium 147 has an er limit of 2 microns for gold, 3 microns for silver, and microns for copper and nickel. Thallium 204, a much "hotter" rce has a much higher high limit and correspondingly a much her low limit as well. Promethium 147 can be used for checking of a micron (.000004 in) of gold on nickel, while thallium's limit is about 2 microns (.00008 in) for the same combination.(28)

In presenting papers, many people make a great effort explain the theory of how and why an instrument operates and the process overlook some practical idea that could be a stant source of difficulty. We have found, and Cooley (29) firmed that an adequate line voltage is important for the trument. A constant voltage transformer should be used ause the efficiency of the beta backscatter instrument is ited below 100 volts, A.C.

In a recent paper, Neve (30) and associates showed t differences can occur on the same instrument. This was omplished by checking the same specimen on the same instrument a one week interval. They found that there were fixturing ferences, misalignment and that loosely seated parts showed kage to radiation with a subsequently reduced count rate and underestimation of the gold thickness. This was all attributed human error rather than instrument failure. There are many ngs that can go wrong with an instrument. Human error only ravates the situation, and it becomes all the more confusing n the ultimate of all human error, infallibility in one's ability, and that is to blame the machine -- and it can't k back, it just keeps on spitting out wrong answers.

All these machines of ingenious and sophisticated trumentation that now spew out data like the tape at a super- ket check out counter should be an answer to our quality control blems -- but is it, really?

Is thickness of plate truly the sole criteria for ting quality? Should it really be? I don't think so.

The most important feature about coating thickness is t it gives us a number to shoot for, yet, this number by no

means tells us all we should know about the function of the coating.

I would presume that the desirability for suitable properties came first and then came the thickness specifica in the expectation that a specified thickness would lead to attainment of one or a combination of those properties. (Th are times though when I think that the thickness numbers ca first and the properties expected only an afterthought.)

Baker and Palumbo(31) made that point in suggestin end point requirements on various physical and chemical pro of the deposits. While the condition of the substrate gene governs the appearance of the deposit, plating conditions h an important bearing on it, too. Is the plating burnt? Is grainy or does it have a color, uncharacteristic of the pla it's supposed to be.

The chemical composition of the coating affects th functioning of the part as far as hardness, **porosity** and re ivity to name a few physical properties. Thickness alone wo tell us anything about the presence of codeposited impuritie like iron in gold. Iron induces porosity and brittleness, a other metallic impurities will effect the solderability of t plate and also its bonding characteristics.

What I am suggesting is that considering the measur ment uncertainty of our thickness measuring devices (and the have them) and while we may be able to compensate somewhat f plate distribution as shown in a bell curve, I feel that it asking a little too much to have you guess in which directio of the plus or minus side of the instrument's accuracy, the answers may fall on a given day.

I'm suggesting that there should not be any argumen whether the plating thickness is 1.25 microns (.00005 in) or 1.20 microns (.000048), 0.75 microns (.00003 in) or 0.71 mic (.000028 in), as long as the bath is of a certified recommen purity and hardness, commensurate with what it should be to insure the soundness of the deposit, and be able to perform functions expected of it.

REFERENCES

Boris B. Joffe - Measurement of Coating Thickness by Beta Backscatter - Facts and Fallacies
1st A.E.S. Symposium on Thickness Testing - Feb.28 - Mar. 1st, 1978

F.Ogburn - Preparation of Calibration Standards for Coating Thickness Instruments
1st A.E.S. Symposium on Thickness Testing - Feb.28 - Mar.1st,1978

S.Lieber - Beta-Backscatter Thickness Testing of Gold
Metal Finishing - Vol.73 #12 - 1975

R.Duva and D.G.Foulke - Properties of Some Gold Electrodeposits
PLATING Vol.55 #10 1968

G.B.Munier - Polymer Codeposited with Gold During Electroplating
PLATING Vol.56 #10 1969

M. Antler - Structuring of Polymer Codeposited in Gold Electroplates
PLATING Vol.60 #5 1973

L.Holt, R.J.Ellis and J. Stanyer - Carbon Inclusions in Gold Electroplates
PLATING Vol.60 #9 1973

R.L.Cooley and K.E.Lemons - Densities of Electroplated Gold
PLATING Vol.56 #5 1969

F.Ogburn - Density of Electrodeposited Metal, ITS SIGNIFICANCE and MEASUREMENT
Chemistry and Physics of Aqueous Gas Solutions
Electrochemical Society, 1975

ASTM - 504-70 - Coulometric Method for Thickness Testing

ASTM - 555-75 - Electrodeposited Metallic Coatings Thickness by the Dropping Test

J.J.Weinstock - Eddy Current, Magnetic Properties and Impedance Measurements Techniques
1st A.E.S. Symposium on Thickness Testing, Feb.28 - Mar.1st, 1978

REFERENCES

13. ASTM - B529-70 - Measurements of Coating Thickne: The Eddy Current Test Method

14. - Unpublished draft of 11/17/75 A: on guide to Method of Measureme: of Thickness of Electrodeposite and related Coatings.

15. ASTM -B530-75 - Measurement of Coating Thickness by the Magnetic Method: Electrodeposited Nickel Coatings on Magnetic and Non-magnetic Su

16. ASTM - B499-75 - Measurement of Coating Thickness by the Magnetic Method; Non Magn Coatings on Magnetic Basic Meta

17. G.A.Wilson - Thickness and Hardness Measurem on Gold Deposits Metal Finishing Vol.58 #6 - 196

18. F. Ogburn - Microscopical Measurement of Th PLATING Vol.59 #12 - 1972

19. W.M. Albrecht - Measuring Thickness of Thin Ele plates 1st A.E.S. Symposium on Thickne: Surface Coatings -Feb.28 -Mar.1:

20. ASTM - B487-75 - Measurement of Thickness by Mic scopial Cross-Section

21. ASTM - B568-72 - Measurement of Thickness by X-R Spectrometry

22. H.A. Heller - Analytical Control in Electropl Technology PLATING Vol.56 #3, 1969

23. F.Ogburn and Smit - Fluorescent X-Ray Methods for Measurement of Coating Thickness PLATING Vol.60 #2 - 1973

24. S.P.G. Melrose and B.S.Cooper - Transactions of the Institute o Metal Finishing Vol. 45, Winter 1967

25. R.L. Meek - Plating Thickness Measurements Beta Backscatter Plating & Surface Finishing Vol #6 - 1975

REFERENCES

Joffe & Miller - Measurement of Coat Thickness on Cylindrical or Spherical Specimen by Beta Backscatter PLATING Vol.62 #6, 1975

A. Ott - What is the Precision of a Coating Thickness Made by Beta Backscatter PLATING Vol.63 #11, 1976

ASTM - 567-72 - Measurement of Coating Thickness by Beta Backscatter Principle

R.L.Cooley - Measuring Gold Thickness PLATING Vol.57 #2, 1970

Neve, Hecox, Mathew & Meek - Plating Thickness Measurement by Beta Backscatter Metal Finishing Vol.76, Nov. 1978

Baker and Palumbo - The Case for End-Point Requirements in Gold Plating Specs for Electronic Equipment PLATING Vol.58 #8 1971

G-5

Electronics II
Session G

A New Approach for Plating Copper, Nickel and Gold Conductors On Thin Film Integrated Circuits

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Paper not available at time of printing of proceedings.

H-1

Electroforming II
Session H

Processing Aids for Nickel Electroforms

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PROCESSING AIDS FOR NICKEL ELECTROFORMS

NTRODUCTION

potential exists for the use of electroforming in the production of commercial ets both for airplane parts and for production tooling. Development work has een initiated to use nickel electroforming for some of these applications on n item by item basis as the specific needs become apparent.

owever, requirements for structurally sound functional parts and high integrity ooling has placed unusual demands on the electroformer which have necessitated ne development of improved plating aids for both the laboratory and the roduction platers.

ISCUSSION

igure #1 - Gravel Guard

igures 1, 2 and 3 are typical electroforming applications.

igure 1 is a leading edge protector for a fiberglass part which is exposed o gravel abrasion during take offs and landings. It is a narrow part, deeply hanneled in cross section with a complex curvature. The process development or electroforming this part was somewhat unique in that the resultant fixtur- ng incorporated electrodepositing to net trim with a number of precision ilot holes included. A 25-to-1 cost savings ratio was achieved over onventional fabrication methods.

igure #2 - Metal Air Duct Fitting

igure 2 illustrates two advantages achievable by electroforming. Transition f metal ducting from an oblong to a rectangular shape while turning through n angle can be a difficult forming problem for conventional means. Electro- orming over a removable mandrel provides a simple means of achieving this ransition. Use of the well-known grow -in technique provides for attachment f the pre-fabricated baffle plates which can be seen inside the duct.

igure #3 - Rotomold Tool for Elbow Duct

igure #3 illustrates a tooling application for electroforming. The tool is two-piece mold used for fabrication of plastic air ducts by the rotational olding process. Tooling for the characteristic hollow cylinder shape offers challenge to electroformers. The challenge lies in incorporating the flange

into each half of the mold so as to have adequate corner strength and dimensional compliance. In this particular mold a steel flange has been brazed to the electroformed nickel.

Figure #4 - Pitted Nickel

Metallurgically speaking, early efforts in nickel electroforming revealed unpleasant surprises in the quality of the metal being deposited from a ba which was apparently well within the recommended operating limits. (Figur Extremely small quantities of contaminants produced unacceptable residual stresses in the deposit as well as inducing pitting and low ductility. Frequently these contaminants are organic materials too low in concentrati to be identified or quantified. Residual stress analysis proved to be the satisfactory procedure to forecast successful electroforming results.

Figure #5 - Stress Instrumentation

To that end the instrumental system illustrated in Figure #5 was designed, built, and patented. Considerable data has been accumulated to verify its reproducibility and ease of operation. Repetitive measurements are within $\pm$ 3%, the helix need not be removed for the life of the metal, individual analysis can be conducted as frequently as every half hour if necessary, a tank operators or online technicians can perform the analyses with a minim of training. The instrument has proven invaluable in predicting successfu electroforming on a deposit mandrel costing thousands of dollars.

Figure #6 - Developmental Plating Equipment

Non-uniform thickness of deposits on simple shapes, as well as complex cor is undesirable in many applications. Rotomold dies are an example of the for uniform wall thickness to assure thermal uniformity. The additions of "robbers" and "shadows" to plating fixtures are helpful techniques for con-trolling thickness. Neither one of these techniques however, lend themsel to quantitative calculations. The illustrated laboratory set up was built gain better insight into positioning of these thickness control aids, part larly shadows. Precision instrumentation such as thermistor temperature controllers, flowmeters and filtering mechanism backed up with particle co allowed extrapolation of test data from 20 liter volumes to multi-thousand liter production tanks. Much technical data other than shadow effects hav been collected from this equipment.

ge #7 - Current Density Meter

ow positioning, however, was still mostly trial and error using this pment. Follow-on efforts have produced a current density meter which is iding very good relationships between meter reading and deposited knesses. Probes of varying lengths and sizes to suit the shapes can be and the readings can be taken on the production part when desired.

re #8 - Current Density Meter in Laboratory Use

lternate procedure of immersing the shadowed deposit mandrel in a con- ive salt solution has proven to be a useful technique. In the laboratory up illustrated in Figure 8, an epoxy mandrel with a silver conductive ing is immersed in a sodium chloride solution.

re #9 - Electroforming with Trees - High Ripple

y electroformer has been dismayed to pull his best effort from his tank to discover "trees" growing outward from several areas on the part. al precautions as to fixturing, current density control, and bath cleanli- sometimes are not sufficient to control these trees.

ier work with effects of ripple on chrome plating led us to investigate DC power supply as a source of poor deposits in nickel. When all operating itions of time, temperature, concentrations and agitation are held constant, ormly cylindrical shapes illustrate the effects of power supply ripple hrome plating quite dramatically. The high ripple power supply restricts chromium plater to a very narrow range of current density in order to luce an acceptable deposit.

re #10 - Bad Chrome Plate with High Ripple

re #11 - Good Chrome with Low Ripple

arison of Figure #10 with Figure #11 shows much improved deposits and a ader range of operating conditions when ripple is reduced. Production e has been doubled in those cases where ripple filters have been added to DC power supplies.

re #12 - Electroforming Without Trace - Low Ripple

re #12 illustrates a laboratory demonstration of the possible improve- ts to nickel deposits by reduction of power supply ripple.

CONCLUSIONS

Improvements in the quality of electroformed parts can be achieved by relatively low expenditures in equipment and instrumentation. The marke potential for high quality structurally sound electro-deposited metals justifies continuing effort for improvements by the electroforming trade It is hoped that these illustrations will encourage that effort.

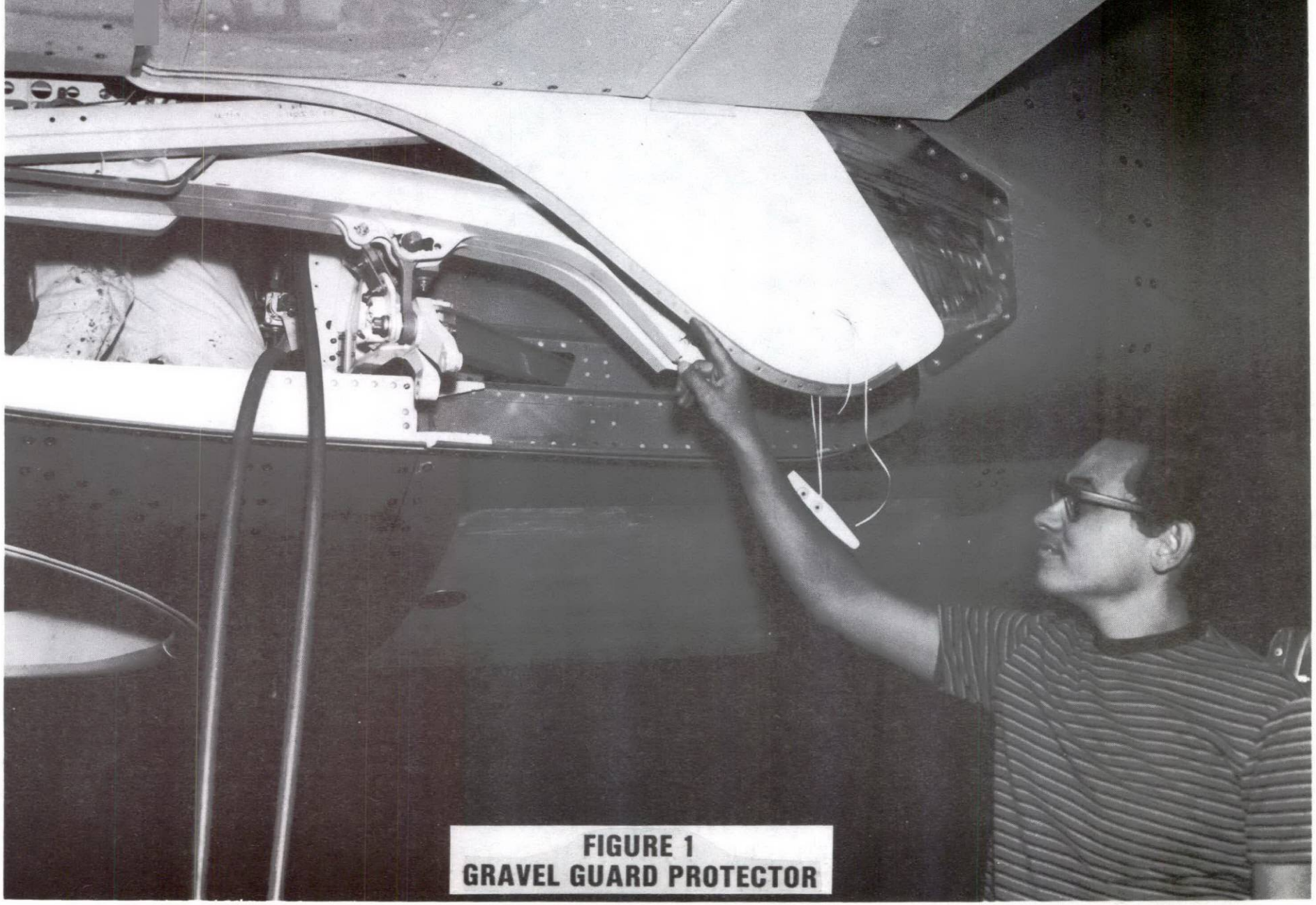


FIGURE 1
GRAVEL GUARD PROTECTOR

737 GRAVEL RUNWAY PROTECTION.
10-6-73
Jax 20711



FIGURE 2
METLAL AIR DUCT FITTING



ROTO-MOLD DIE
45114868
11-7-74

FIGURE 3
ROTOMOLD TOOL FOR ELBOW DUCT

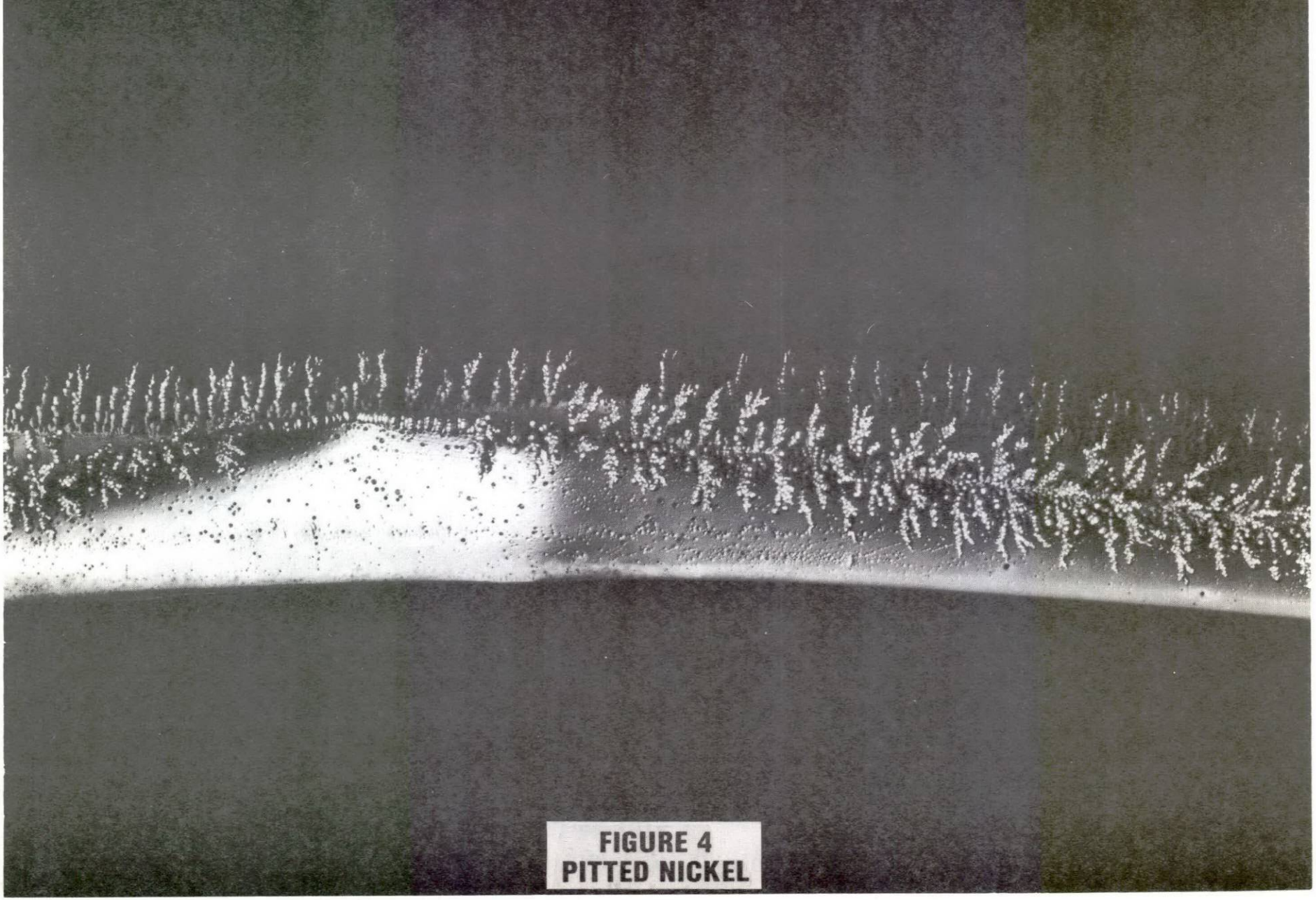


FIGURE 4
PITTED NICKEL

ELECTRONIC BATH IMBALANCE 3 SB03240
2-27-75

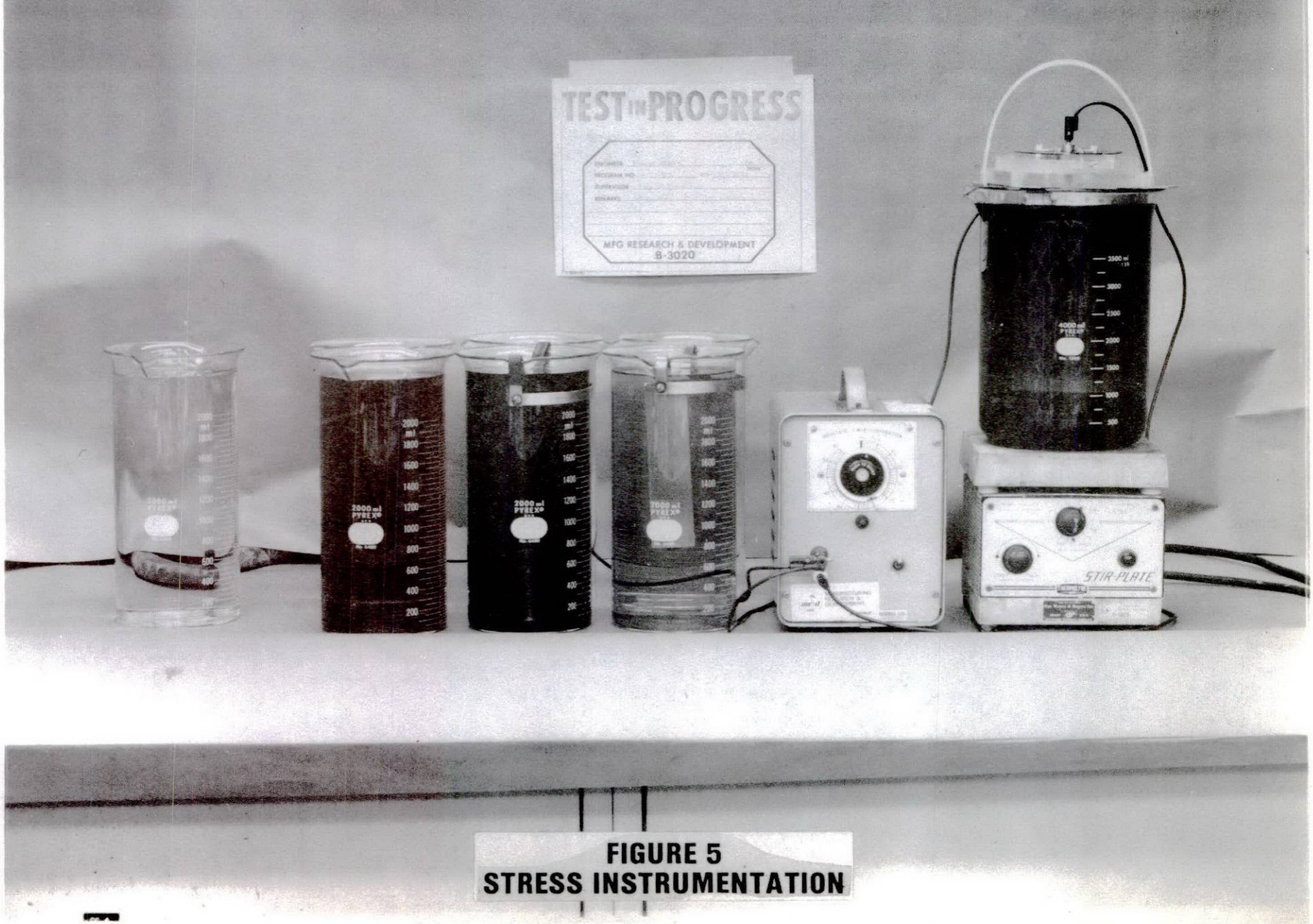


FIGURE 5
STRESS INSTRUMENTATION

FIGURE FIRE-PROPOSING 2-6-76 04435

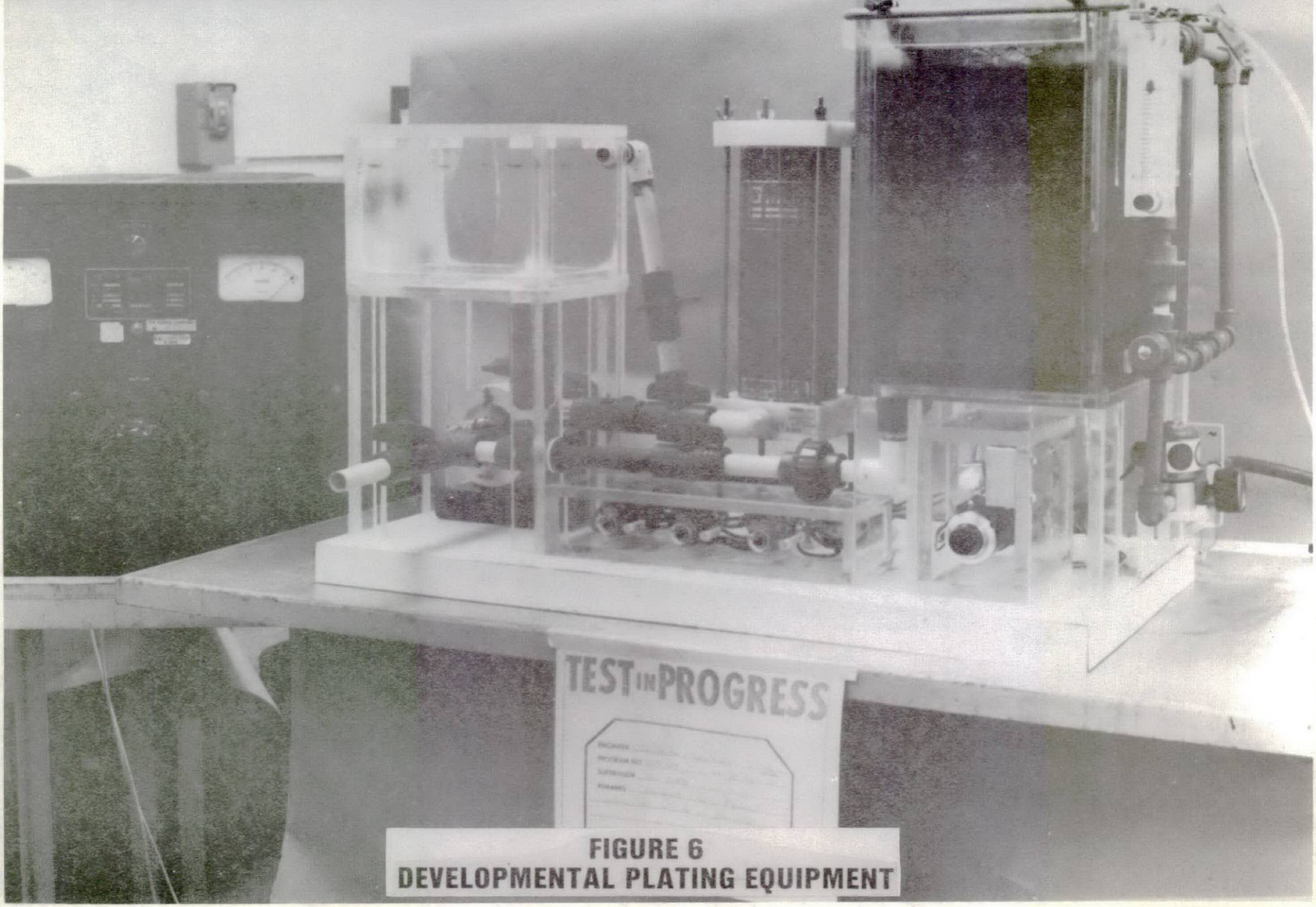


FIGURE 6
DEVELOPMENTAL PLATING EQUIPMENT

DEVELOPMENTAL PLATING EQUIP.
7-11-75
SSK 12553

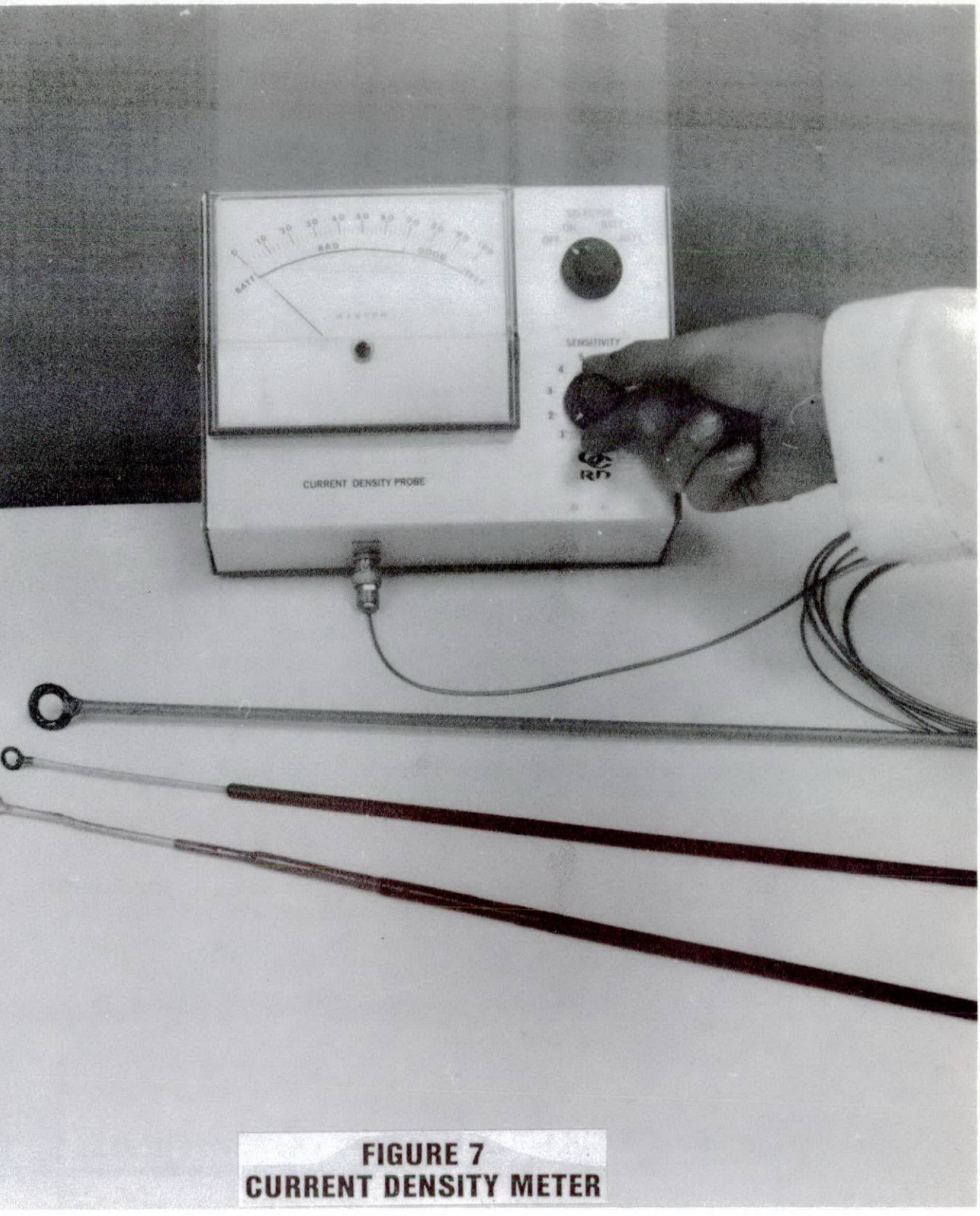


FIGURE 7
CURRENT DENSITY METER



FIGURE 8
CURRENT DENSITY METER IN LABORATORY USE

CURRENT DENSITY PROBE TEST
1-20-78

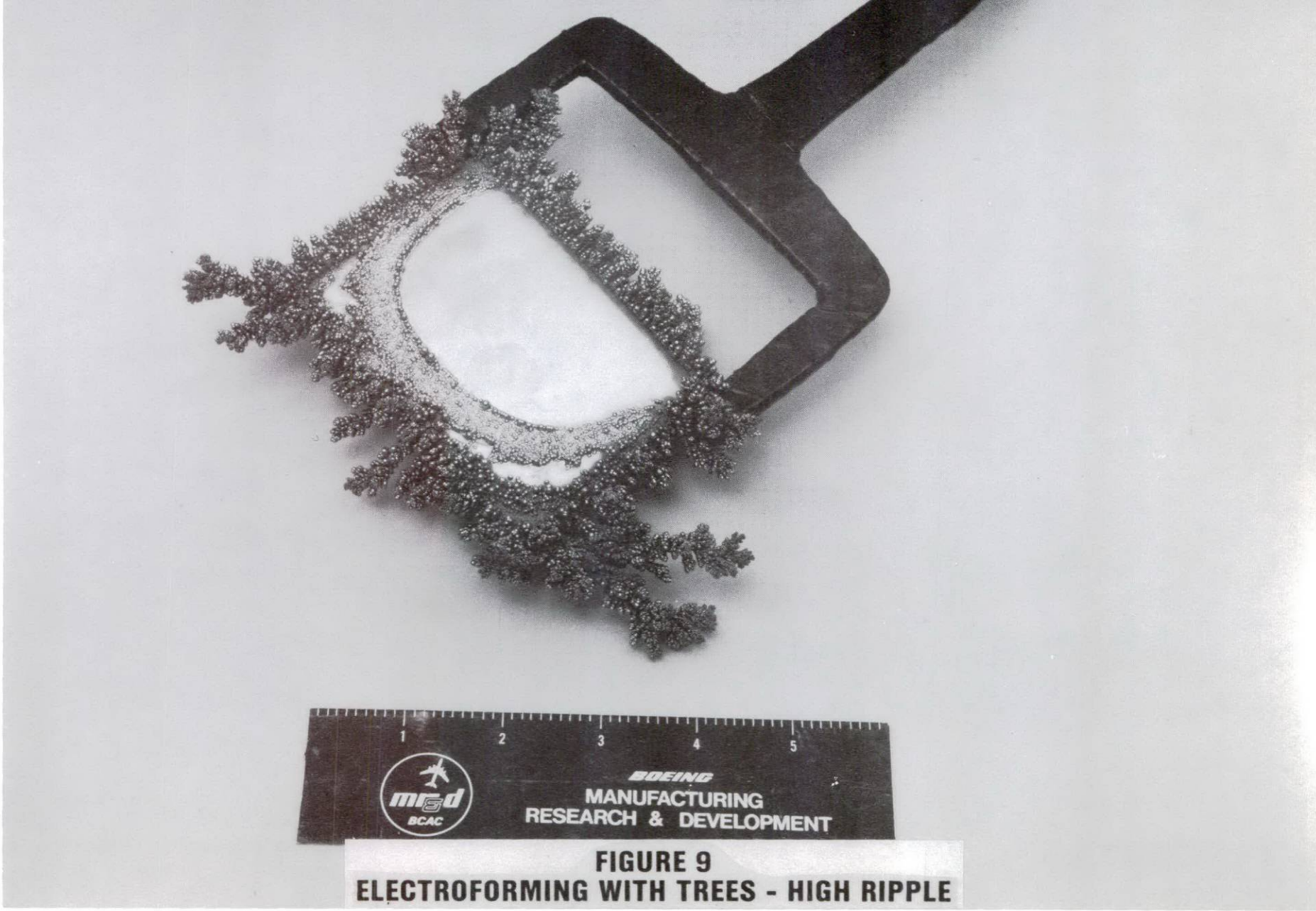
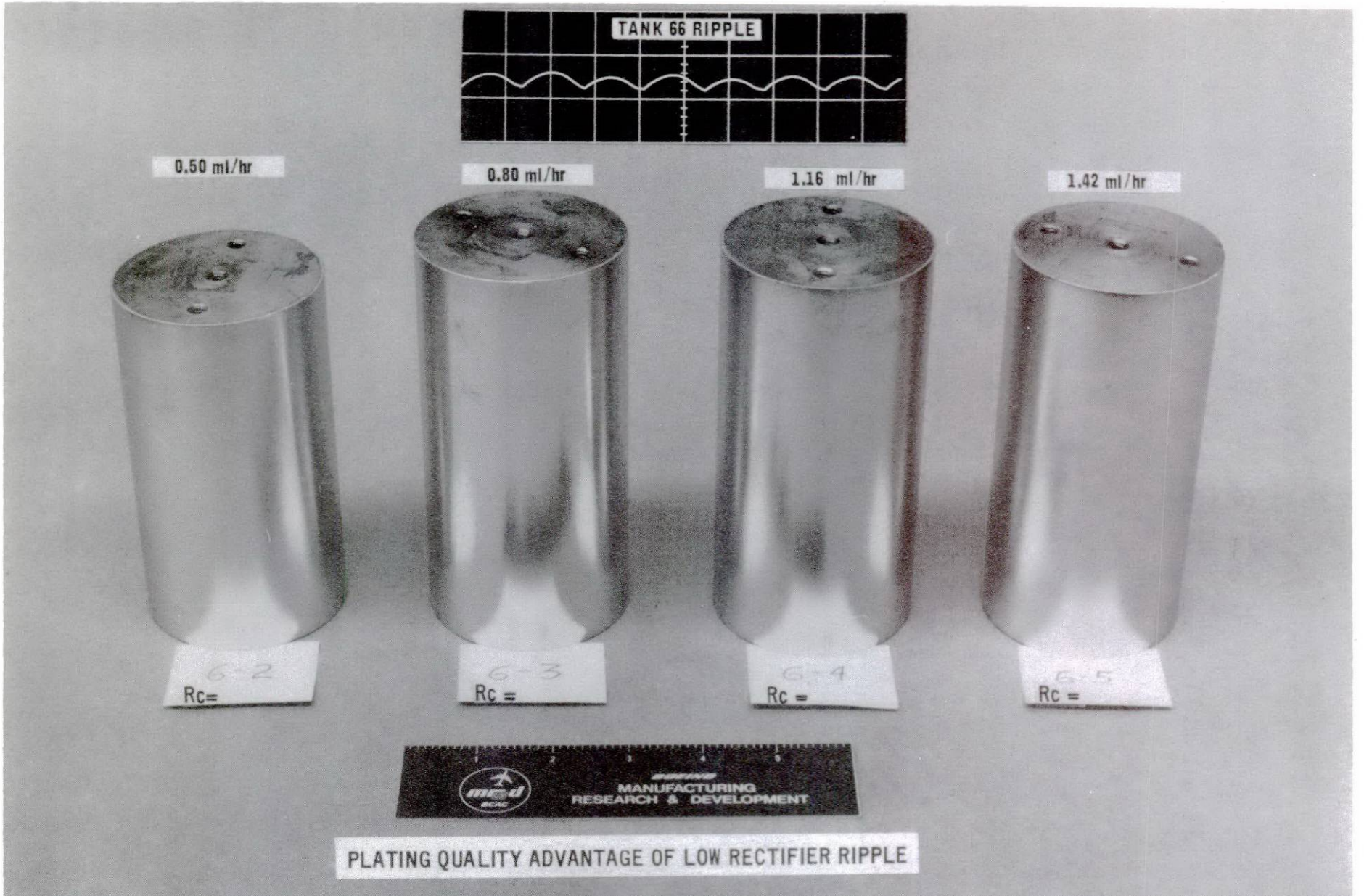


FIGURE 9
ELECTROFORMING WITH TREES - HIGH RIPPLE

BOEING 10-31-78
SBK 09321



FIGURE 10
BAD CHROME PLATE WITH HIGH RIPPLE



PLATING QUALITY ADVANTAGE OF LOW RECTIFIER RIPPLE

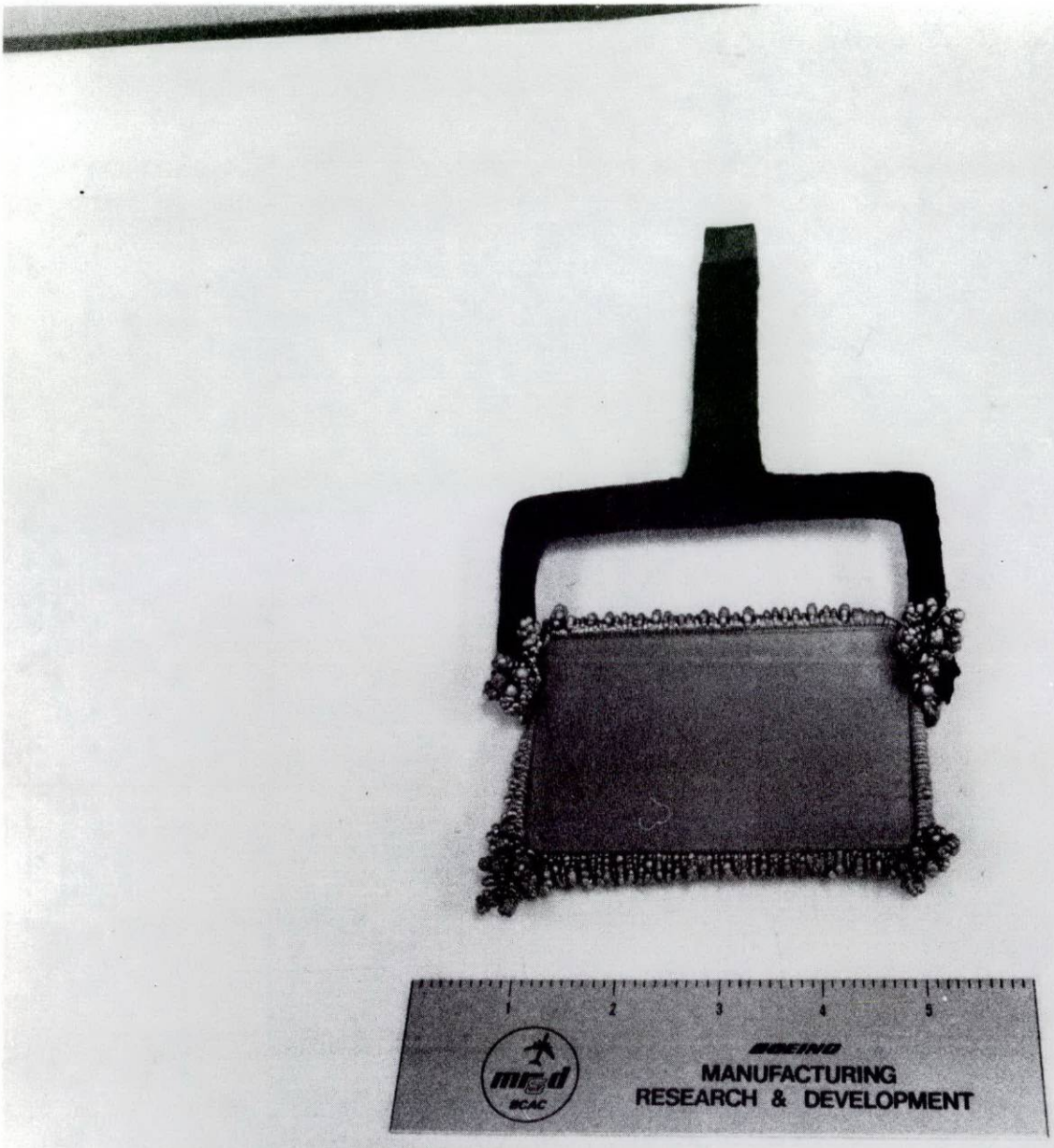


FIGURE 12
ELECTROFORMING WITHOUT TREES - LOW RIPPLE

H-2

Electroforming II
Session H

Electroforming a Mold For Casting Plastic Fresnel Lenses

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r hearing all of these rousing success stories and descriptions of
ant techniques and brillant solutions to problems, I feel a little
ed, being here to tell you a nonsuccess story.

egin at the beginning, at the Sandia Corporation's Albuquerque Laboratory
e is a program aimed at harnessing solar energy. Now, it is common
edge that solar energy collected with a simple, flat plate is of low
ty, as an engineer would say. To be of high quality, capable of being
iently converted into other forms of energy, mechanical or electrical,
must be at a high temperature (quality and temperature being, for all
ical purposes, synonomous). To raise the temperature of collected
ine one must concentrate it, and this means focusing either with mirrors
th lenses. At Sandia Albuquerque, one focusing device being developed
e Fresnel lens.

just a word about lenses and the rationale behind the Fresnel lens. An
ary focusing lens has either one or two spherical surfaces, and if the
is very large it must be quite thick. It had occurred to the Comte de
n in 1748[1] that a lens could be greatly reduced in weight by dividing
ontinuous lens surface into a succession of concentric rings (Figure 1).
20, A. J. Fresnel, developer of the wave theory of light, used this
iple to build lenses for lighthouse beacons. Until that time, mirrors
een used for this purpose. Such lenses are used for many purposes today
ll of you have likely seen Fresnel lenses of considerable size that are
actured for the hobby trade.

ill note that a Fresnel lens of a few steps, as might be used for a
house lense, is still quite a thick structure. To get the very thin
el lenses of substantial area it is necessary to have many shallow
(Figure 2). Fabrication of such a device is obviously a difficult
r. However, if a mold can be made, there is the possibility of
cating it many times in a clear, acrylic, plastic material.

he problem is, how to fabricate a mold on which to cast the plastic
s? One approach is to fabricate, in metal, a positive which is just

like the desired lens and then to electroform a negative off this mand from which lenses can be cast. The thing that got us, that is, the Oa Ridge Y-12 Plant (a) into the picture is the capability of the Plant diamond turn metals to a mirror surface. Diamond turning is a machini technique in which the tool bit is a single-crystal diamond honed to a incredibly sharp and precise edge. A capability for using this techni was developed in the Y-12 Plant several years ago. This is in keeping the Plant's mission to stay current with, or be the cutting edge of, t state-of-the-art in metal fabricating techniques. This is to meet the increasingly critical tolerance demands in fabricating metal piece par for Department of Energy work (Figure 3). A spin-off of this technolo has been the fabrication of metal mirrors for the Air Force and for th Los Alamos Scientific Laboratory's laser induced fusion work. By this technique, metal mirrors have been fabricated which experts have decla to be, in the as-machined state, the equivalent of any metal mirror th have ever seen, fabricated by whatever method. Equivalent here refers reflectivity and to resistance to damage by high-energy laser beams.

Well, word gets around and the people of Sandia Albuquerque came to th Y-12 Plant for help in fabricating a mold for casting Fresnel lenses. was finally established that, yes, it should be possible to machine th positive by diamond turning. And, yes, we have an electroforming capability so we can make you a nickel, casting mold. Then, we were a "What would you like for a mandrel material?". We knew that diamond t has one very definite limitation -- there are only certain metals whic be cut successfully. There is copper, gold, silver, and aluminum, and just about completes the list. We knew that in some applications copp used for an electroforming mandrel and is given a passivating treatmen makes it possible to release the electroform, but we were not familia

(a) Operated for the Department of Energy by Union Carbide Corporation-Nuclear Division under Contract W-7405 eng 26

technique and had our doubts that any surface treatment could be used
out degrading the surface finish. So, we said, "Make it out of
inum". Now, we had done a good deal of electroforming on aluminum and
eved that we should not have any problem in electroforming, but we did
some reservations about how the electroform should be parted from the
rel.

reparation for machining the 28-inch-diameter, real part (Figure 4), the
ine shop fabricated a test piece approximately 6-inches in diameter. This
rel was available for making a test electroform, which we did in the
lopment Laboratory, using tooling and fixturing of the type we planned
se on the real part. We had considered all along that we would not be
to prepare the diamond-turned surface for plating by any method which
ired contact with a solid material, even cotton gauze would scratch the
r-finished aluminum surface. So we rinsed the surface with solvent,
owed that with a water solution of a wetting agent, and went into the
ing bath with current on. We plated at a current density of 25 asf, for
t 100 hours. To part the electroform from the mandrel, we simply set it
o the electroform was supported at three points and struck one sharp blow
he center with a rubber hammer. The mandrel dropped off cleanly.

mandrel did not have the high reflectivity after electroforming that it
had before, and the mandrel side of the electroform was surprisingly
. As the time approached to electroform the full-scale part, we got
serious about the matter of precisely how we would prepare the mandrel
plating. Some work on cleaning mirror surfaces, done by Charlene
rds of our Plastics and Adhesives Development Group, had shown that a
icular brand of trichloroethane is a good solvent which does not degrade
er surfaces, so we chose that for degreasing. We knew we did not want
se an ordinary detergent because they are generally high pH solutions
likely to be corrosive toward aluminum. We concocted a solution of a
t chain, non-ionic surfactant to promote wetting, and a long chain,
ionic surfactant to emulsify oily residues. We found that when these
rials were used in sequence, i.e. the organic solvent followed by the
ing solution, on a small diamond-turned aluminum specimen, that the

surface was wet very well by the surfactant solution; but, when the surface was rinsed with demineralized water, a water break occurred promptly when the flow of water stopped. If we plated a specimen clean in this manner in a nickel sulfamate bath, going in with current on, we observed a considerable amount of gassing at the cathode, and the nicke covered the aluminum surface completely only after several minutes. If the specimen was plated until the nickel was fairly thick, when the nickel electroform was removed the aluminum was found to be corroded ov a considerable area, and the nickel was not mirror-like in the area whe the aluminum was corroded. We tried starting at high-current density a at low current density, and going into the bath without rinsing, i.e. the surface wet with the surfactant solution, and almost every time fou aluminum mandrel corroded and the nickel surface of poor quality. We c cluded that the diamond turning must put a thin, stable oxide film on t aluminum surface which is then so passive that in some areas it will no plate until corrosion by the plating solution has removed the film. Th is some reason to believe that diamond turning may generate an oxide fi of appreciable thickness because diamond-turned copper surfaces remain bright and highly reflective for years, in an ordinary air environment, before any color change is observed. As we wondered what to do about t situation, Harold Patterson of the Y-12 Plant production job shop sugge treating the aluminum with 17.5 wt. % nitric acid solution, as is commo done in preparation of aluminum for zincating and electroplating. It h not occurred to any of the rest of us that this treatment could possibl be used without damage to the surface finish. When a diamond-turned su was solvent degreased with trichloroethane, rinsed with an aqueous surf solution, and then dipped for only 30 seconds in the nitric acid soluti a good water break test was obtained on rinsing and a good nickel plate obtained. The nickel covered promptly, and when the electroform was re there was no evidence of corrosion of the aluminum surface. Both the aluminum and the nickel were bright and highly reflective.

Of course, "highly reflective" is not a very meaningful term. We took small diamond-turned aluminum mirror ("small" is used here for a standa size, which is 1.52 inches in diameter) and cleaned it, then pickled ju half of it in the nitric acid for 30 seconds. We then had it examined

optical testing group using an interference microscope to compare the led and not-pickled areas. They concluded that there was no discernible erence. The entire surface of this specimen was then pickled, and when ed, gave a good water break test. The specimen was then nickel plated. diamond-turned surface covered promptly, and when the electroform was ved, both the aluminum and nickel surfaces were found to be in good ition. So we added a nitric acid pickle to our procedure and it looked thing like this: (Table I)

e went through this procedure on the real mandrel, everything seemed to oing along O.K. until we were drying the part. At this point, I looked fully at the flat diamond-turned area outside the Fresnel rings and ead of having a bright specular look, it appeared sort of dull and life- . The thought went through me like an icy projectile, "My God, we've ed the thing!". Maybe we had, I still don't know because no lenses have cast from the electroform as yet, but there was nothing to do but go d. The diamond turning of the part had been a once in a lifetime pro- tion. There would neither be time available on the super precision ines, nor money to pay for it, to do the job over again -- not for years ay. The air we were using was instrument air, which should have been n and dry, with a final filter just after the pressure regulator.

ything else went pretty well that first day. We got the back plate bolted taped off the sides, attached the annular shield and the picture-frame ld, and applied the RTV caulking (Figure 5). The reason for caulking the plate was to assure that solution would not leak under the plate and, in very long time that the part would be in the plating bath, cause severe osion of the back side of the aluminum mandrel. The caulking on the back of the annular shield prevents nickel plate from growing under the shield forming large trees on the back side.

aration of the part for plating was made on a Friday afternoon. Monday ing the plating bath was made ready for operation and the part was given final preparation. From the very first, it had been noticed that there a small area, a few square inches, on the grooves which was contaminated ome way. Repeated applications of solvent and surfactant solution with a

cotton gauze had failed to remove this contamination and it still would wet, not even with the surfactant solution. It was decided to treat the mandrel for one minute with the nitric acid solution. The face of the p was rinsed with the surfactant solution, followed by a demineralized wat rinse, and then it went into the nitric acid tank. This was a new, clea nitric acid solution. We waited with baited breath and watched fearfull any sign of bubbles. We did not see a single bubble. The part was remo from the acid, rinsed and transported immediately to the plating tank. part was lowered into the plating bath with current on and the current w set at 10 asf. After plating for four hours, the current was raised to and after 24 hours, to 20 asf. We wanted at least 60 mils of plate; we have felt better about 80; and we actually let the part plate approximat 100 hours, just to give us a little fat. As always, after a long platin operation like that, we wondered a bit about what we would have. Here i picture of the plated side of the electroform (Figure 6). You can see t the masking and shielding controlled the plate quite well; there is just little incipient treeing at the bottom as the part hung in the plating b looking at the deep tank.

The final act in an electroforming scenario is generally parting the ele form from the mandrel. Now, in this particular case, the electroform wa be backed up by a half-inch thick steel plate, adhesively bonded to the surface. We planned to use this plate to push the electroform off the m (Figure 7). We believed that parting could prove a problem at a tempera higher than the temperature at which the electroforming was done because the aluminum would expand and lock on the electroform around the outer e Also, if the temperature were lower than the plating temperature, we exp that the electroform would lock onto the almost vertical sides of the gr which in aggregate, amounts to a substantial area. So we removed the ma with its electroform, to an area where the air temperature was about the as the temperature of the plating bath, allowed the system to equilibrat overnight, and started to push off the electroform. Each screw was turn in sequence -- 1/4 turn at a time. After a round or two, there was a "p sound. But, unfortunately, it was not the electroform parting from the it was the steel plate parting from the epoxy adhesive. Now this left u no way to push off the electroform except around the edge. There was an wide, practically flat flange where the electroform had built up against

lar shield. We had a push-off ring fabricated and prepared to push off electroform with this device. Because we expected the electroform to and bind in the center if pushed off in this manner, we first thermally ed the assembly to 120° F (49° C) in a large, walk-in oven. After ing overnight, the assembly was allowed to cool to room temperature. the screws were tightened, the electroform came off with very little rt.

appearance of the mandrel and of the electroform was not an inspiring t. In spite of our precautions, plating solution had obviously gotten r the electroform and caused considerable corrosion of the mandrel, ure 8) and staining of the nickel (Figure 9). This must have occurred ome time after the electroform had an appreciable thickness. If this rue, the electroform must have cupped slightly due to residual tensile ss. We had provided a generous radius at the edge of the part to fen the electroform in an effort to avoid this problem. Another thing ight have done would have been to add to the plating bath enough saccharin, ome other such agent, to have reduced the stress to close to zero.

good was the electroform? We really don't know. The proof of the pudding n how good a lens can be cast from it. To date, none have been cast. factors that will affect the fitness of the electroform for its intended are flatness and finish. We don't know just how flat the electroform is ts present, unsupported state, and we know of no way of putting it in a condition for bonding on another back-up plate. The part does not exhibit ular reflection which leads us to believe that the surface will prove to ather poor and that lenses made from it will scatter a good percentage of incident light.

e had it to do over again, there are a few things we would do differently. ould not use the surfactant or any aqueous solution in precleaning the rel. This would also eliminate the compressed air drying. At the time the part is given its final preparation, just before plating, it would lushed with surfactant solution, rinsed, and nitric acid pickled. We d adjust the stress in the bath to close to zero. Even now, I am not

sure how we should go about parting the electroform from the mandrel. W believe that using the back-up plate to push off the electroform is a viable technique. But some testing of the adhesive system and the metho of surface preparation should be done to assure that the bond will hold.

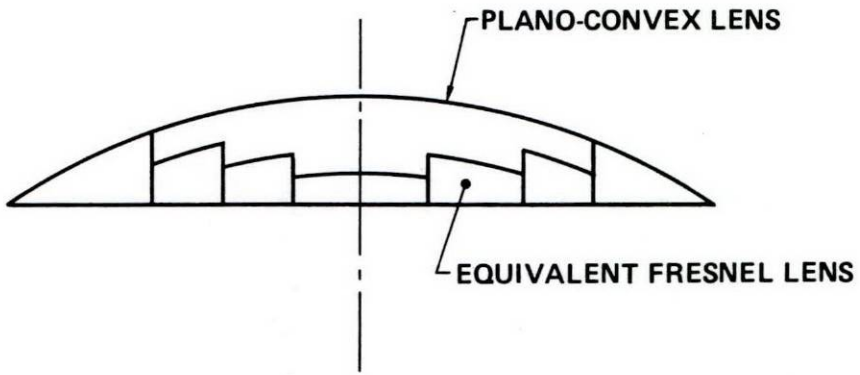
REFERENCE

1. Encyclopedia Britanica; Volume 13, p. 953;
Encyclopedia Britanica, Incorporated, 1967

TABLE I

1. Hang the part in a vertical position from the shop crane.
2. Solvent degrease.
3. Rinse with surfactant solution.
4. Water rinse.
5. Dry with compressed air.
6. Tape sides.
7. Attach and caulk the backing plate.
8. Place and caulk side shield.
9. Attach shadow ring shield.
10. Rinse with surfactant solution.
11. Water rinse.
12. Nitric acid pickle.
13. Water rinse.
14. Go into sulphamate nickel plating bath with current on.

PRINCIPLE OF THE FRESNEL LENS



THIN FRESNEL LENS

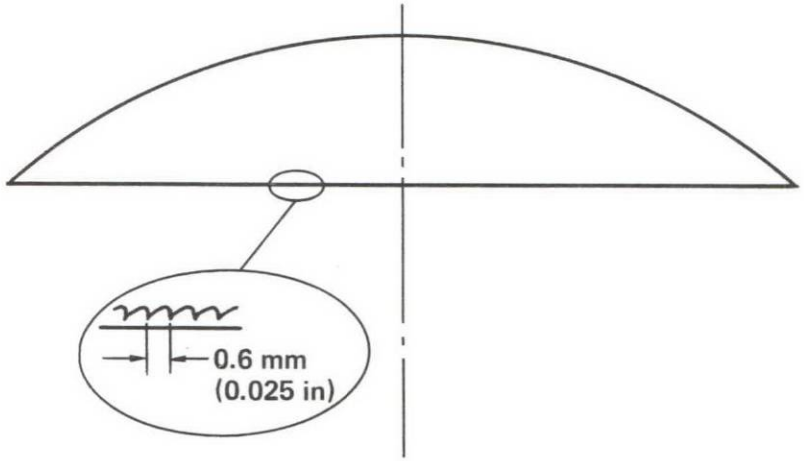
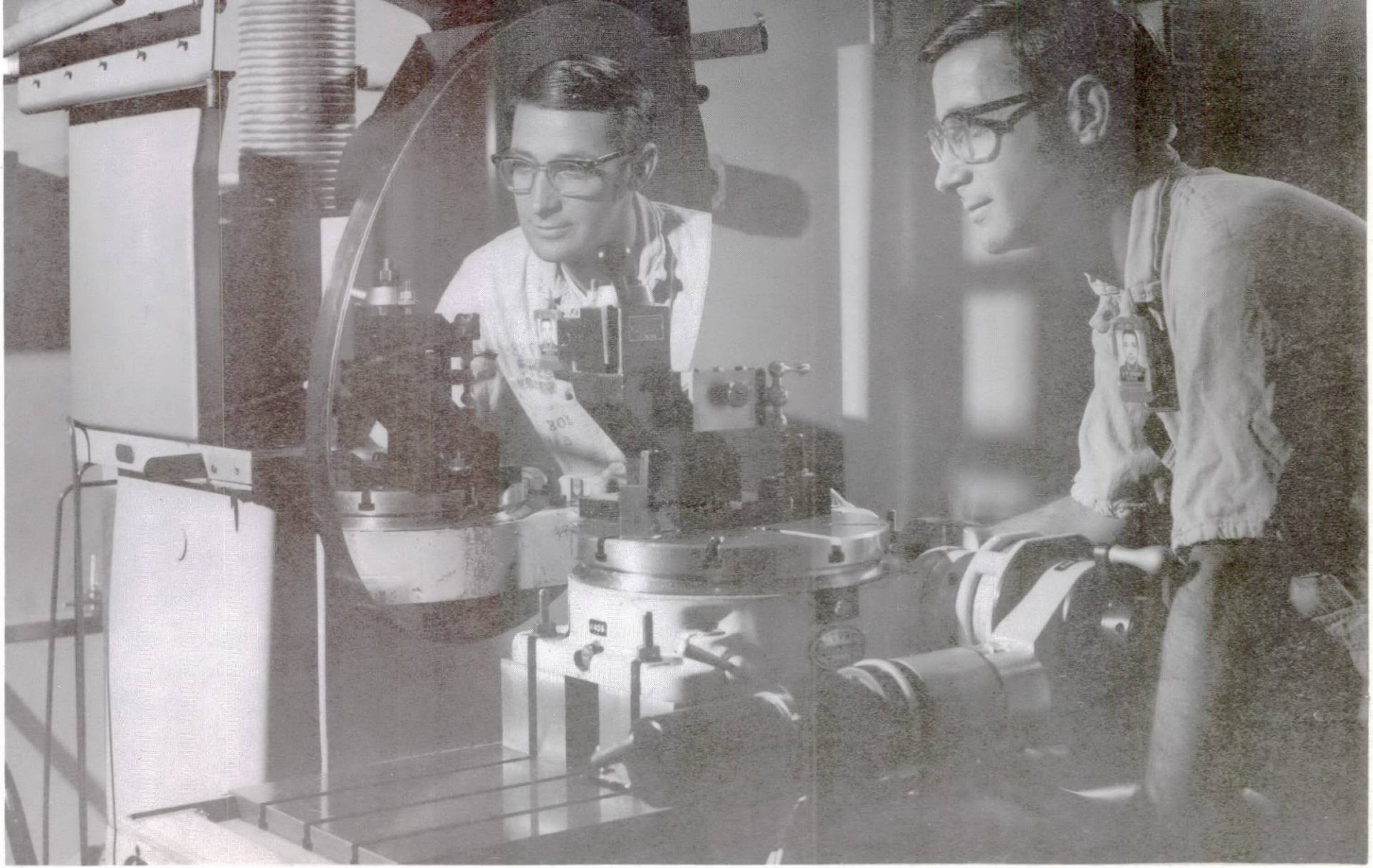


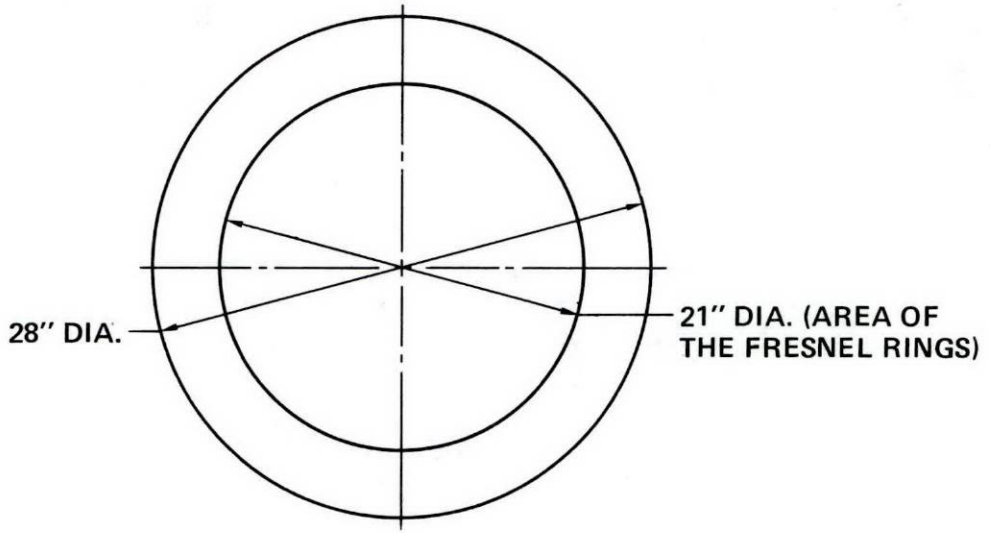
Figure 2

FIGURE 3

SUPER PRECISION MACHINE FOR DIAMOND
TURNING OPTICAL SURFACES



FRESNEL LENS MANDREL



MANDREL IS 6061 ALUMINUM SLAB 3 INCHES THICK

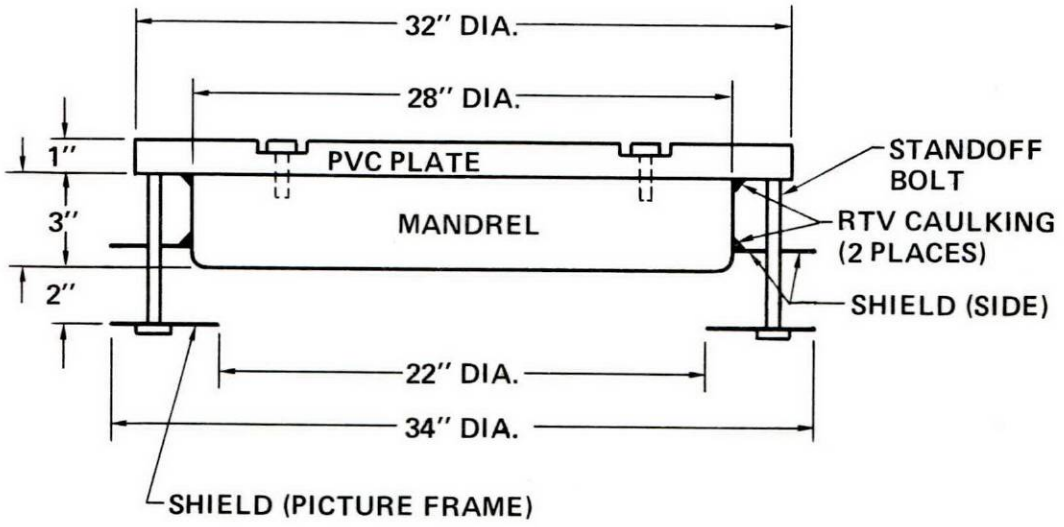

32" DIA.
28" DIA.
1"
PVC PLATE
STANDOFF BOLT
3"
MANDREL
RTV CAULKING (2 PLACES)
2"
SHIELD (SIDE)
22" DIA.
34" DIA.
SHIELD (PICTURE FRAME)

Figure 5

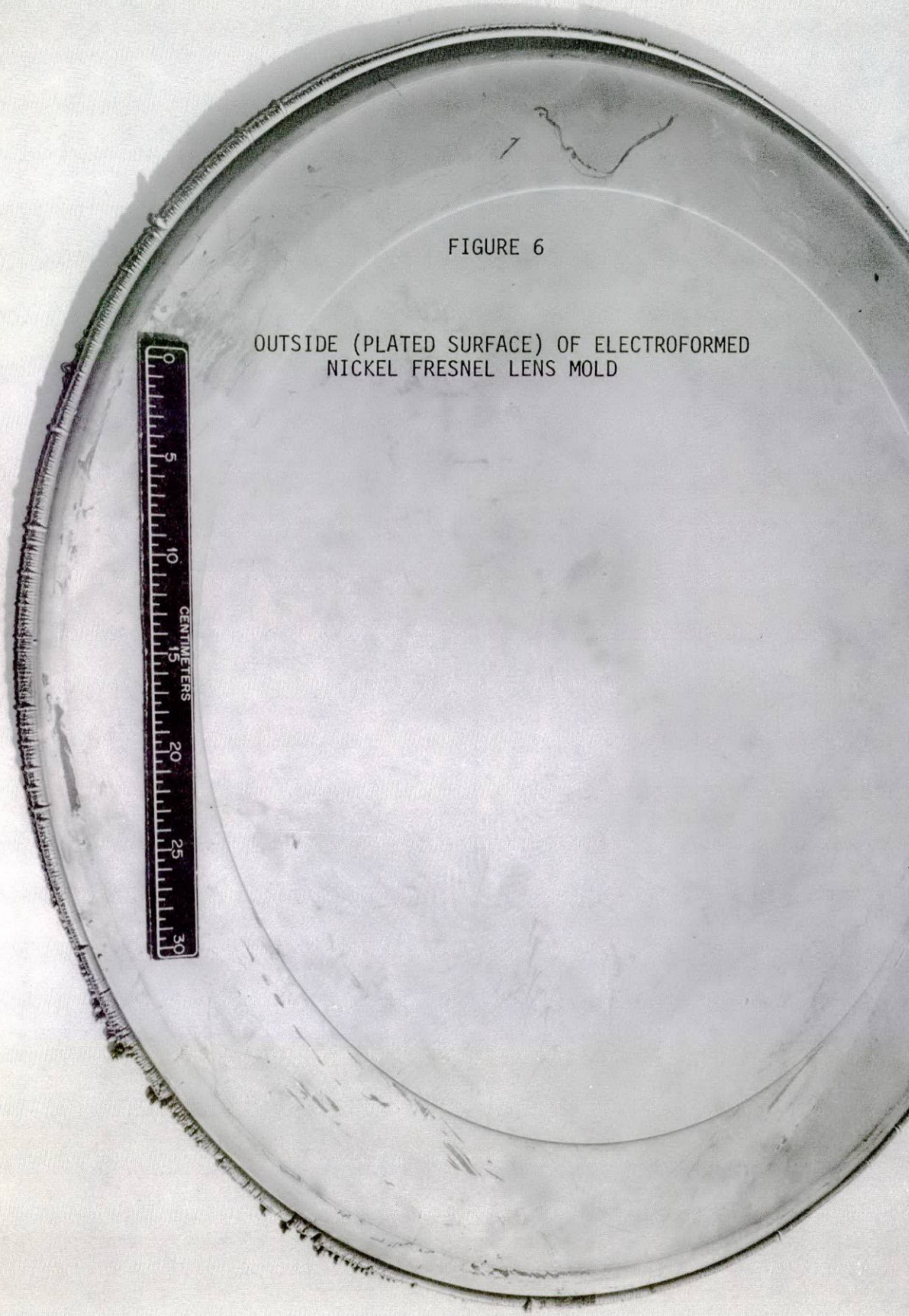


FIGURE 6

OUTSIDE (PLATED SURFACE) OF ELECTROFORMED
NICKEL FRESNEL LENS MOLD

SET-UP FOR PARTING THE ELECTROFORM

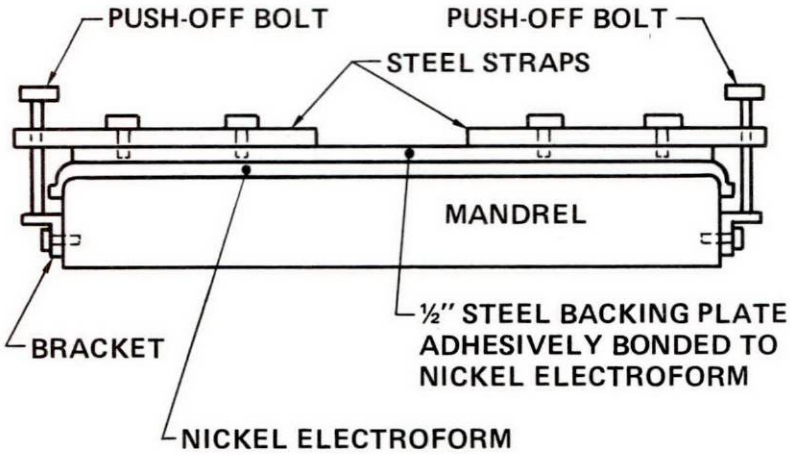


Figure 7

FIGURE 8

ALUMINUM MANDREL FOR ELECTROFORMING FRESNEL LENS MOLD AFTER USE

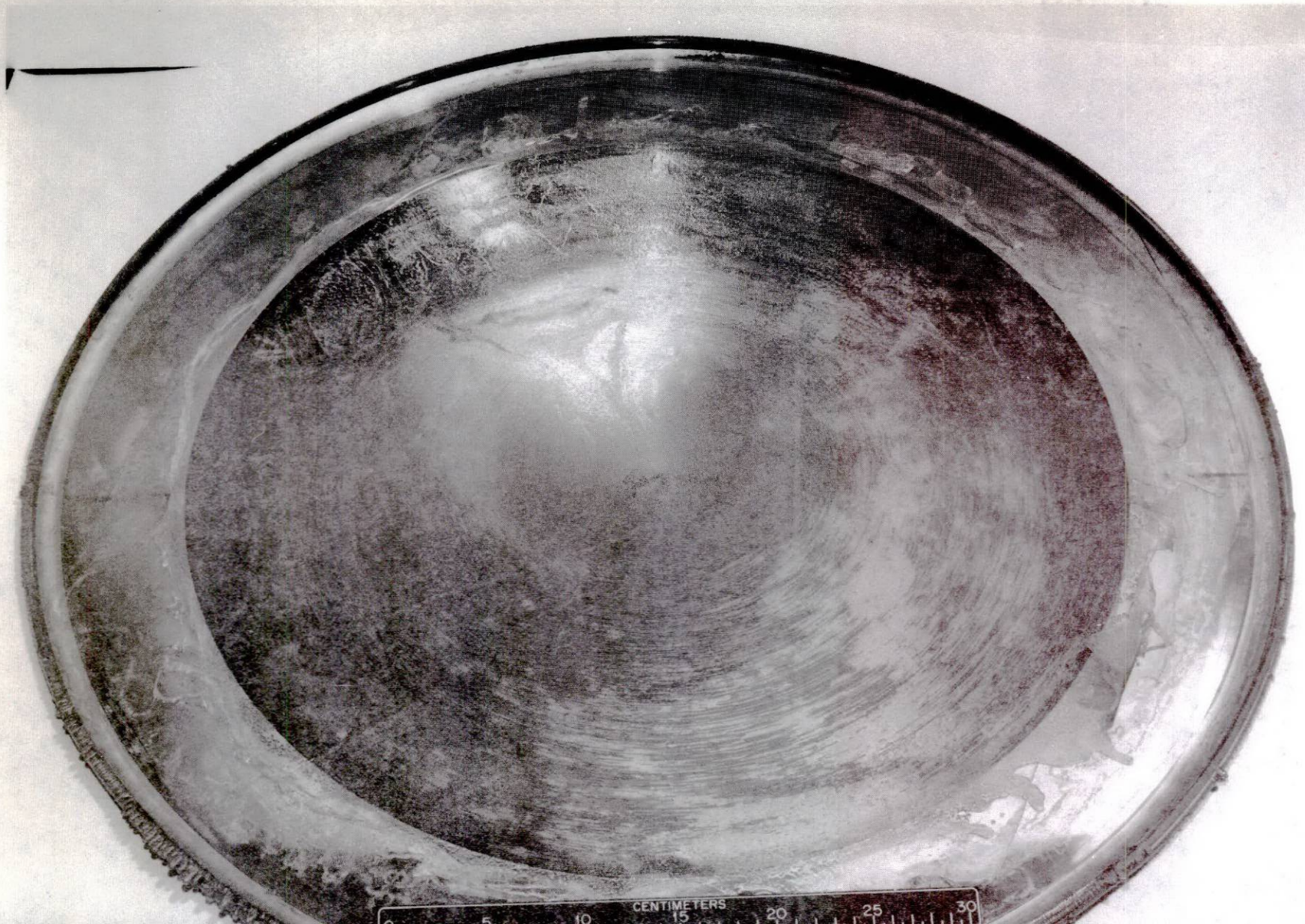
(Note that surface has been given a protective plastic coating which has bubbled considerably)


CENTIMETERS
0
5
10
15
20
25
30

FIGURE 9

MANDREL SIDE OF ELECTROFORMED NICKEL FRESNEL LENS MOLD

(Note that surface has been given a protective plastic coating which has bubbled considerably)


CENTIMETERS
5
10
15
20
25
30

H-3

Electroforming II
Session H

Electroforming Copper and Nickel In Large Thicknesses

G. Malone
Bell Aerospace Co.
Division of Textron
Buffalo, New York

ELECTROFORMING COPPER AND NICKEL IN LARGE THICKNESSES

G. A. Malone
Manufacturing Engineering Dept.
Bell Aerospace - Textron
Buffalo, New York

The following described work was performed on a ct for the US Air Force Rocket Propulsion Laboratory, s Air Force Base, California. The objective of this work e electroform fabrication of two rocket nozzles for simula- f atmospheric re-entry conditions experienced by certain tics missiles. The nozzles are large in size, having a of thirty inches, a large end diameter of about twenty , and a total wall thickness varying from 0.885 to 1.150 . The nozzle wall contains 120 cooling passages which are nch wide and up to 0.60 inch in depth. The inner section h nozzle is copper (containing the channels) and the outer is nickel.

Aluminum mandrels machined to the hot gas wall side ions for the nozzles formed the starting form for the elec- m. The mandrels were solvent wiped and detergent cleaned fixturing for rotation on a conductive center shaft. This was in turn attached to a copper shaft through a mercury n order to conduct over 450 amperes required in the copper tion. The entire unit was supported on a structural frame ning thrust bearings to carry the weight of 1,200 pounds ed after electroforming. Movement of this assembly was ac- shed with an overhead hoist.

Copper electroforming was performed in a 450 gallon tional acid sulfate bath containing 27 to 30 ounces per of copper sulfate and 9 to 10 ounces (by weight) per gallon gent grade sulfuric acid and OFHC anodes. Since thick deposits from such a bath become rough and porous after 0.075 inch of build-up, periodic reverse deposition was em- . It was thus possible to electroform nearly the entire thickness without numerous interruptions for costly and onsuming machining operations.

The copper electrolyte was continuously carbon l and filtered to 10 microns. The bath temperature was ined at 92°F. The mandrel was rotated at 10 to 15 revolu- per minute and a battery of electrolyte sprays was posi- vertically next to the cathode to provide solution agita- n all surfaces being electroformed. The current density was ined at 45 amperes per square foot. A 5:1 periodic reversal was used with the reversal time being about 4 seconds. The was eventually increased to 7:1 without undue roughness in up.

The electroformed copper was template machined on ne lathe and the channels were milled with a side-cutting the required contour depths. The copper electroform was ed prior to wax-fill of the channels for nickel electro- . The wax was applied by wrapping shrink tape around the

outside of the slotted nozzle, closing the bottom end of ea channel in an aluminum manifold, attaching a pipe with fu ne the manifold, and pouring the molten wax into the funnel. wax penetrated to full depth in the channels and forced air as it rose in the passages. The wax was sanded to the copp surface profile and silvered to make it conductive.

The copper surfaces were anodically electroe in 65 percent by volume phosphoric acid at 100 amperes per foot for about five minutes. The hardware was rinsed and t ferred to a bath of 35 percent by volume sulfuric acid where amperes per square foot cathodic current was applied for su activation. Keeping cathodic voltage applied, the copper w double rinsed and transferred to the nickel sulfamate electr ing tank. This bath contained 10 ounces per gallon of nick (as metal), 4 ounches per gallon of boric acid, and approxi 1.8 grams per liter of nickel chloride. Sulfur depolarized nickel anode chips in double bagged titanium anode baskets s plied nickel. This bath was continuously carbon treated an tered to 10 microns.

The electroform was inspected and restarted a every five or six days. Current density on the first nozzle 40 amperes per square foot. This was decreased to 30 ampere square foot on the second nozzle because of excessive surfac roughness. Pitting was not experienced due to agitation by tion of the cathode and the use of high volume electrolyte s on the part.

Each nozzle was machined for final contour an manifold feed passages to the coolant channels prior to deli

H-1

Electroforming II
Session H

Processing Aids for Nickel Electroforms

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Boeing Commercial Airplane Co.
Seattle, Washington

PROCESSING AIDS FOR NICKEL ELECTROFORMS

ODUCTION

tential exists for the use of electroforming in the production of commercial
both for airplane parts and for production tooling. Development work has
initiated to use nickel electroforming for some of these applications on
tem by item basis as the specific needs become apparent.

ver, requirements for structurally sound functional parts and high integrity
ing has placed unusual demands on the electroformer which have necessitated
development of improved plating aids for both the laboratory and the
uction platers.

USSION

re #1 - Gravel Guard

res 1, 2 and 3 are typical electroforming applications.
re 1 is a leading edge protector for a fiberglass part which is exposed
ravel abrasion during take offs and landings. It is a narrow part, deeply
neled in cross section with a complex curvature. The process development
electroforming this part was somewhat unique in that the resultant fixtur-
incorporated electrodepositing to net trim with a number of precision
t holes included. A 25-to-1 cost savings ratio was achieved over
entional fabrication methods.

re #2 - Metal Air Duct Fitting

re 2 illustrates two advantages achievable by electroforming. Transition
etal ducting from an oblong to a rectangular shape while turning through
ngle can be a difficult forming problem for conventional means. Electro-
ing over a removable mandrel provides a simple means of achieving this
sition. Use of the well-known grow -in technique provides for attachment
he pre-fabricated baffle plates which can be seen inside the duct.

re #3 - Rotomold Tool for Elbow Duct

re #3 illustrates a tooling application for electroforming. The tool is
o-piece mold used for fabrication of plastic air ducts by the rotational
ing process. Tooling for the characteristic hollow cylinder shape offers
allenge to electroformers. The challenge lies in incorporating the flange

into each half of the mold so as to have adequate corner strength and dimensional compliance. In this particular mold a steel flange has bee brazed to the electroformed nickel.

Figure #4 - Pitted Nickel

Metallurgically speaking, early efforts in nickel electroforming reveal unpleasant surprises in the quality of the metal being deposited from a which was apparently well within the recommended operating limits. (F Extremely small quantities of contaminants produced unacceptable residu stresses in the deposit as well as inducing pitting and low ductility. Frequently these contaminants are organic materials too low in concentr to be identified or quantified. Residual stress analysis proved to be satisfactory procedure to forecast successful electroforming results.

Figure #5 - Stress Instrumentation

To that end the instrumental system illustrated in Figure #5 was desig built, and patented. Considerable data has been accumulated to verify reproducibility and ease of operation. Repetitive measurements are wi $\pm$ 3%, the helix need not be removed for the life of the metal, individu analysis can be conducted as frequently as every half hour if necessary tank operators or online technicians can perform the analyses with a m of training. The instrument has proven invaluable in predicting succes electroforming on a deposit mandrel costing thousands of dollars.

Figure #6 - Developmental Plating Equipment

Non-uniform thickness of deposits on simple shapes, as well as complex is undesirable in many applications. Rotomold dies are an example of for uniform wall thickness to assure thermal uniformity. The additions "robbers" and "shadows" to plating fixtures are helpful techniques for trolling thickness. Neither one of these techniques however, lend ther to quantitative calculations. The illustrated laboratory set up was bu gain better insight into positioning of these thickness control aids, p larly shadows. Precision instrumentation such as thermistor temperatu controllers, flowmeters and filtering mechanism backed up with particle allowed extrapolation of test data from 20 liter volumes to multi-thous liter production tanks. Much technical data other than shadow effects been collected from this equipment.

#7 - Current Density Meter

positioning, however, was still mostly trial and error using this
nt. Follow-on efforts have produced a current density meter which is
ng very good relationships between meter reading and deposited
sses. Probes of varying lengths and sizes to suit the shapes can be
d the readings can be taken on the production part when desired.

#8 - Current Density Meter in Laboratory Use

rnate procedure of immersing the shadowed deposit mandrel in a con-
salt solution has proven to be a useful technique. In the laboratory
illustrated in Figure 8, an epoxy mandrel with a silver conductive
is immersed in a sodium chloride solution.

#9 - Electroforming with Trees - High Ripple

lectroformer has been dismayed to pull his best effort from his tank
discover "trees" growing outward from several areas on the part.
precautions as to fixturing, current density control, and bath cleanli-
metimes are not sufficient to control these trees.

work with effects of ripple on chrome plating led us to investigate
power supply as a source of poor deposits in nickel. When all operating
ons of time, temperature, concentrations and agitation are held constant,
ly cylindrical shapes illustrate the effects of power supply ripple
me plating quite dramatically. The high ripple power supply restricts
omium plater to a very narrow range of current density in order to
an acceptable deposit.

#10 - Bad Chrome Plate with High Ripple

#11 - Good Chrome with Low Ripple

son of Figure #10 with Figure #11 shows much improved deposits and a
range of operating conditions when ripple is reduced. Production
s been doubled in those cases where ripple filters have been added to
power supplies.

#12 - Electroforming Without Trace - Low Ripple

#12 illustrates a laboratory demonstration of the possible improve-
o nickel deposits by reduction of power supply ripple.

CONCLUSIONS

Improvements in the quality of electroformed parts can be achieved by relatively low expenditures in equipment and instrumentation. The ma potential for high quality structurally sound electro-deposited metal justifies continuing effort for improvements by the electroforming tr It is hoped that these illustrations will encourage that effort.

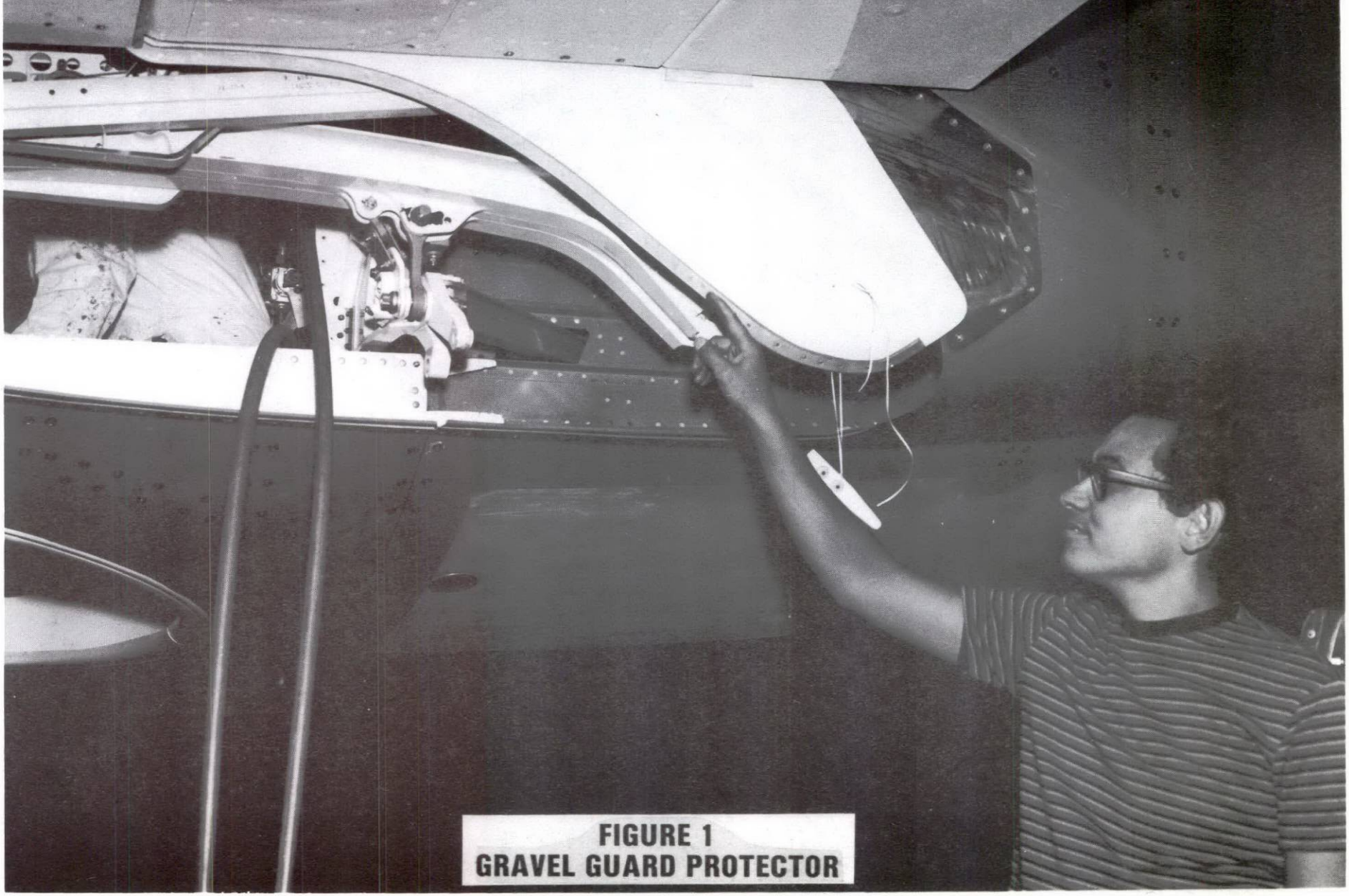


FIGURE 1
GRAVEL GUARD PROTECTOR

737 GRAVEL RUNWAY PROTECTION.
10-8-73

3RK 20711

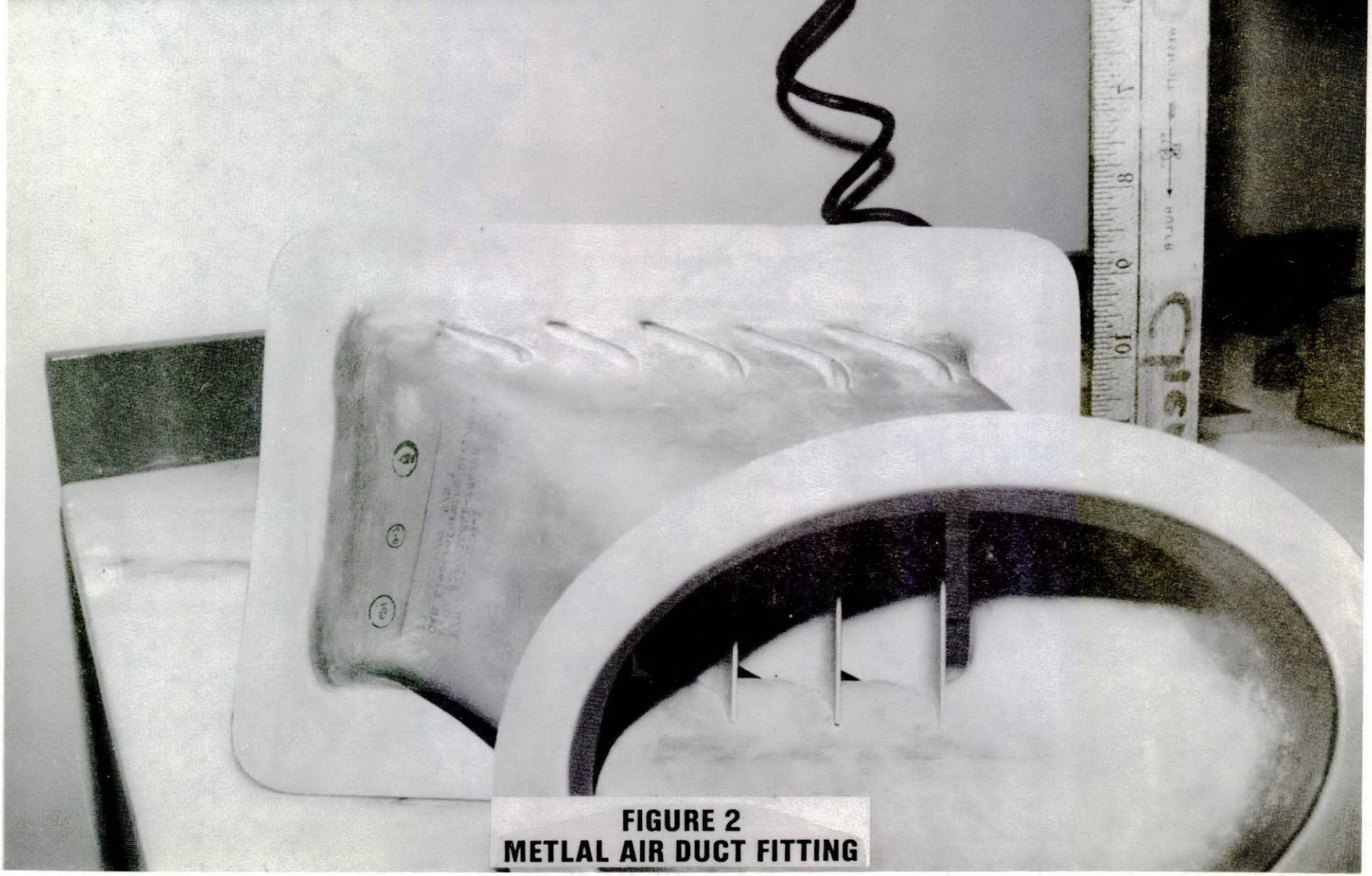


FIGURE 2
METLAL AIR DUCT FITTING



FIGURE 3
ROTOMOLD TOOL FOR ELBOW DUCT

ROTO-MOLD DIE
4SR14868
11-7-74

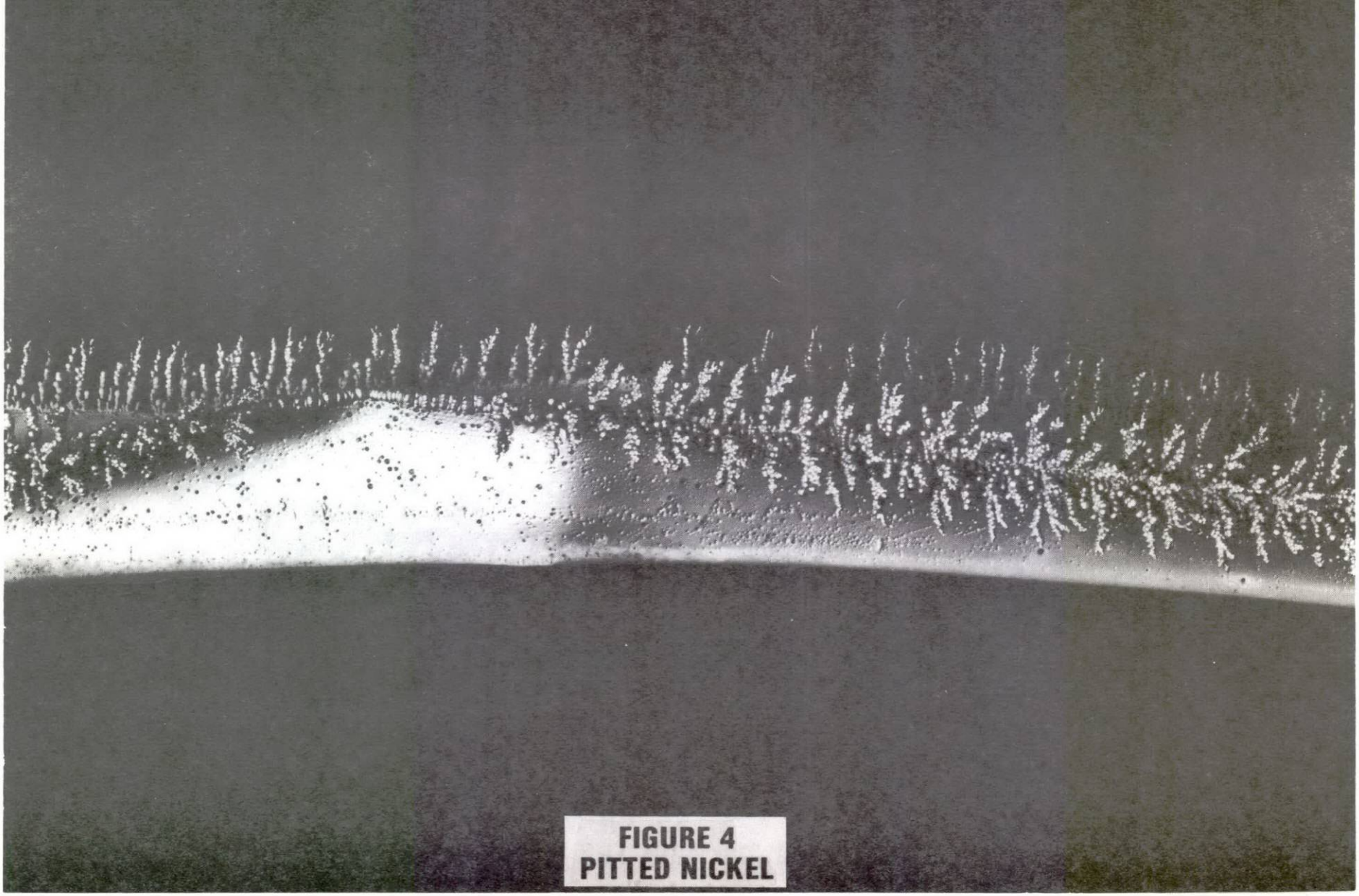


FIGURE 4
PITTED NICKEL

ELECTRONIC BATH IMBALANCE 5,383,240
2-27-75

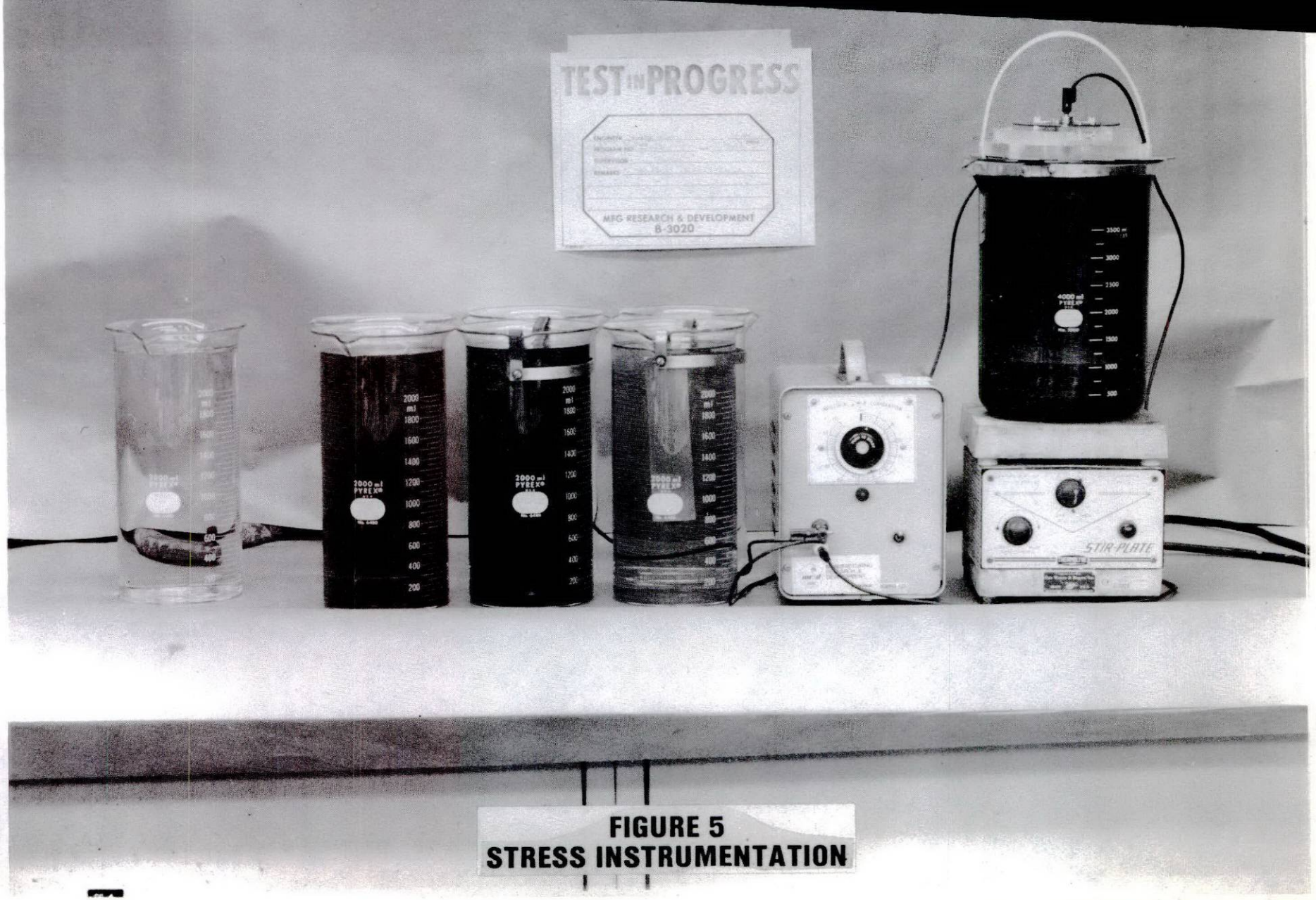


FIGURE 5
STRESS INSTRUMENTATION

NICKEL ELECTROFORMING 2-6-76 6MX 04435

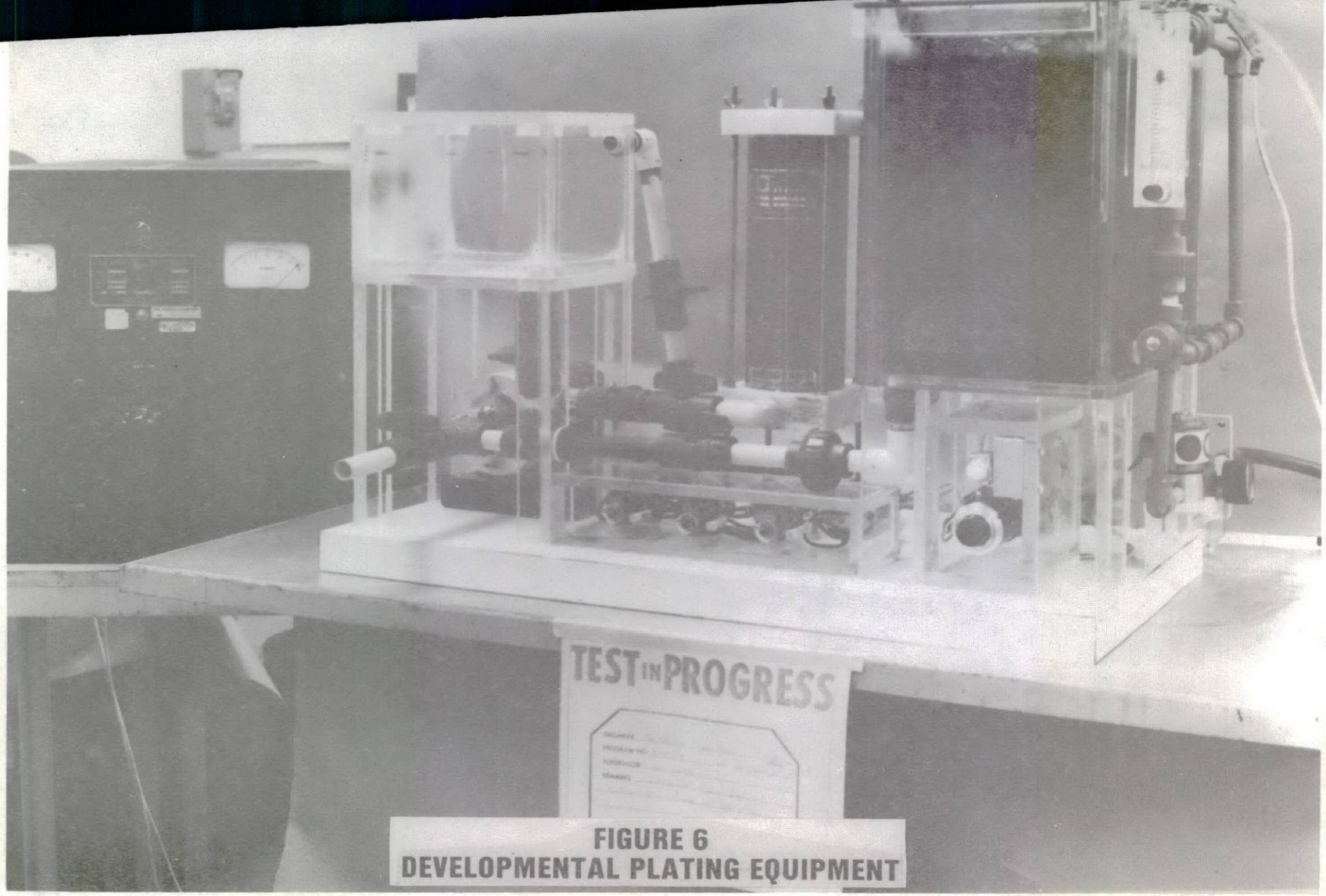


FIGURE 6
DEVELOPMENTAL PLATING EQUIPMENT

DEVELOPMENTAL PLATING EQUIP.
7-11-75
BBK 12553

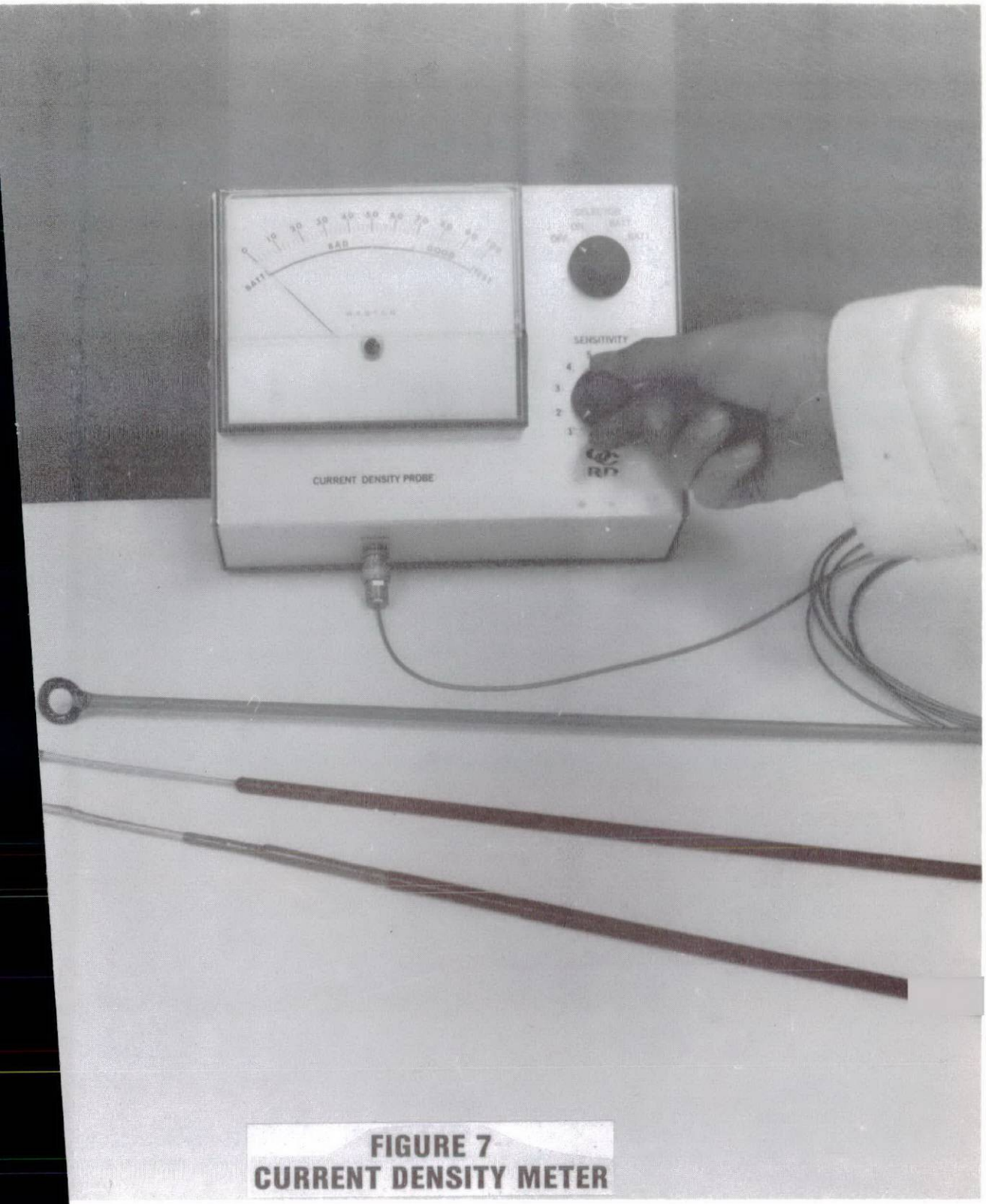


FIGURE 7
CURRENT DENSITY METER



FIGURE 8
CURRENT DENSITY METER IN LABORATORY USE

CURRENT DENSITY P
1-20-78

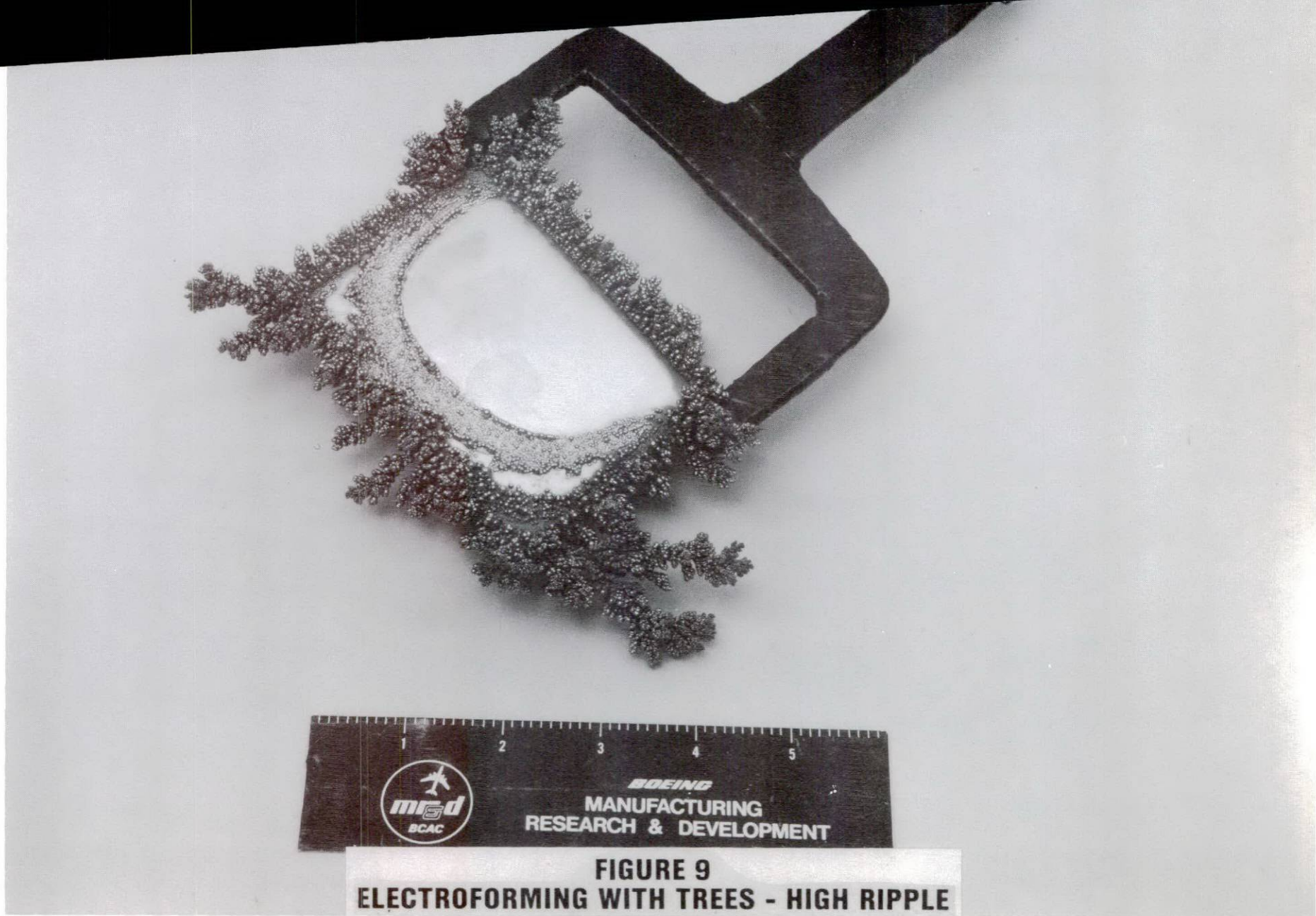


FIGURE 9
ELECTROFORMING WITH TREES - HIGH RIPPLE

NICKEL PLATING
10-31-78
BSK 09921

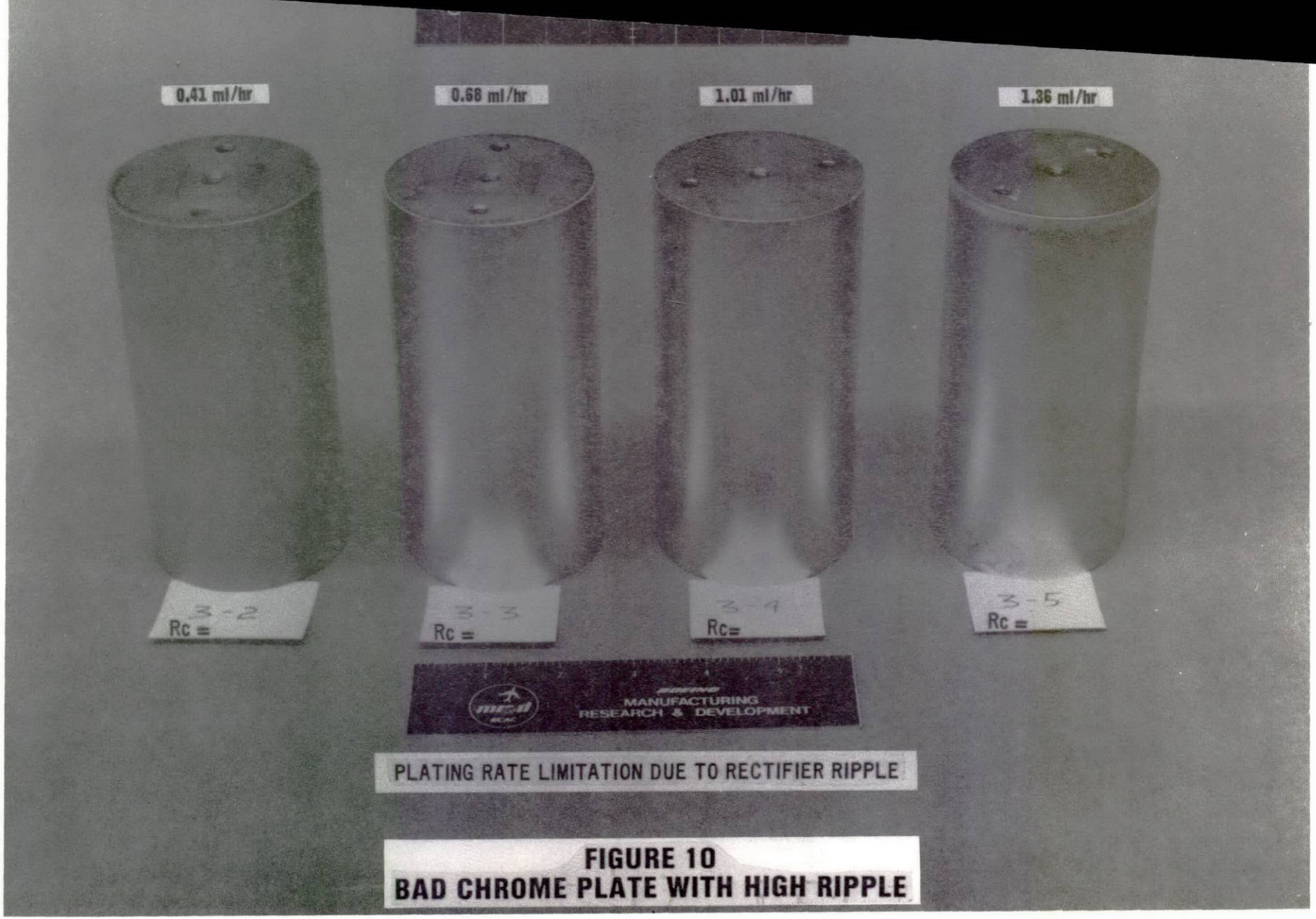
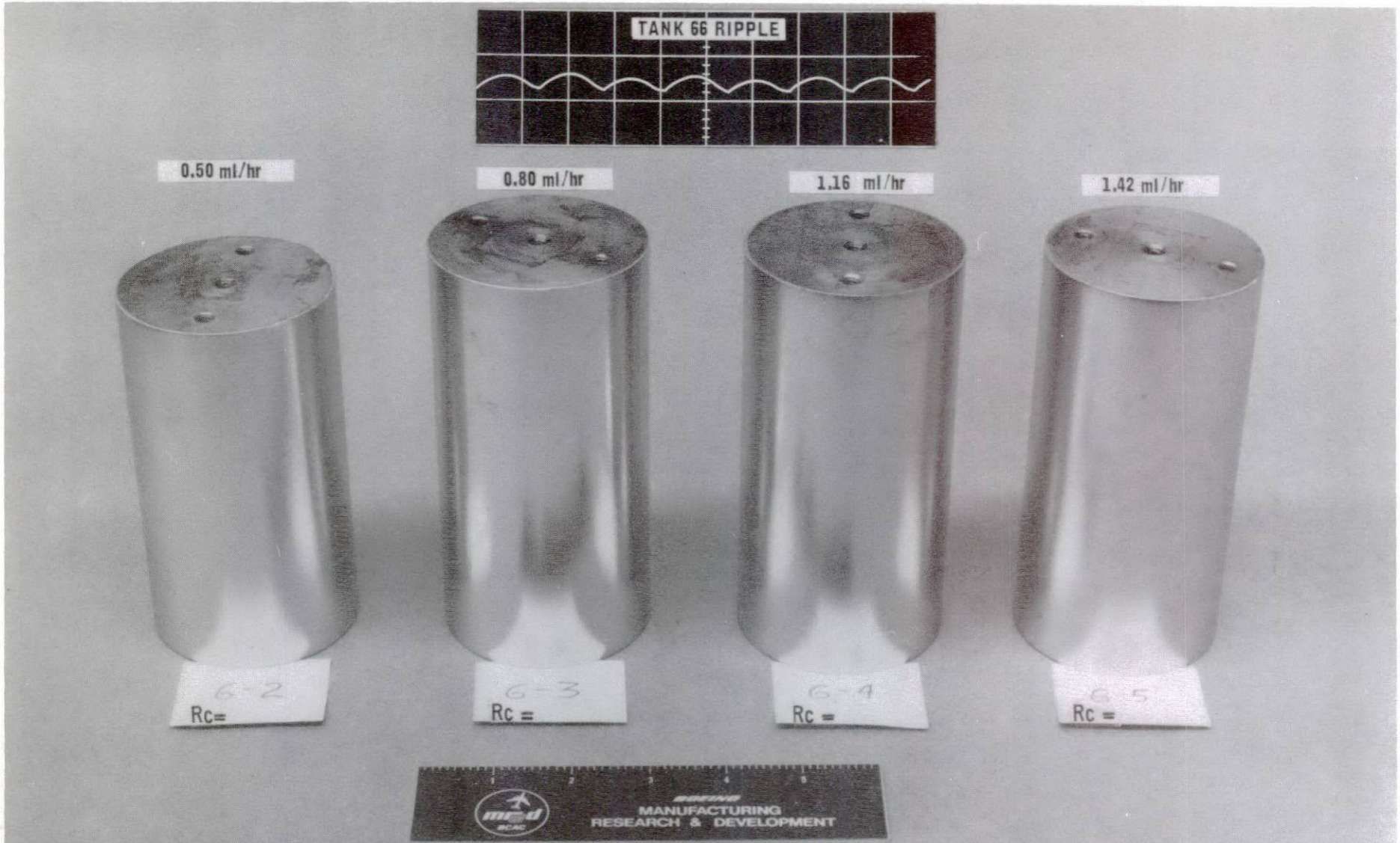


FIGURE 10
BAD CHROME PLATE WITH HIGH RIPPLE



PLATING QUALITY ADVANTAGE OF LOW RECTIFIER RIPPLE

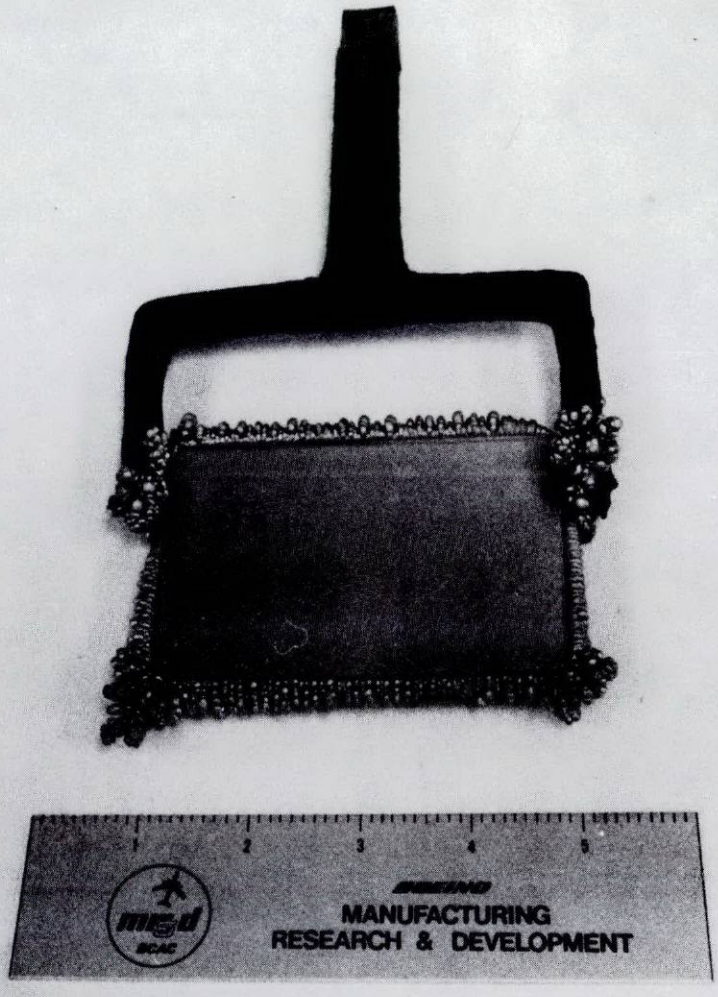


FIGURE 12
ELECTROFORMING WITHOUT TREES - LOW RIPPLE

H-2

Electroforming II
Session H

Electroforming a Mold For Casting Plastic Fresnel Lenses

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and H. E. Patterson
Union Carbide Corp.
Nuclear Division
Oak Ridge, Tennessee

ter hearing all of these rousing success stories and descriptions of egant techniques and brillant solutions to problems, I feel a little ashed, being here to tell you a nonsuccess story.

begin at the beginning, at the Sandia Corporation's Albuquerque Laboratory ere is a program aimed at harnessing solar energy. Now, it is common owledge that solar energy collected with a simple, flat plate is of low ality, as an engineer would say. To be of high quality, capable of being ficiently converted into other forms of energy, mechanical or electrical, t must be at a high temperature (quality and temperature being, for all ctical purposes, synonomous). To raise the temperature of collected shine one must concentrate it, and this means focusing either with mirrors with lenses. At Sandia Albuquerque, one focusing device being developed he Fresnel lens.

just a word about lenses and the rationale behind the Fresnel lens. An nary focusing lens has either one or two spherical surfaces, and if the is very large it must be quite thick. It had occurred to the Comte de n in 1748[1] that a lens could be greatly reduced in weight by dividing ontinuous lens surface into a succession of concentric rings (Figure 1). 20, A. J. Fresnel, developer of the wave theory of light, used this iple to build lenses for lighthouse beacons. Until that time, mirrors een used for this purpose. Such lenses are used for many purposes today l of you have likely seen Fresnel lenses of considerable size that are ctured for the hobby trade.

l note that a Fresnel lens of a few steps, as might be used for a use lense, is still quite a thick structure. To get the very thin lenses of substantial area it is necessary to have many shallow Figure 2). Fabrication of such a device is obviously a difficult However, if a mold can be made, there is the possibility of ting it many times in a clear, acrylic, plastic material.

problem is, how to fabricate a mold on which to cast the plastic One approach is to fabricate, in metal, a positive which is just

like the desired lens and then to electroform a negative off this mandrel from which lenses can be cast. The thing that got us, that is, the Oak Ridge Y-12 Plant (a) into the picture is the capability of the Plant to diamond turn metals to a mirror surface. Diamond turning is a machining technique in which the tool bit is a single-crystal diamond honed to an incredibly sharp and precise edge. A capability for using this technique was developed in the Y-12 Plant several years ago. This is in keeping with the Plant's mission to stay current with, or be the cutting edge of, the state-of-the-art in metal fabricating techniques. This is to meet the increasingly critical tolerance demands in fabricating metal piece parts for Department of Energy work (Figure 3). A spin-off of this technology has been the fabrication of metal mirrors for the Air Force and for the Los Alamos Scientific Laboratory's laser induced fusion work. By this technique, metal mirrors have been fabricated which experts have declared to be, in the as-machined state, the equivalent of any metal mirror they have ever seen, fabricated by whatever method. Equivalent here refers to reflectivity and to resistance to damage by high-energy laser beams.

Well, word gets around and the people of Sandia Albuquerque came to the Y-12 Plant for help in fabricating a mold for casting Fresnel lenses. It was finally established that, yes, it should be possible to machine the positive by diamond turning. And, yes, we have an electroforming capability so we can make you a nickel, casting mold. Then, we were asked "What would you like for a mandrel material?". We knew that diamond turning has one very definite limitation -- there are only certain metals which can be cut successfully. There is copper, gold, silver, and aluminum, and that just about completes the list. We knew that in some applications copper is used for an electroforming mandrel and is given a passivating treatment which makes it possible to release the electroform, but we were not familiar

(a) Operated for the Department of Energy by Union Carbide Corporation-Nuclear Division under Contract W-7405 eng 26

e technique and had our doubts that any surface treatment could be used thout degrading the surface finish. So, we said, "Make it out of uminum". Now, we had done a good deal of electroforming on aluminum and lieved that we should not have any problem in electroforming, but we did ve some reservations about how the electroform should be parted from the ndrel.

preparation for machining the 28-inch-diameter, real part (Figure 4), the chine shop fabricated a test piece approximately 6-inches in diameter. This drel was available for making a test electroform, which we did in the elopment Laboratory, using tooling and fixturing of the type we planned use on the real part. We had considered all along that we would not be e to prepare the diamond-turned surface for plating by any method which uired contact with a solid material, even cotton gauze would scratch the r-finished aluminum surface. So we rinsed the surface with solvent, owed that with a water solution of a wetting agent, and went into the ing bath with current on. We plated at a current density of 25 asf, for t 100 hours. To part the electroform from the mandrel, we simply set it the electroform was supported at three points and struck one sharp blow e center with a rubber hammer. The mandrel dropped off cleanly.

andrel did not have the high reflectivity after electroforming that it ad before, and the mandrel side of the electroform was surprisingly As the time approached to electroform the full-scale part, we got erious about the matter of precisely how we would prepare the mandrel ating. Some work on cleaning mirror surfaces, done by Charlene s of our Plastics and Adhesives Development Group, had shown that a ular brand of trichloroethane is a good solvent which does not degrade surfaces, so we chose that for degreasing. We knew we did not want an ordinary detergent because they are generally high pH solutions ely to be corrosive toward aluminum. We concocted a solution of a hain, non-ionic surfactant to promote wetting, and a long chain, ic surfactant to emulsify oily residues. We found that when these s were used in sequence, i.e. the organic solvent followed by the solution, on a small diamond-turned aluminum specimen, that the

surface was wet very well by the surfactant solution; but, when the surface was rinsed with demineralized water, a water break occurred promptly when the flow of water stopped. If we plated a specimen cleaned in this manner in a nickel sulfamate bath, going in with current on, we observed a considerable amount of gassing at the cathode, and the nickel covered the aluminum surface completely only after several minutes. If the specimen was plated until the nickel was fairly thick, when the nickel electroform was removed the aluminum was found to be corroded over a considerable area, and the nickel was not mirror-like in the area where the aluminum was corroded. We tried starting at high-current density and at low current density, and going into the bath without rinsing, i.e. wi the surface wet with the surfactant solution, and almost every time found aluminum mandrel corroded and the nickel surface of poor quality. We co cluded that the diamond turning must put a thin, stable oxide film on th aluminum surface which is then so passive that in some areas it will not plate until corrosion by the plating solution has removed the film. The is some reason to believe that diamond turning may generate an oxide fil of appreciable thickness because diamond-turned copper surfaces remain bright and highly reflective for years, in an ordinary air environment, before any color change is observed. As we wondered what to do about t situation, Harold Patterson of the Y-12 Plant production job shop sugge treating the aluminum with 17.5 wt. % nitric acid solution, as is commo done in preparation of aluminum for zincating and electroplating. It h not occurred to any of the rest of us that this treatment could possib be used without damage to the surface finish. When a diamond-turned s was solvent degreased with trichloroethane, rinsed with an aqueous sur solution, and then dipped for only 30 seconds in the nitric acid solut a good water break test was obtained on rinsing and a good nickel plat obtained. The nickel covered promptly, and when the electroform was there was no evidence of corrosion of the aluminum surface. Both the aluminum and the nickel were bright and highly reflective.

Of course, "highly reflective" is not a very meaningful term. We too small diamond-turned aluminum mirror ("small" is used here for a stan size, which is 1.52 inches in diameter) and cleaned it, then pickled half of it in the nitric acid for 30 seconds. We then had it examin

r optical testing group using an interference microscope to compare the ckled and not-pickled areas. They concluded that there was no discernible fference. The entire surface of this specimen was then pickled, and when nsed, gave a good water break test. The specimen was then nickel plated. e diamond-turned surface covered promptly, and when the electroform was moved, both the aluminum and nickel surfaces were found to be in good ndition. So we added a nitric acid pickle to our procedure and it looked mething like this: (Table I)

we went through this procedure on the real mandrel, everything seemed to going along O.K. until we were drying the part. At this point, I looked efully at the flat diamond-turned area outside the Fresnel rings and tead of having a bright specular look, it appeared sort of dull and life-s. The thought went through me like an icy projectile, "My God, we've ned the thing!". Maybe we had, I still don't know because no lenses have cast from the electroform as yet, but there was nothing to do but go d. The diamond turning of the part had been a once in a lifetime pro-tion. There would neither be time available on the super precision ines, nor money to pay for it, to do the job over again -- not for years y. The air we were using was instrument air, which should have been and dry, with a final filter just after the pressure regulator.

thing else went pretty well that first day. We got the back plate bolted aped off the sides, attached the annular shield and the picture-frame d, and applied the RTV caulking (Figure 5). The reason for caulking the late was to assure that solution would not leak under the plate and, in ry long time that the part would be in the plating bath, cause severe ion of the back side of the aluminum mandrel. The caulking on the back f the annular shield prevents nickel plate from growing under the shield rming large trees on the back side.

tion of the part for plating was made on a Friday afternoon. Monday the plating bath was made ready for operation and the part was given al preparation. From the very first, it had been noticed that there nall area, a few square inches, on the grooves which was contaminated way. Repeated applications of solvent and surfactant solution with a

cotton gauze had failed to remove this contamination and it still would not wet, not even with the surfactant solution. It was decided to treat the mandrel for one minute with the nitric acid solution. The face of the part was rinsed with the surfactant solution, followed by a demineralized water rinse, and then it went into the nitric acid tank. This was a new, clean nitric acid solution. We waited with baited breath and watched fearfully f any sign of bubbles. We did not see a single bubble. The part was removed from the acid, rinsed and transported immediately to the plating tank. The part was lowered into the plating bath with current on and the current was set at 10 asf. After plating for four hours, the current was raised to 15 and after 24 hours, to 20 asf. We wanted at least 60 mils of plate; we wo have felt better about 80; and we actually let the part plate approximatel 100 hours, just to give us a little fat. As always, after a long plating operation like that, we wondered a bit about what we would have. Here is picture of the plated side of the electroform (Figure 6). You can see th the masking and shielding controlled the plate quite well; there is just little incipient treeing at the bottom as the part hung in the plating ba looking at the deep tank.

The final act in an electroforming scenario is generally parting the ele form from the mandrel. Now, in this particular case, the electroform wa be backed up by a half-inch thick steel plate, adhesively bonded to the surface. We planned to use this plate to push the electroform off the m (Figure 7). We believed that parting could prove a problem at a tempera higher than the temperature at which the electroforming was done becaus the aluminum would expand and lock on the electroform around the outer Also, if the temperature were lower than the plating temperature, we ex that the electroform would lock onto the almost vertical sides of the g which in aggregate, amounts to a substantial area. So we removed the m with its electroform, to an area where the air temperature was about th as the temperature of the plating bath, allowed the system to equilibr overnight, and started to push off the electroform. Each screw was tu in sequence -- 1/4 turn at a time. After a round or two, there was a sound. But, unfortunately, it was not the electroform parting from th it was the steel plate parting from the epoxy adhesive. Now this lef no way to push off the electroform except around the edge. There was wide, practically flat flange where the electroform had built up agai

nnular shield. We had a push-off ring fabricated and prepared to push off he electroform with this device. Because we expected the electroform to lex and bind in the center if pushed off in this manner, we first thermally ycled the assembly to 120° F (49° C) in a large, walk-in oven. After eating overnight, the assembly was allowed to cool to room temperature. hen the screws were tightened, the electroform came off with very little ffort.

he appearance of the mandrel and of the electroform was not an inspiring ght. In spite of our precautions, plating solution had obviously gotten der the electroform and caused considerable corrosion of the mandrel, igure 8) and staining of the nickel (Figure 9). This must have occurred some time after the electroform had an appreciable thickness. If this true, the electroform must have cupped slightly due to residual tensile ess. We had provided a generous radius at the edge of the part to ffen the electroform in an effort to avoid this problem. Another thing might have done would have been to add to the plating bath enough saccharin, some other such agent, to have reduced the stress to close to zero.

good was the electroform? We really don't know. The proof of the pudding n how good a lens can be cast from it. To date, none have been cast. factors that will affect the fitness of the electroform for its intended are flatness and finish. We don't know just how flat the electroform is s present, unsupported state, and we know of no way of putting it in a condition for bonding on another back-up plate. The part does not exhibit lar reflection which leads us to believe that the surface will prove to ther poor and that lenses made from it will scatter a good percentage of ncident light.

had it to do over again, there are a few things we would do differently. ld not use the surfactant or any aqueous solution in precleaning the l. This would also eliminate the compressed air drying. At the time he part is given its final preparation, just before plating, it would shed with surfactant solution, rinsed, and nitric acid pickled. We djust the stress in the bath to close to zero. Even now, I am not

sure how we should go about parting the electroform from the mandrel. We believe that using the back-up plate to push off the electroform is a viable technique. But some testing of the adhesive system and the methods of surface preparation should be done to assure that the bond will hold.

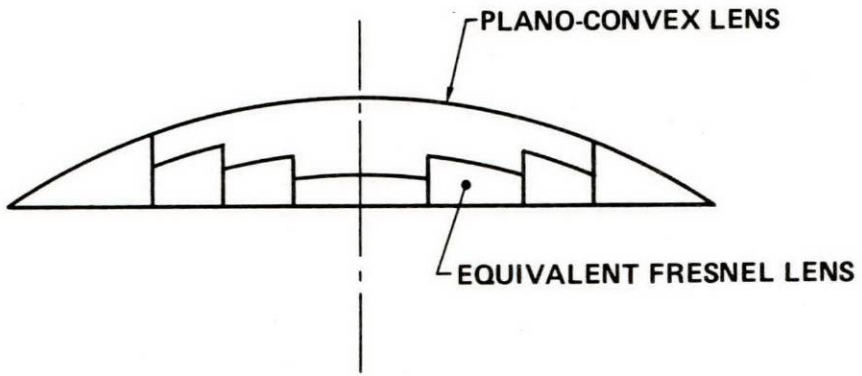
REFERENCE

1. Encyclopedia Britanica; Volume 13, p. 953;
Encyclopedia Britanica, Incorporated, 1967

TABLE I

1. Hang the part in a vertical position from the shop crane.
2. Solvent degrease.
3. Rinse with surfactant solution.
4. Water rinse.
5. Dry with compressed air.
6. Tape sides.
7. Attach and caulk the backing plate.
8. Place and caulk side shield.
9. Attach shadow ring shield.
10. Rinse with surfactant solution.
11. Water rinse.
12. Nitric acid pickle.
13. Water rinse.
14. Go into sulphamate nickel plating bath with current on.

PRINCIPLE OF THE FRESNEL LENS



THIN FRESNEL LENS

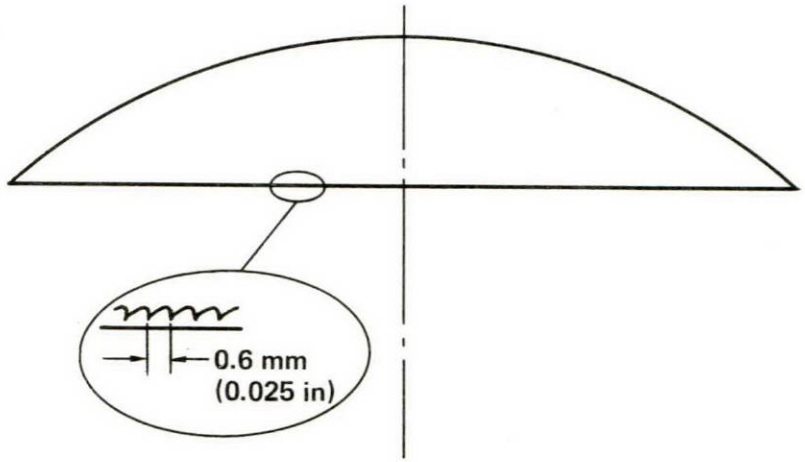


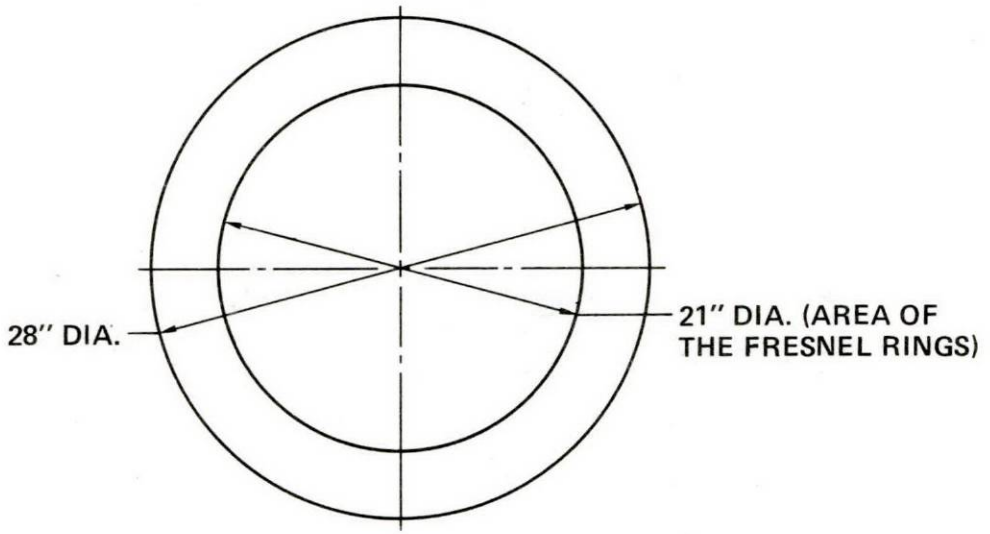
Figure 2

FIGURE 3

SUPER PRECISION MACHINE FOR DIAMOND
TURNING OPTICAL SURFACES



FRESNEL LENS MANDREL



MANDREL IS 6061 ALUMINUM SLAB 3 INCHES THICK

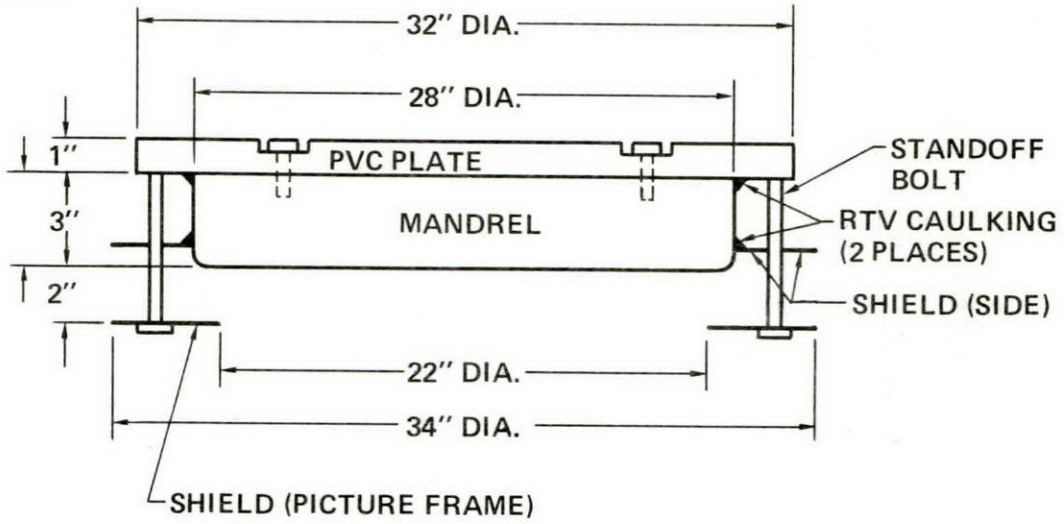

32" DIA.
28" DIA.
1"
PVC PLATE
STANDOFF BOLT
3"
MANDREL
RTV CAULKING (2 PLACES)
2"
SHIELD (SIDE)
22" DIA.
34" DIA.
SHIELD (PICTURE FRAME)

Figure 5

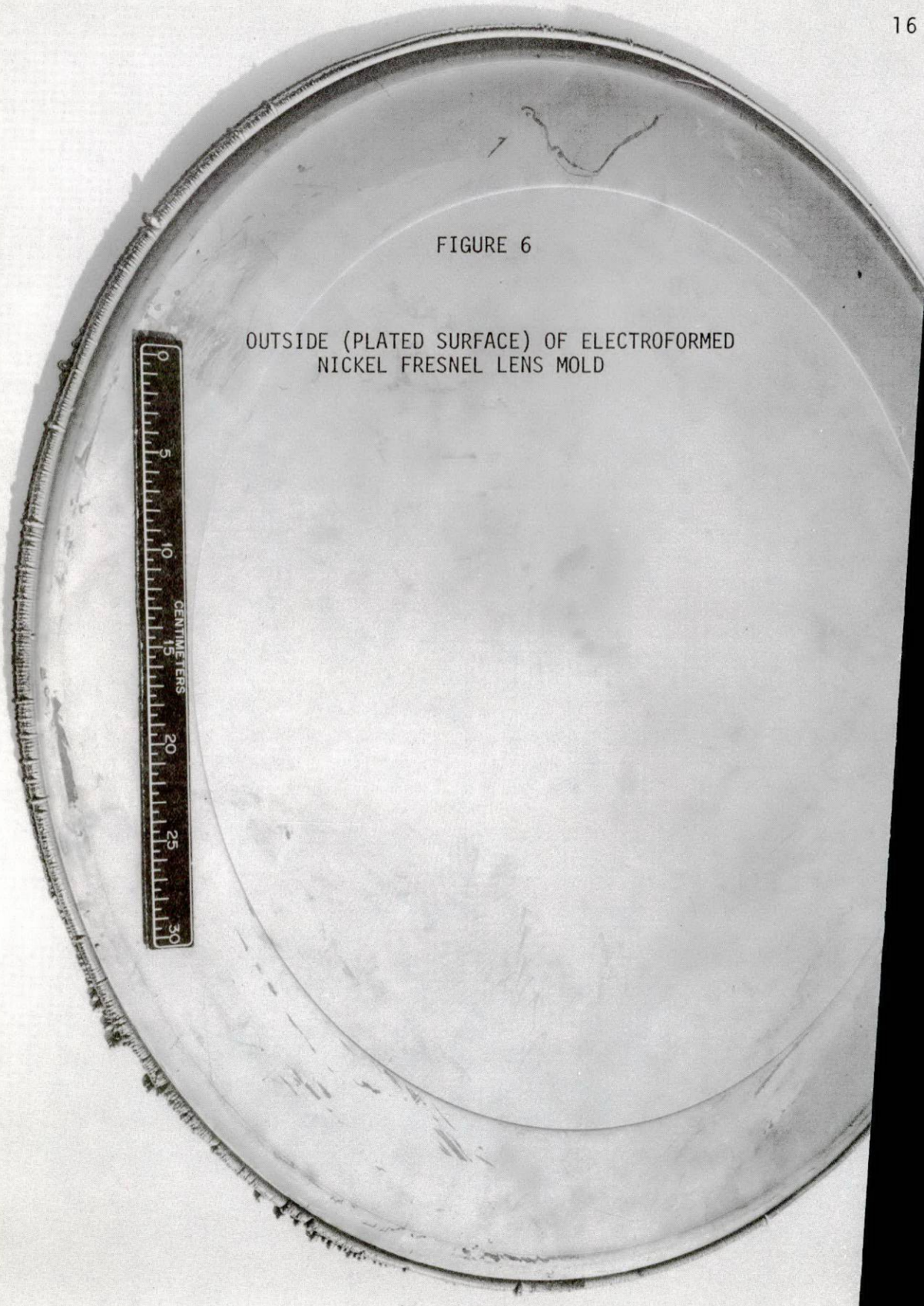


FIGURE 6

OUTSIDE (PLATED SURFACE) OF ELECTROFORMED
NICKEL FRESNEL LENS MOLD

SET-UP FOR PARTING THE ELECTROFORM

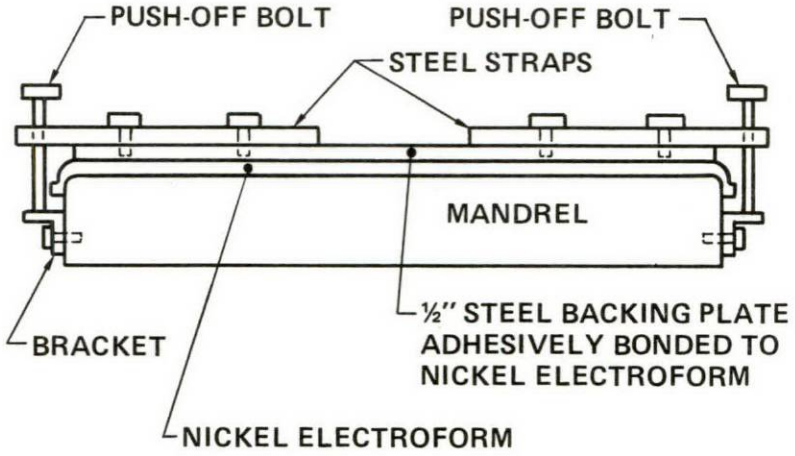


Figure 7

FIGURE 8

ALUMINUM MANDREL FOR ELECTROFORMING FRESNEL LENS MOLD AFTER USE

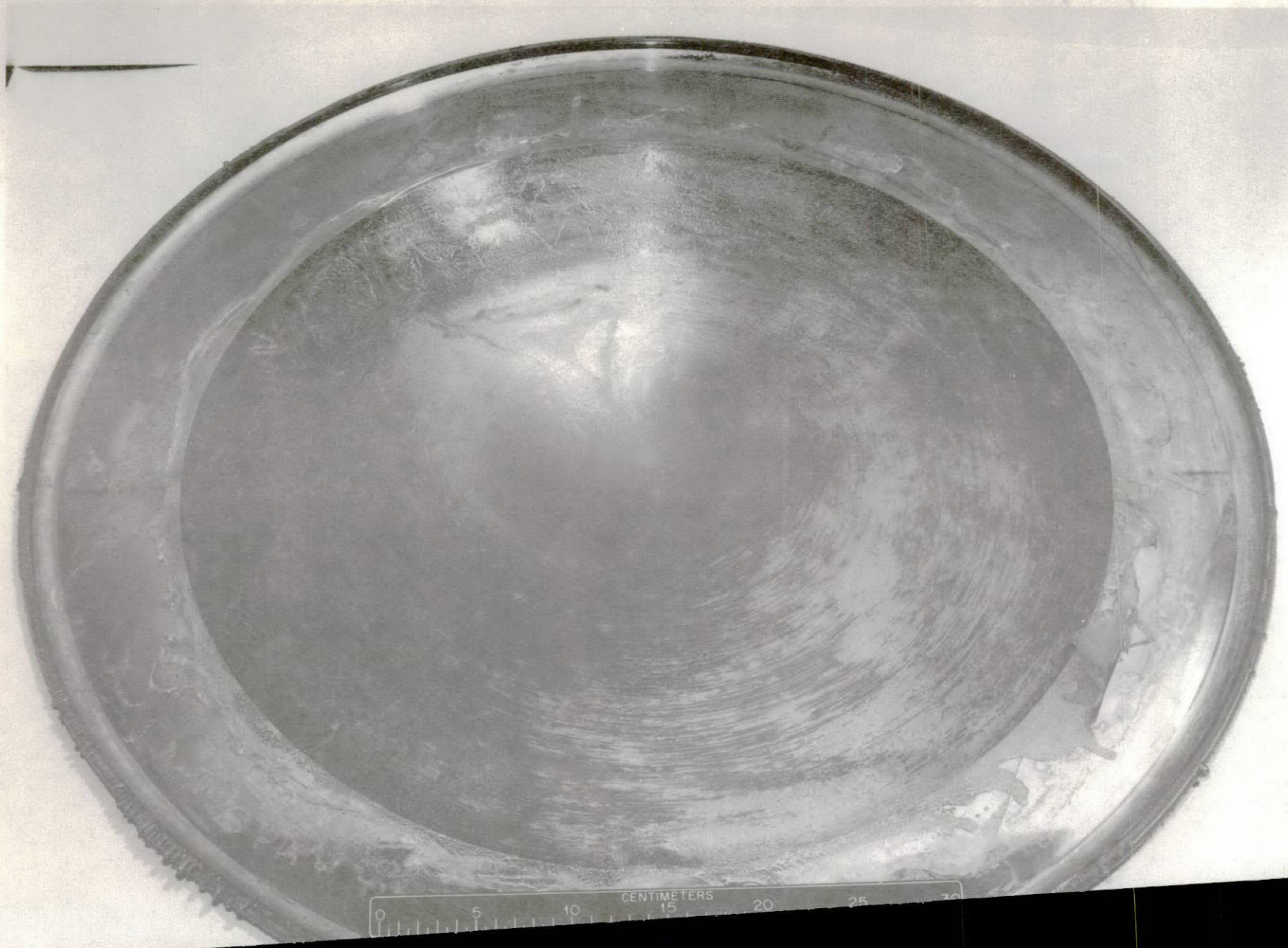
(Note that surface has been given a protective plastic coating which has bubbled considerably)


CENTIMETERS
0
5
10
15
20
25
30

FIGURE 9

MANDREL SIDE OF ELECTROFORMED NICKEL FRESNEL LENS MOLD

(Note that surface has been given a protective plastic coating which has bubbled considerably)


CENTIMETERS
0
5
10
15
20
25

H-3

Electroforming II
Session H

Electroforming Copper and Nickel In Large Thicknesses

G. Malone
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ELECTROFORMING COPPER AND NICKEL IN LARGE THICKNESSES

G. A. Malone
Manufacturing Engineering Dept.
Bell Aerospace - Textron
Buffalo, New York

The following described work was performed on a
ıtract for the US Air Force Rocket Propulsion Laboratory,
ards Air Force Base, California. The objective of this work
the electroform fabrication of two rocket nozzles for simula-
n of atmospheric re-entry conditions experienced by certain
listics missiles. The nozzles are large in size, having a
gth of thirty inches, a large end diameter of about twenty
es, and a total wall thickness varying from 0.885 to 1.150
es. The nozzle wall contains 120 cooling passages which are
inch wide and up to 0.60 inch in depth. The inner section
ach nozzle is copper (containing the channels) and the outer
l is nickel.

Aluminum mandrels machined to the hot gas wall side
nsions for the nozzles formed the starting form for the elec-
rm. The mandrels were solvent wiped and detergent cleaned
fixturing for rotation on a conductive center shaft. This
was in turn attached to a copper shaft through a mercury
in order to conduct over 450 amperes required in the copper
ition. The entire unit was supported on a structural frame
ining thrust bearings to carry the weight of 1,200 pounds
ted after electroforming. Movement of this assembly was ac-
ished with an overhead hoist.

Copper electroforming was performed in a 450 gallon
tional acid sulfate bath containing 27 to 30 ounces per
of copper sulfate and 9 to 10 ounces (by weight) per gallon
gent grade sulfuric acid and OFHC anodes. Since thick
deposits from such a bath become rough and porous after
.075 inch of build-up, periodic reverse deposition was em-
. It was thus possible to electroform nearly the entire
thickness without numerous interruptions for costly and
nsuming machining operations.

The copper electrolyte was continuously carbon
and filtered to 10 microns. The bath temperature was
ned at 92°F. The mandrel was rotated at 10 to 15 revolu-
r minute and a battery of electrolyte sprays was posi-
vertically next to the cathode to provide solution agita-
all surfaces being electroformed. The current density was
ed at 45 amperes per square foot. A 5:1 periodic reversal
s used with the reversal time being about 4 seconds. The
s eventually increased to 7:1 without undue roughness in
.

The electroformed copper was template machined on
lathe and the channels were milled with a side-cutting
e required contour depths. The copper electroform was
prior to wax-fill of the channels for nickel electro-
The wax was applied by wrapping shrink tape around the

outside of the slotted nozzle, closing the bottom end of each channel in an aluminum manifold, attaching a pipe with funnel t the manifold, and pouring the molten wax into the funnel. The wax penetrated to full depth in the channels and forced air out as it rose in the passages. The wax was sanded to the copper surface profile and silvered to make it conductive.

The copper surfaces were anodically electroetche in 65 percent by volume phosphoric acid at 100 amperes per squa foot for about five minutes. The hardware was rinsed and trans ferred to a bath of 35 percent by volume sulfuric acid where 1(amperes per square foot cathodic current was applied for surfac activation. Keeping cathodic voltage applied, the copper was double rinsed and transferred to the nickel sulfamate electrof ing tank. This bath contained 10 ounces per gallon of nickel (as metal), 4 ounches per gallon of boric acid, and approximat 1.8 grams per liter of nickel chloride. Sulfur depolarized nickel anode chips in double bagged titanium anode baskets sup plied nickel. This bath was continuously carbon treated and f tered to 10 microns.

The electroform was inspected and restarted abo every five or six days. Current density on the first nozzle w 40 amperes per square foot. This was decreased to 30 amperes square foot on the second nozzle because of excessive surface roughness. Pitting was not experienced due to agitation by r tion of the cathode and the use of high volume electrolyte sp on the part.

Each nozzle was machined for final contour and manifold feed passages to the coolant channels prior to deliv

I-1

Light Metals Finishing III
Session I

Surface Treatment of Magnesium

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Abstract

In this paper, the following three topics will be reported. These

(1) New patents on the surface treatment of magnesium in Japan.

(2) New methods for surface treatment of magnesium by the present authors.

(3) Basic experiments on magnesium films formed by the convensional methods.

New patents on surface treatment of magnesium in Japan

Standard methods of surface treatment of magnesium in Japan are specified by the Japanese Industrial Standard (JIS). This specification (JIS-H-8651) is almost as same as the DOW methods or MIL Specification. Table 1 shows JIS Specification on the surface treatment of magnesium.

New patents (From 1966 to 1977) on surface treatment of magnesium Japan are listed in Table 2. Some examples of these patents are plained in the following.

ample 1] 41-15285 (Fuji Steel Co., Ltd.)

Bath Composition

$MgSO_4$	1 M
Mg_2SO_4	1 M
H_2O	1 L
pH	7.5

Condition of electrolysis

Cathod :	Si-Steel
Temp. :	30°C
Current density :	10A/dm^2
Electrolyzing time :	1 min.

Aging

(Several hours at 1050°C in H_2 gas)

e 2] 43-12253 (Japanese defence ministry)

Mixture of organic paint and boron oxide is painted on magnesium.

[Example 3] 48-31459 (Japan-Bell Hawel Co., Ltd.)

Bath Composition

$Ca(OH)_2$	3 g/ℓ
pH	12 ∿ 12.5

Condition of electrolysis

Anodizing voltage : 10 ∿ 120V (D.C.)
Temp. : 0 ∿ 35°C
Anodizing time : 15 ∿ 120 min.
Cathod : Stainless steel

[Example 4] 48-39135 (Japanese person)

This process is the three steps treatments. Galvani
in the Zn - Sn mixed melt → Electroplating of Ti →
Diffusion treatment at 80 ∿ 200°C for 30 ∿ 60 min.

[Example 5] 51-17133 (KOKAI) (Japan defence ministry and Japan
Kihatsu Oil Co., Ltd.)

When magnesium powder is kept in 0.2 wt. % KOH or i
0.1 ∿ 1.0 wt. % NaOH aqueous solution, change of ma
powder can not be observed for 2,000 hours.

[Example 6] 52-95546 (Japan-Parkerizing Co., Ltd.)

Condition of dipping

Tannic acid : 5 g/ℓ
Titanium ammonium fluoride : 4 g/ℓ
pH : 5.0
Temperature : 50°C
Dipping time : 60 sec.

Aging

Temp. : 290°C
Aging time : 45 sec.

ew methods for surface treatment of magnesium by the present uthors

New surface treatment methods of magnesium are studied by the resent authors. These methods are,

(1) Two steps electrolysis method

(2) Anodizing method by the step voltage

(3) Anodizing method by alternating voltage superimposed on direct voltage

these experiments, AZ91C magnesium alloy is used as experimental terials. Table 3 shows experimental conditions for pretreatment magnesium alloy.

Two steps electrolysis method

This treatment method of magnesium is the application of he electrolytic coloring method of anodized aluminum. irst, the film is formed on magneisum by the convensional methods OW 9, DOW 12, DOW 17 or HAE method). Then, these films are ectrolyzed in the aqueous solution containing metal ions by the ternating voltage. Table 4 shows the experimental conditions of e second AC treatment. The experimental results are shown in le 5. Fig. 1 shows the current-time curves during AC treatment.

dizing method by the step voltage

Magnesium alloy is anodized by the step voltage which is n in Fig. 2 Bathes for anodizing are DOW 12, DOW 17 and HAE es. Experimental results are shown in Table 6 and Fig. 3.

2.3 Anodizing methods by the alternating voltage superimposed on direct voltage

Magnesium alloy is anodized by the alternating voltage superimposed on direct voltage in the DOW 12, DOW 17 and HAE bathes, respectively. Table 7 and Fig. 4 show experimental results.

3. Basic experiments on magnesium films formed by the convensional methods.

Characters of film on magnesium formed by the conversional methods (DOW 9, DOW 12, DOW 17 and HAE) are studied.

Fig. 5 shows the X-ray diffraction charts of films. Photo. 1 shows the surface observed by the scanning electronmicroscope. Charts of Auge electronmicroscopy are shown in Fig. 6 ∿ Fig. 10.

Table 1 Japanese Industrial Standard for surface treatment of magnesium (JIS-H-8651)

Type of surface treatment (JIS)	Reference
Type 1A	MIL Spec. Type 1
Type 1B	I.G. Method
Type 2	MIL Spec. Type 2
Type 3	MIL Spec. Type 3
Type 4	Selenious acid method
Type 5	MIL Spec. Type 4
Type 6	MIL Spec. Type 5

Table 2 New patents on surface treatment of magnesium in Japan (From 1966 to 1977)

No. of patent	Title of patent	Assignee
41-2525 (1966)	Surface celaner for magnesium alloy	DOW Chem. Co.
41-15285 (1966)	Film formation of magnesium compound on steel	Fuji Steel Co Ltd.
43-7858 (1968)	Chemical milling of magnesium alloy	DOW Chem. Co.
43-12253 (1968)	Painting on magnesium alloy	Japanese defe ministry
43-22371 (1968)	Chemical conversion film on magnesium alloy	U.K. Atomic Energy Autho (England)
44-19965 (1969)	Chemical conversion film on magneisum alloy	DOW Chem. Co
48-31459 (1973)	Anodizing of magnesium alloy	Japan-Bell H Co., Ltd.
48-39135 (1973)	Galvanizing of magneisum alloy	Private pers (Japan)
50-133126 (1975)	Acid cleaning of magnesium	(Sweden)
51-17133 (KOKAI, 1976)	Preservation method of magnesium powder	Japanese def ministry and Nippon Kiha Co., Ltd.
51-24986 (1976)	Formation of diffusion film on magnesium	Chrom-alloy Ltd. (U.S.A.)
52-95546 (KOKAI, 1977)	Chemical conversion film on magnesium	Japan-Parke Co., Ltd.

Table 3 Experimental conditions of pretreatment of magnesium alloy

	Bath composition		Conditions of pretreatment
Alkaline	NaOH	100 g/ℓ	90°C dipping for 10 ∿ 20 min.
cid cleaning	55% HNO_3	100 mℓ/ℓ	15 ∿ 40°C
	$Fe(NO_3)_3 \cdot 9H_2O$	50 g/ℓ	dipping for 1 ∿ 3 min.
	KF	5 g/ℓ	
shing			flowing water 10 min.

Table 4 Experimental conditions of the the second AC electrolysis

	Bath composition		Electrolysis
ath	$NiSO_4 \cdot 6H_2O$	30 g/ℓ	1 ∿ 20V (AC) 20°C 2 min.
	H_3BO_3	30 g/ℓ	
ath	$SnSO_4$	5 g/ℓ	
n Bath	$SnSO_4$	5 g/ℓ	
	$NiSO_4$	20 g/ℓ	
	H_2SO_4	5 g/ℓ	
h	$CuSO_4$	10 g/ℓ	
	H_2SO_4	5 g/ℓ	

Table 5 Experimental results by the two steps electrolysis method

First treatment	Second treatment (AC electrolysis)			
	Ni Bath	Sn Bath	Ni-Sn Bath	Cu Bat
DOW 9	12 ∿ 15V(AC) grey	15V black	15V black	15V black
DOW 12	12 ∿ 15V grey	12 ∿ 15V grey	12 ∿ 15V black	15V Greeni grey
DOW 17	12 ∿ 15V Dark grey	12 ∿ 15V Greenish grey	15V black	15V Green blac
HAE	15V grey	12 ∿ 15V Yellowish white	15V black	×

Table 6 Experimental results of the anodizing by the step voltage

Bath	(A) type voltage	(B) type voltage
DOW 12	E_1 = 25V, t_1 = 5 min. E_2 = 4V, t_2 = 25 min. Silver	E_1 = 8V, t_1 = 30 sec E_2 = 2V, t_1 = 5 sec Anodizing time = 30 min. Greyish silver
OW 17	E_1 = 30V, t_1 = 5 min. E_2 = 8V, t_2 = 25 min. Green	E_1 = 6V, t_1 = 30 sec E_6 = 1V, t_6 = 10 sec Anodizing time = 30 min. Green
AE	E_1 = 20V, t_1 = 5 min. E_2 = 6V, t_2 = 25 min. Greyish white	E_1 = 20V, t_1 = 30 sec E_2 = 2V, t_2 = 5 sec Greyish white

Table 7 Experimental results of anodizing by alternating voltage superimposed on the direct voltage

Bath	Results
DOW 12	DC = -10V, AC = 20V, Anodizing time 30 min. (Greyish silver)
DOW 17	DC = -10V, AC = 15V, Anodizing time 30 min. (Greenish white)
HAE	DC = -10V, AC = 20V, Anodizing time 30 min. (Yellowish brown)

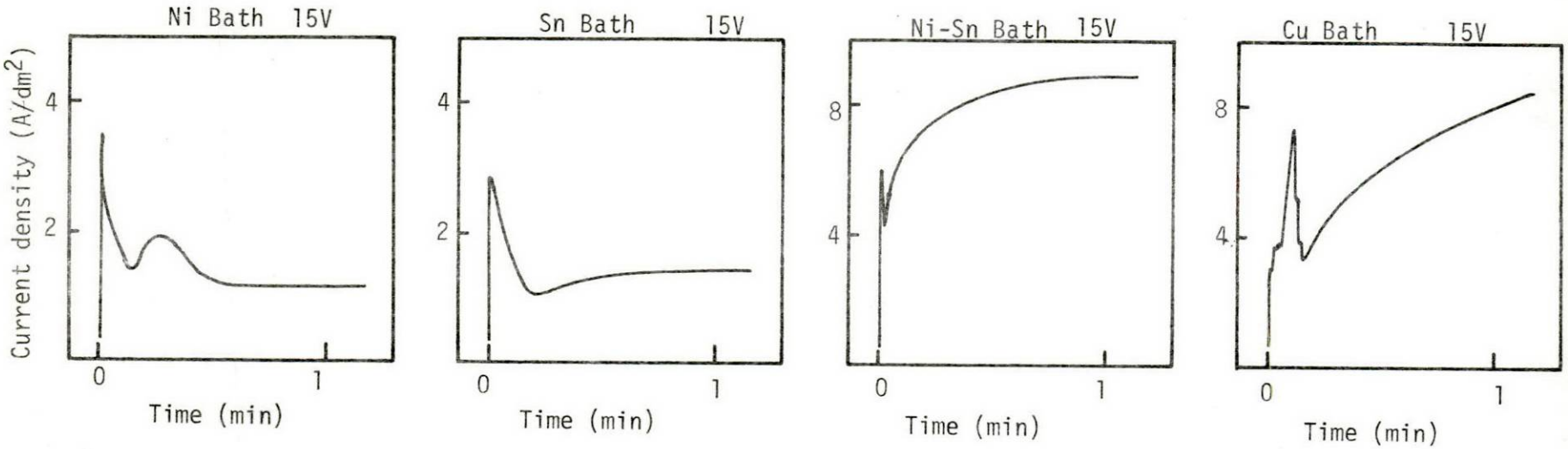


Fig.1 Current - time curves during A.C. electrolysis in a metalic solt solution.

(Magnesium oxid film is formed by Dow 12)

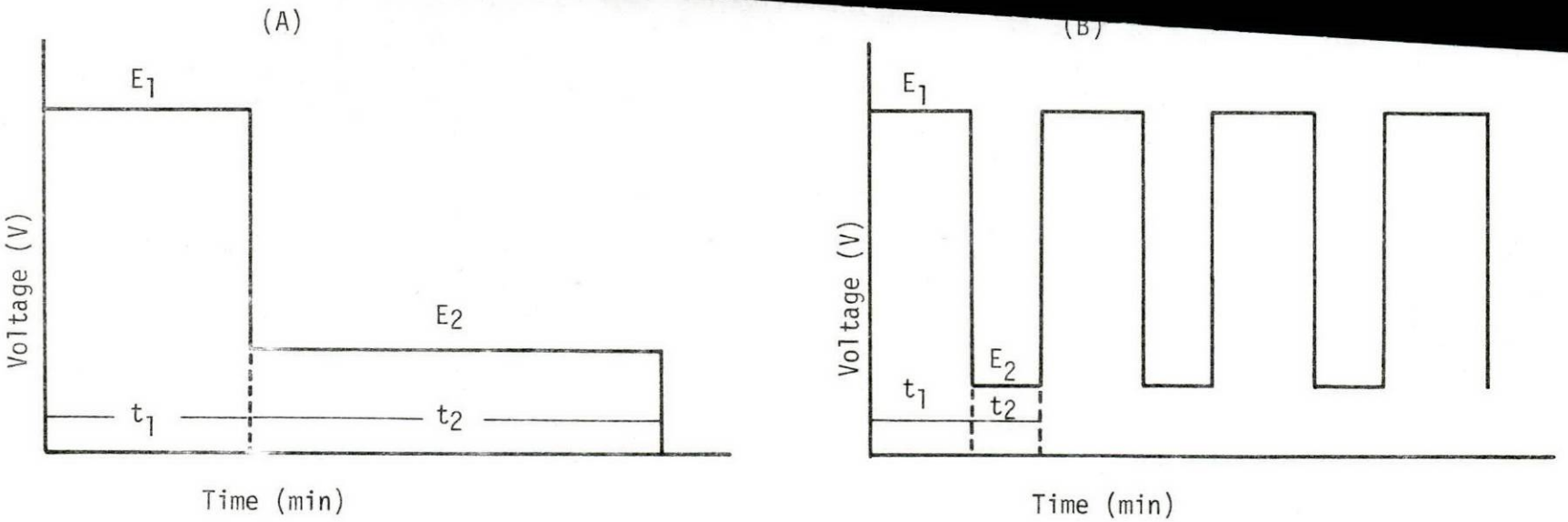


Fig.2 Step voltage.

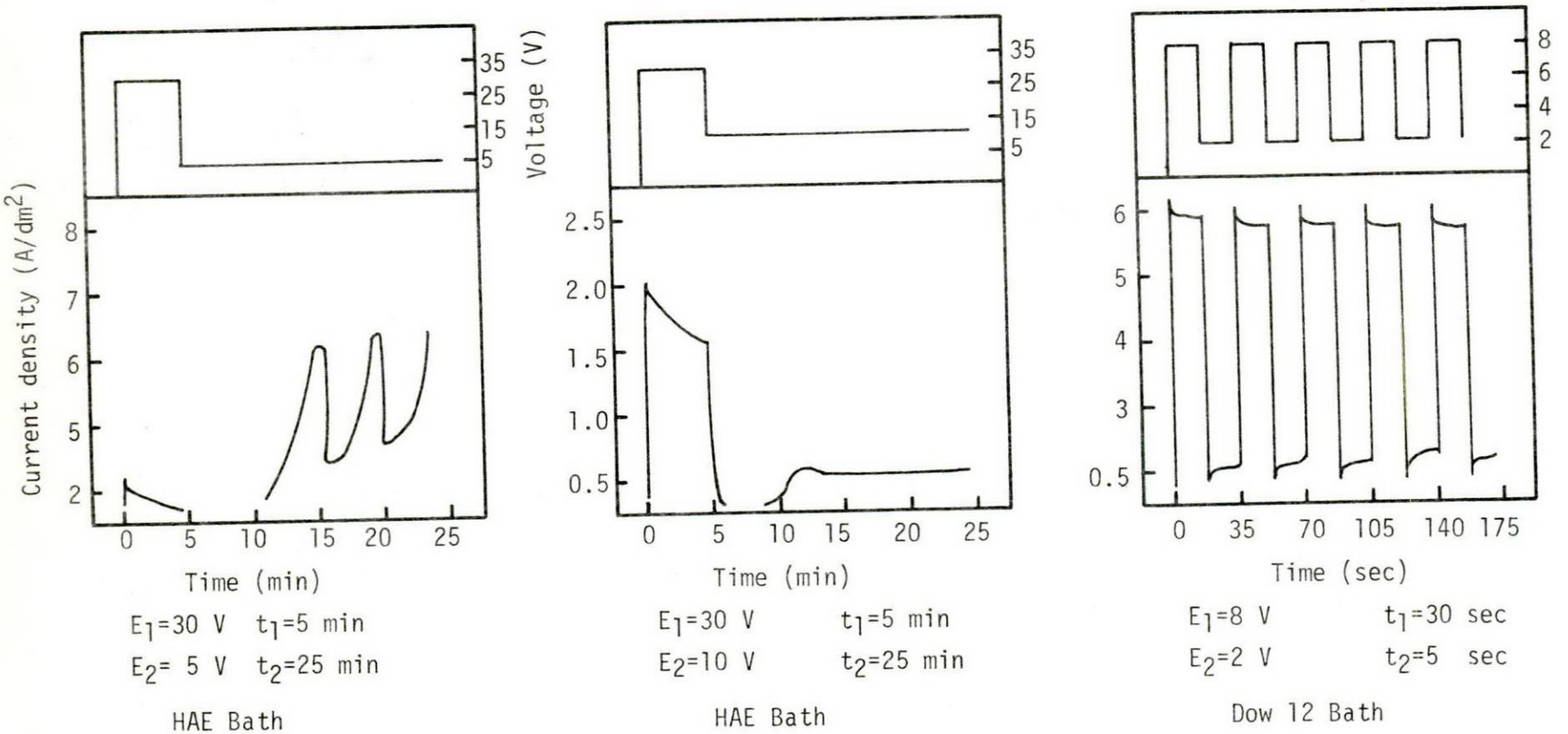
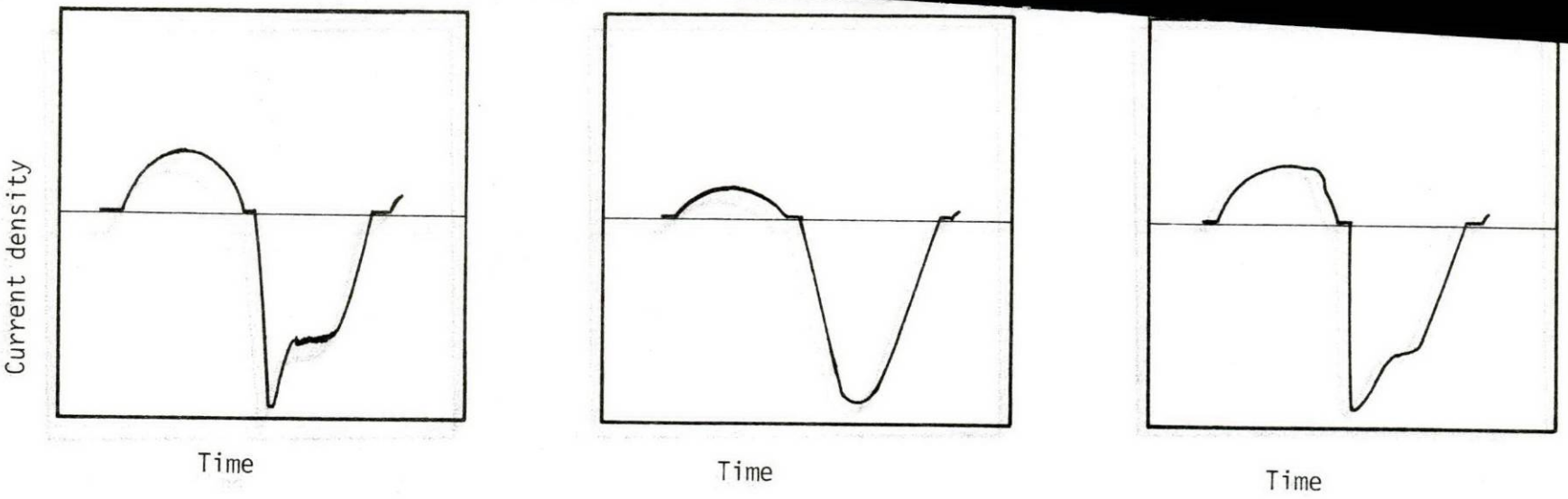


Fig.3 Experimental results of anodizing by the step voltage



D.C. = -10 V
A.C. = 20 V

Dow 12 Bath

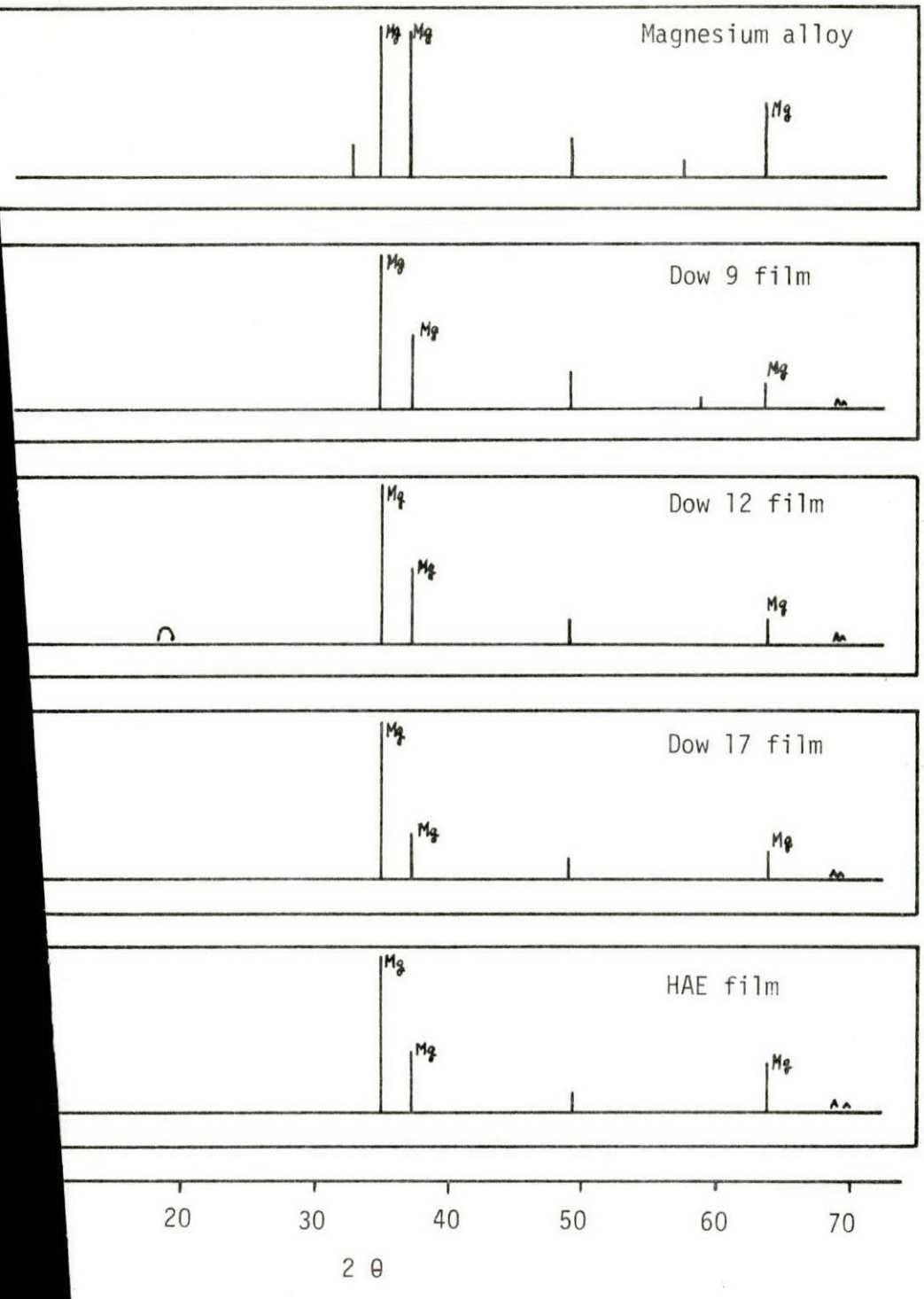
D.C = -10 V
A.C.= 15 V

Dow 17 Bath

D.C. = -10 V
A.C. = 20 V

HAE Bath

Fig.4 Current wave forms during anodizing with the alternating voltage superimposed on direct voltage.



ay diffraction charts of magnesium oxide films formed by the
vensional methods. (cathod Cu)

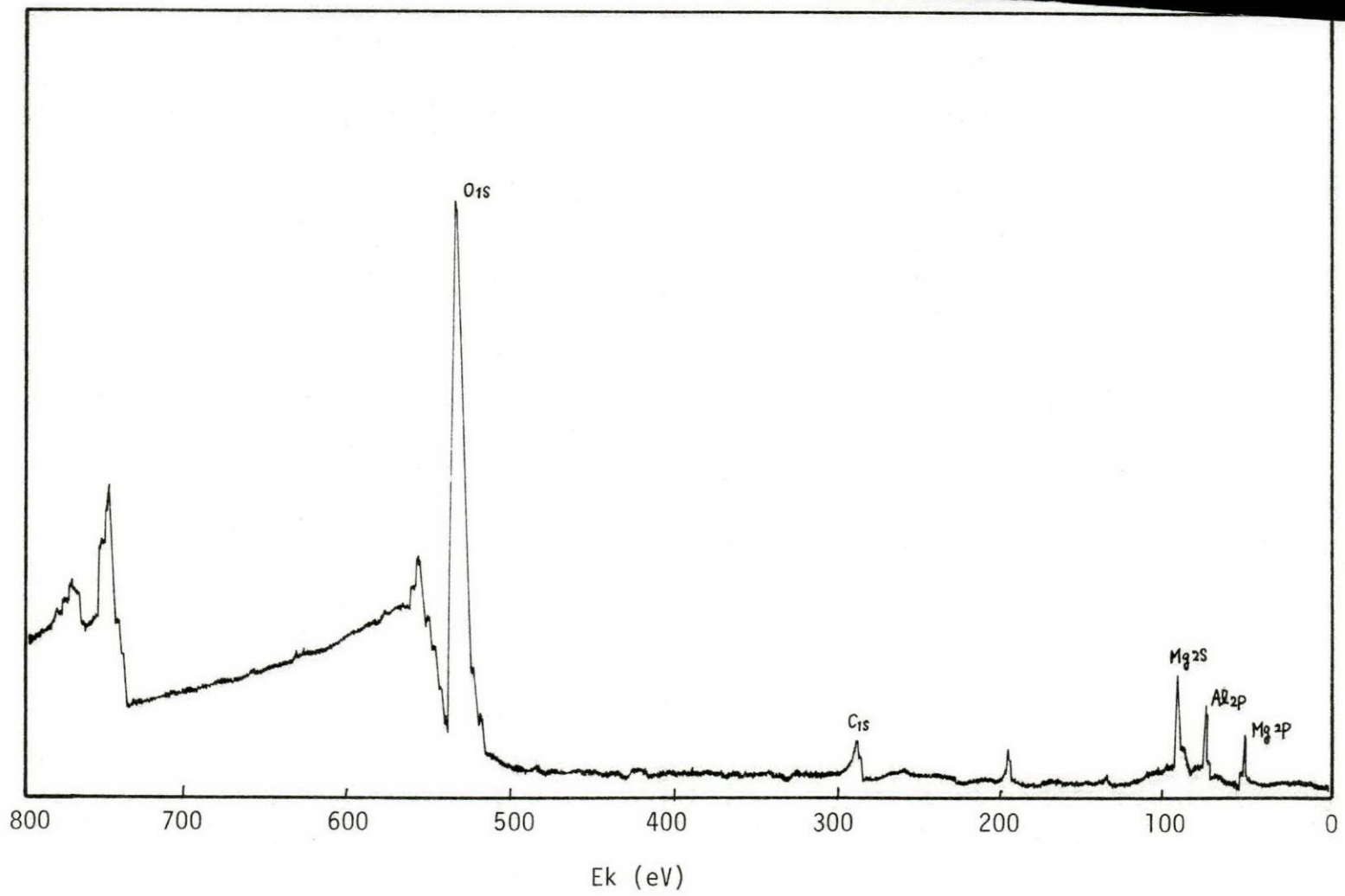


Fig.6 ESCA spectrum of a magnesium alloy.

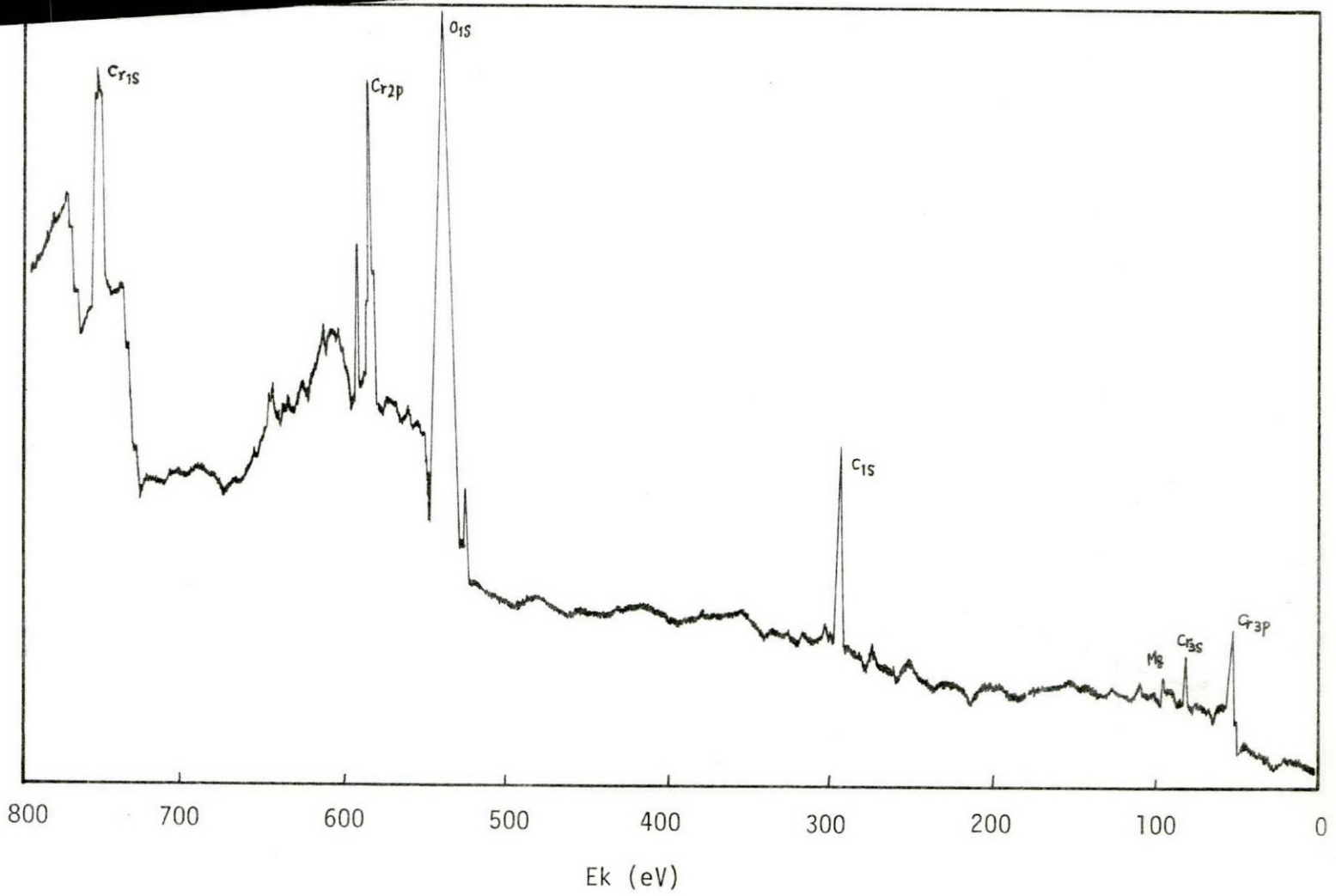


Fig.7 ESCA spectrum of a magnesium alloy. (Anodized by Dow 9 bath.)

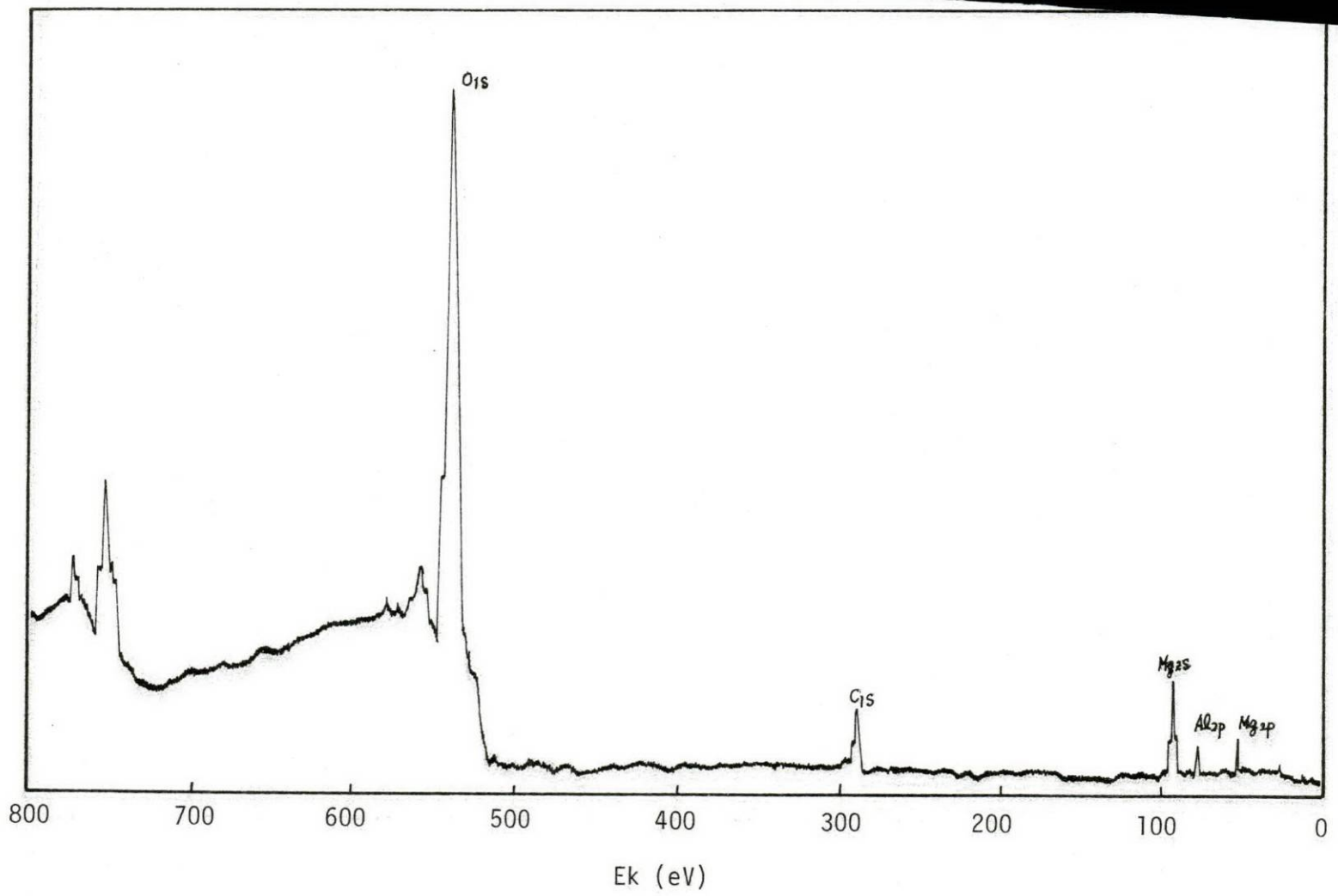


Fig.8 ESCA spectrum of a magnesium alloy. (Anodized by Dow 12 bath.)

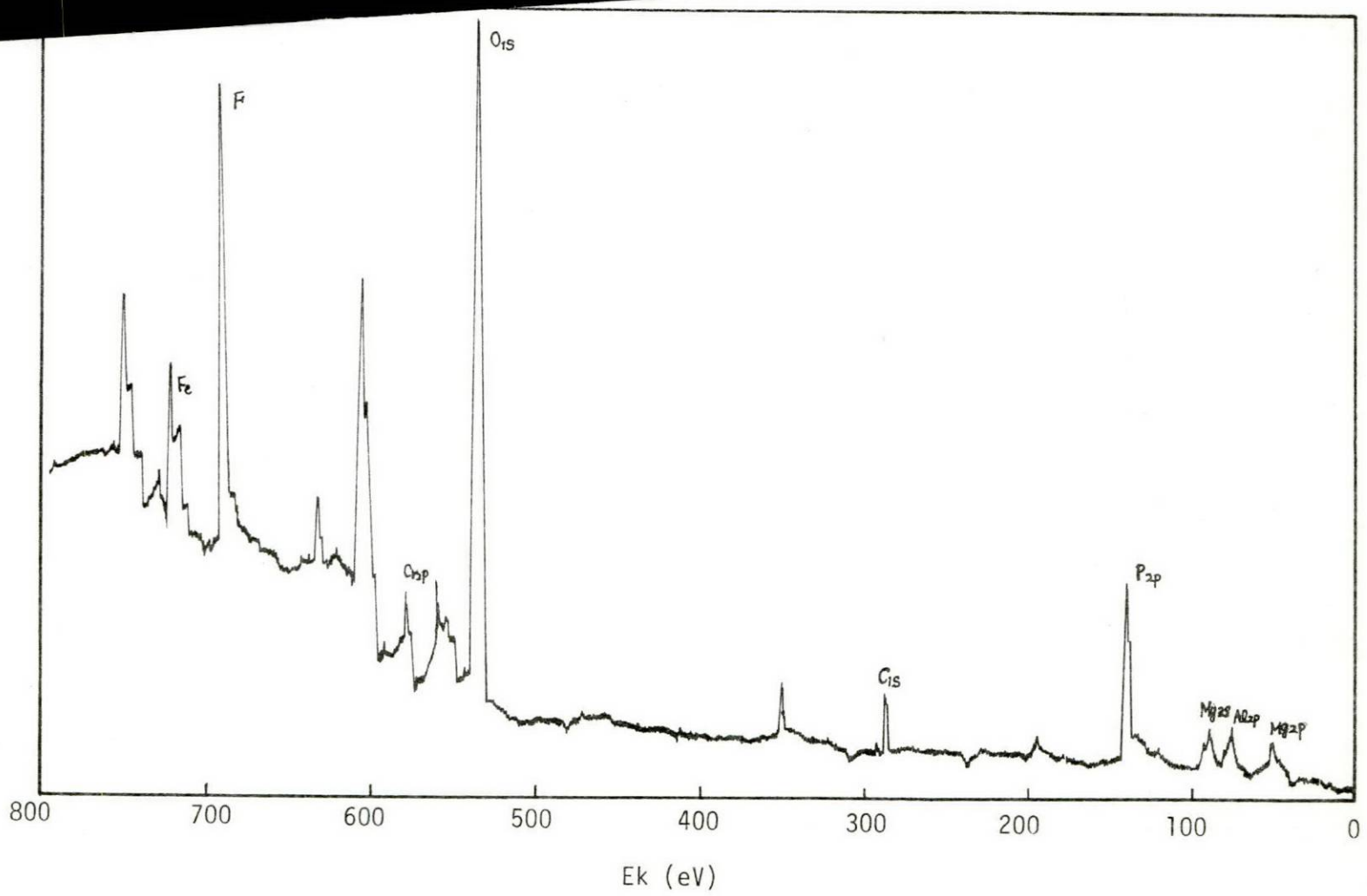


Fig.9 ESCA spectrum of a magnesium alloy. (Anodized by Dow 17 bath.)

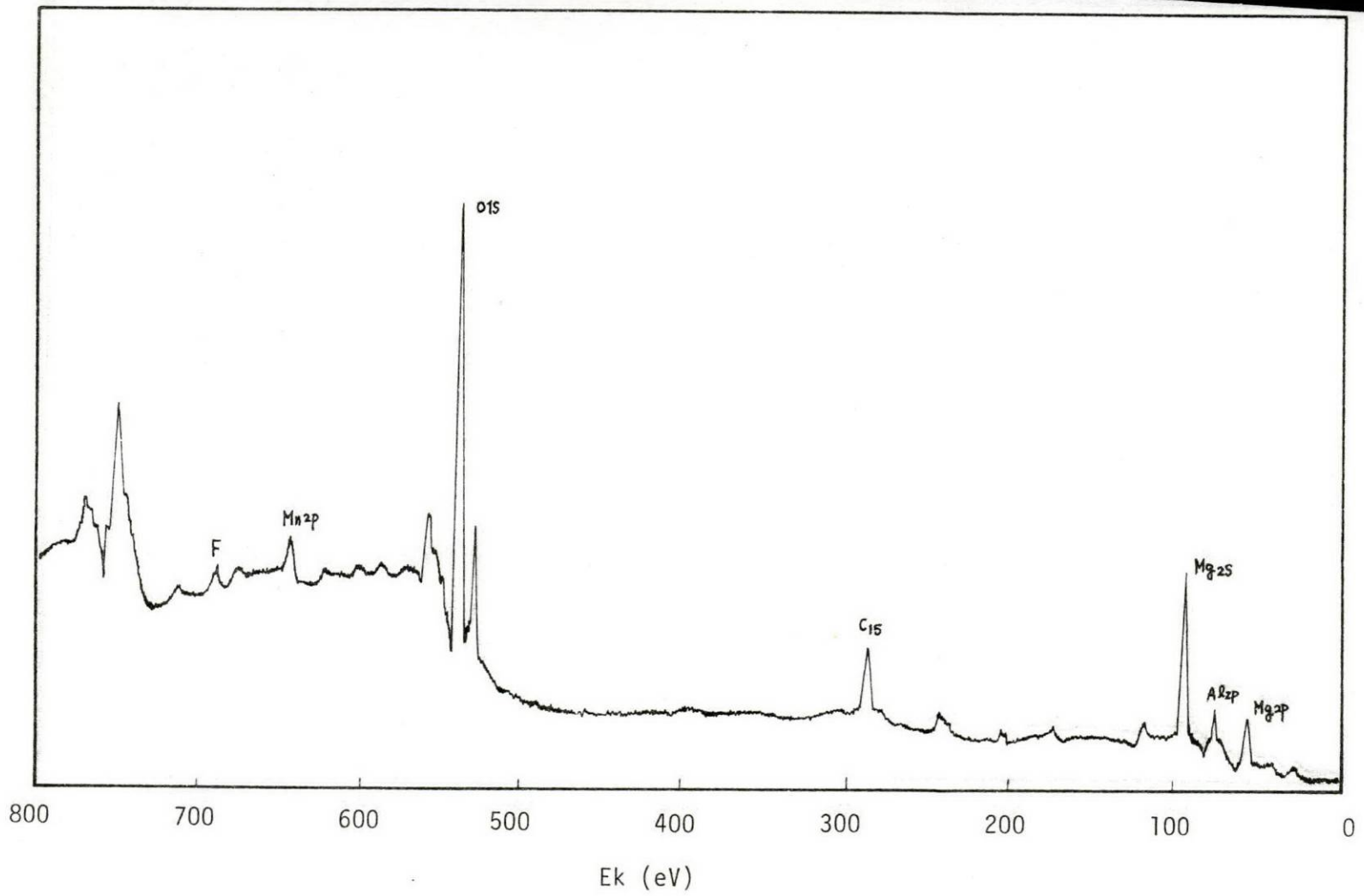
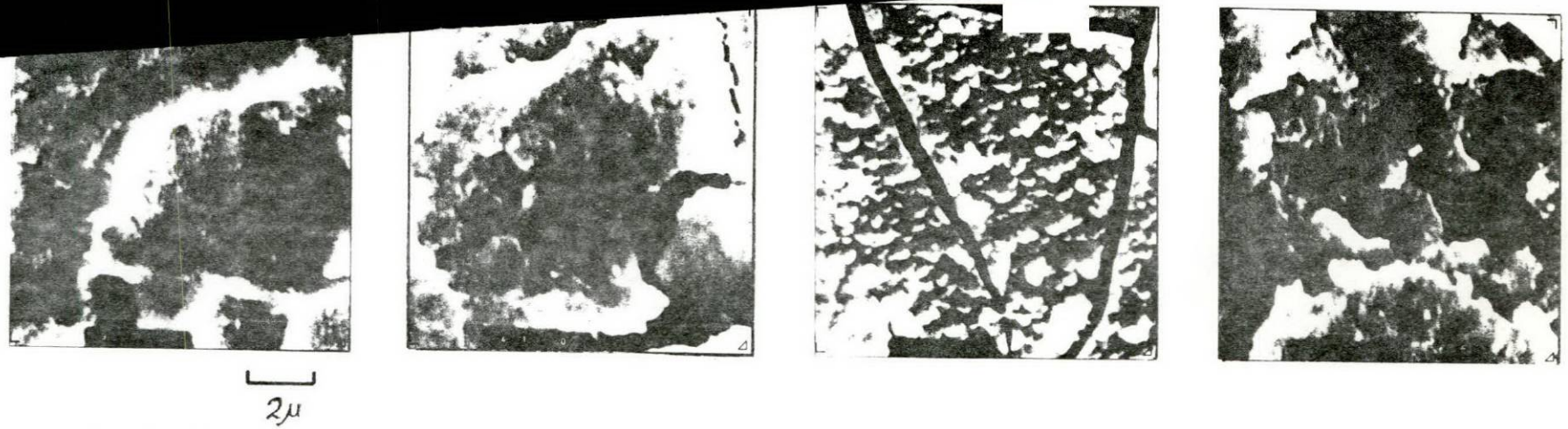


Fig.10 ESCA spectrum of a magnesium alloy. (Anodized by HAE bath.)



Dow 9 film | Dow 12 film | Dow 17 film | HAE film

Photo 1 Surface of magnesium oxide films formed by the convensional method.

I-2

Light Metals Finishing III
Session I

Electrolytic Coloring of Anodized Aluminum With Nickel Sulfate

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ELECTROLYTIC COLORING OF ANODIZED ALUMINUM WITH NICKEL SULFATE

By T. Sato and S. Sakai

Some basic experiments on electrolytic coloring of anodized aluminum with nickel sulfate are reported. These experiments are cathodic polarization of aluminum oxide film in a nickel sulfate aqueous solution by direct current, polarization of oxide film by alternating current, effects of oxide film on metal deposition and origin of colors by the electrolytic coloring process.

Introduction

When anodic oxide film on aluminum is electrolyzed in the solution containing metal ions, oxide film is colored. This coloring process was invented by Cabonie in 1936[1]. In 1940, one German engineer also invented an electrolytic coloring method of anodized aluminum[2]. But these electrolytic coloring methods had not been industrialized. In 1960, Asada made another patent of electrolytic coloring of anodized aluminum in Japan and in some other countries[3-7]. Then, the electrolytic coloring process by the alternating current was industrialized in Japan. This technology was introduced all over the world by ALCAN. Electrolytic coloring by the direct current was also industrialized in Japan in the early 1970's[8-10].

Technical reviews of the electrolytic coloring have been reported by Wernick and Pinner[11], Hermann[12], Sheasby and Cooke[13], and Shenoi et la[14]. These papers are good papers. But there are a few theoretical discussions in these papers.

In this paper, theories of electrolytic coloring of anodized luminum with nickel sulfate is reported.

lectrochemistry of electrolytic coloring

lectric plating and electrolytic coloring

Fig. 1 shows the electrolylic coloring process. First, aluminum 9.5% Aℓ) is anodized in a sulfuric acid bath (15 wt.% H_2SO_4) and ide film is formed on aluminum. The thickness of porous layer is ut 9 μm and that of barrier layer is about 150 Å. Diameter of e is about 100 Å and the thickness of pore wall is about 300 Å[11].

At the second step, the oxide film is electrolyzed in the solut containing metal ions. Metal ions are electrodeposited and oxi film is colored. So, electrochemical reaction during electroly coloring of anodized aluminum is written in equation (1).

$$M^{n+} + ne \longrightarrow M \qquad (1)$$

Equation (1) is as same as electrochemical reaction of ele plating. Theories of electric plating is well studied, because history of electric plating is more than 100 years. Some theor electric plating is useful to understand the mechanism of elec lytic coloring of anodized aluminum.

2.2 Ionics of electrolytic coloring

When nickel sulfate is dissolved in the distilled water, solution is clean and green-colored. The green color is due t presence of $[Ni\ (OH_2)_6]^{2+}$ in the bulk solution. When anodic film on aluminum is cathodically polarized in the nickel sulf single solution (30 g/ℓ $NiSO_4 \cdot 6H_2O$), green precipitate is obs on anodic oxide film. At oxide/solution interface, hydrogen are reduced to hydrogen gas. So, in this area, the concentra hydrogen ion is low and pH at the interface is high. Then, hydroxide is formed at the interface.

When boric acid is added to the nickel sulfate single s pH in the bulk solution does not change so much. But nickel deposited in the pores of oxide film, when oxide film is ele in the nickel sulfate-boric acid mixed bath (30 g/ℓ $NiSO_4 \cdot 6H$ H_3BO_3). And oxide film is colored brown. In this case, the precipitate ($Ni(OH)_2$) is not observed on the oxide film. B

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addition of boric acid, pH at the interface is kept constant. So, nickel hydroxide is not formed at the interface, and nickel ions can be reduced smoothly. It is often said that boric acid is a pH buffer reagent. And remember that boric acid is not only a pH buffer reagent but also complexing agent for nickel ions. Because, if the other pH buffer reagents are added to the nickel sulfate bath instead of boric acid, good results can not be obtained in the nickel plating and also in the electrolytic coloring of oxide film.

Cathodic polarization by direct current

Fig. 2 shows the cathodic polarization characteristics of aluminum oxide film in a nickel sulfate--boric acid mixed bath[15]. This polarization curve is measured by the linear voltage sweep method. In Fig. 2 three cathodic current peaks are observed at - 4 V, - 13 V and - 18 V respectively. When sulfuric acid is added to the coloring bath (pH = 2.0), oxide film is not colored and only the first cathodic current peak is observed at - 4 V and the first peak is very large. So, the first peak is due to the reduction of hydrogen ions.

When the concentration of nickel sulfate is changed, the third current peak is changed. And when oxide film is electrolyzed in the ammonium sulfate--boric acid mixed bath, oxide film is not colored, and the first and second current peaks are observed. But the third peak is not observed. So, the third current peak at - 18 V is due to the reduction of nickel ions.

When ammonium or sodium cations are added to the nickel sulfate bath, the second peak are changed large. But the origin of the second peak at - 13 V is unknown. Fig. 2 shows that the cathodic

voltage more than - 10 V is necessary for nickel deposition. I
tric plating, a few volt is enough for metal deposition. In th
electrolytic coloring the higher cathodic voltage is necessary
metal deposition. Because there is a barrier layer on aluminum
trode. And we must remember that electric field (or electric v
age) does not drop linearly in the barrier layer. When the thi
of barrier layer is half, the coloring voltage is not half. So
voltage drop in the cathode is shown as Fig. 3. In Fig. 3, η_c
is a total over voltage at cathode, η_{oxide} is a voltage drop i
barrier layer, and η_{HL} is the over voltage in Helmholz layer.
barrier layer, there are space charge layer, so the voltage dr
the barrier layer is not linear[16].

2.4 Polarization of oxide film by alternating current

When aluminum oxide film is electrolyzed in the nickel s
boric acid mixed bath by alternating voltage (50 Hz), deform
rent waveform is observed on the synchroscope (Fig. 4(B)).
current waveform is divided into two parts, that is, i_{NF} and
Fig. 4(B'). Current i_{NF} is the current to be charged or to
charged by oxide film. i_{NF} makes only physical change, and
chemical changes do not occur by this current. Current i_{NF}
called a non-Faradic current or a capacitive current. Curr
called a Faradic current or a reaction current. Change of
the change of impedance in the electrolysis system, and ch
i_F means change of reaction rate[17,18]. Change of impedanc
discussed in the next chapter, and Fig. 5 shows the chang
against the electrolyzing time[19]. In nickel sulfate sing

in nickel sulfate--boric acid mixed bath, i_F decrease and is almost zero after 4 minutes. While i_F is almost constant in ammonium sulfate--boric acid mixed bath or in sodium sulfate--boric acid mixed bath. These differences are due to the different electrochemical reactions. In the latter cases, the cathodic reactions are only reduction of hydrogen ions. Radius of hydrogen ions are small, so these hydrogen ions can enter into the barrier layer and reduced at metal/oxide interface. This reaction occurs at constant rate, so i_F is almost constant. In the cases of nickel sulfate single bath and of nickel sulfate--boric acid mixed bath, nickel ions are reduced at oxide/solution interface. After some deposition of nickel, reduction reaction ceases, so i_F is almost zero after a few minutes. In Na_2SO_4-H_3BO_3 bath, an anodic current peak is observed after 5 minutes. This anodic current means that barrier layer is anodically dissolved by Na^+ ions.

The effects of frequency of alternating voltage are studied[20]. When frequency is lower than 100 Hz, the shade of color is almost same. At 250 Hz, the color are a little lighter and cathodic current peak is small. When the frequency of alternating voltage is higher than 500 Hz, oxide film is not colored and cathodic current peaks are not observed.

Effects of anodic voltage of alternating voltage on electrolytic coloring is studied[21]. Asymmetrical voltage, shown in Fig. 6 (), is applied on oxide film in the $NiSO_4$-H_3BO_3 mixed bath. In these experiments, cathodic voltage is kept constant and only the anodic voltage is changed from 17 V to 0 V. When asymmetrical voltage is applied on oxide film, current waveforms shown in Fig. 6

(B) are observed. When anodic voltage is small, not only anod current but also the cathodic current peak are small. Anodic effects on the rate of cathodic reaction.

2.5 Effects of oxide film on metal deposition

In electric plating, metal ions deposit on metal surface. Electron is supplied to metal ions from metal surface. In the trolytic coloring of anodized aluminum, metal ions electrodepo on oxide surface. Then the effects of oxide film on metal dep tion are studied. Fig. 7 shows the relationship between the thickness of porous layer and cathodic current[22]. When the t ness of porous layer is thinner than 2 μm, cathodic current b ions is very high and oxide film is not colored by cathodic p rization. When porous layer is thinner than 6.5 μm, the firs the second cathodic current peaks are observed, but the thir is not observed and oxide film is not colored. When the thi of porous layer is thicker than 9 μm, three current peaks ar observed and oxide film is colored. In the electrolytic col with direct current, the thickness of porous layer is very portant.

Fig. 8 shows the effects of the thickness of barrier l the electrolytic coloring with direct current[22]. In these ments, the thickness of porous layer are constant, and only thickness of barrier layer is changed by the "Recovery Eff proposed by Wood et la[23]. When the thickness of barrier l thinner, cathodic current peaks appear at lower voltage.

Fig. 9 shows the impedance of oxide film in a nickel

boric acid mixed bath[24]. Before the electrolytic coloring with cathodic current, impedance of oxide film is 6.3 $K\Omega \cdot cm^2$. When cathodic voltage is applied on oxide film, the impedance decreases suddenly (1.2 $K\Omega \cdot cm^2$), and during cathodic polarization, the impedance increases gradually. This impedance consists of impedance of barrier layer, Faradic impedance and impedance of electrodeposited materials. After cathodic polarization oxide film is colored, and the impedance of oxide film is larger than the impedance which was measured before the electrolytic coloring. Increase of impedance after cathodic polarization is due to deposition of metallic colloids in the pores of oxide film and change of electric character of barrier layer.

Origin of colors by electrolytic coloring

Origin of colors in general

There are many colored materials in the world. The origin of these colors are mainly grouped into two classes. These are "color by dispersion of light" and "color by absorption of light". Sky looks blue. There are many fine particles in the sky. These fine particles disperse the light. Then, sky looks blue. So, the origin of blue sky is due to the dispersion of light. Some kinds of colloid suspension show red, yellow, green or blue colors respectively. These colors are also due to the dispersion of light by colloidal particles.

Origin of blue ink is not as same as origin of blue sky. Blue ink absorbs yellow and red colors, so the ink looks blue.

Origin of colored oxide film by organic dyestuff is due to the

absorption of light. Origin of color by integral coloring is no studied well. Some one says that the origin of integral colorin is due to the absorption of light by aluminum complex compound i the oxide film. While, the other says that origin of color is due to the dispersion of light by carbon colloids or by aluminum colloids in the oxide film[25].

3.2 Origin of colors by electrolytic coloring

When aluminum oxide film is electrolyzed in a metallic sal solution, metal deposits in the pores of oxide film. It was sa in the early studies that metal oxide or other metal compound deposited in the pores of oxide film, and that these compounds absorbed the light and oxide film is colored[17].

Recently by new instrument analysis methods, Ni, Co, Sn, and Ag are deposited in the pore as metal[13]. Then, the origi color by electrolytic coloring is due to the metal colloids d ited in the pores of oxide film. This mechanism will be disc in detail. In electronmicroscopic scale, the thickness of ba layer is not uniform as shown in Fig. 10 (A). When this oxi is electrolyzed in the metal salt solution, metal deposit li osition shown in Fig. 10 (B). There is a size distribution electrodeposited metal. Because of this size distribution, range of wave length of dispersed light is wide. So, oxide looks brown. When the coloring time is longer than the usu ing time, much metal deposit and size distribution of metal are more wide, so oxide film looks black. Size distributio electrodeposited metal is different by kinds of metal. So

color by nickel and brown color by tin looks different a little.

According to the above mentioned hypothesis for colors by electrolytic coloring, primary colors like blue, green, or red must be colored when the size distribution of metal colloids is narrow (Fig. 10 (C)). We can get pink, green, violet and blue colors with nickel sulfate[26]. When aluminum is anodized in a sulfuric acid bath at lower voltage, the thickness of barrier layer is thin and the difference of thickness of barrier layer are very small. In this case, the size of electrodeposited metal is uniform. Then, the range of wave length of dispersed light is narrow and oxide film looks pink, red, green or blue. Table 1 shows results of this experiment.

Possibility of new colors by electrolytic coloring

Usually yellow, brown and black colors are obtained by the electrolytic coloring. These days, new colors like green, blue or red are required by architects and so on. There are two ways to make a new color by electrolytic coloring. These principles are,

(A) Modification of barrier layer

(B) Formation of colored compound in the oxide film

Now, some examples of principle (A) and (B) will be introduced as follows. There is a famous patent by Dr. Asada and ALCAN[27,28]. According to this patent, oxide film is formed in a usual bath. Then, this oxide film is again anodized in a phosphoric acid bath, and at the third step oxide film is electrolyzed in the metal salt solution. Blue and gray colors can be made. The present authors think that the principle of this patent are schematically shown in Fig. 11. The thickness of barrier layer formed in a sulfuric acid

bath is not uniform as shown in Fig. 11 (A). When this oxide fi is again anodized in the phosphoric acid bath, the thickness of barrier layer is to be thick, because the anodizing voltage is higher in a phosphoric acid bath. And also the difference of thickness of barrier layer is small, so electrodeposited metal colloids are uniform and oxide film looks gray or blue (Fig. 11 (C)).

Recently two new patents are reported. In these patents, o film is formed in a sulfuric acid bath, and then this oxide fil again anodized in a chromic acid bath[29] or in an organic acid b And at third step, these oxide film is electrolyzed in a metal solution. Then, blue, green, or violet color is obtained. The authors think that principles of new patents are almost as same the principle of Dr. Asada's patent.

There is other interesting patent[31]. Oxide film is made sulfuric acid bath, and then this oxide film is dipped in a wa sulfuric acid solution. At third step, this oxide film is ele lytically colored. Colors are blue, green, pink and so on. T authors think that the principle of this process is to make th thickness of barrier layer uniform by dissolution of oxide fi a warm sulfuric acid solution.

When oxide films, anodized in a chromic acid bath or in phoric acid bath, are electrolyzed in the nickel sulfate bath pastel-blue color is obtained[32]. In this case metal deposits branched pores of oxide film.

Another principle to make new colors is "Formation of c compound in the oxide film". Usually the origin of electrol

colored film is due to the dispersion of light by the electrodeposited metal particles. So, this principle is different from the usual electrolytic coloring method.

When aluminum oxide film is electrolyzed in a barium nitrate bath by alternating current, oxide film is colored opaque white[32]. In this case, the origin of color is due to the formation of $BaSO_4$ in the pores of oxide film. Barium sulfate is an insoluble white compound.

When oxide film is electrolyzed in a sulfuric acid bath containing small amount of Cu^{2+} ions, green film is obtained. The origin of green film is due to the formation of CuS[32].

Aluminum is anodized in an oxalic acid bath, then this oxide film is electrolyzed in a $KMnO_4$ solution. Pink colored film is obtained. Pink color is due to the formation of $MnCO_3$. Pink color was not stable and decolored after a few days, because $MnCO_3$ decomposed into MnO.

According to a German patent[33], blue color is obtained by electrolytic coloring of oxide film in a molybdenum salt bath. The origin of blue color may be due to molybdenum oxide (Molybdenum blue).

Conclusions

Electrolytic coloring of anodized aluminum is rather new technology and this technology is popular in European countries and Japan.

Electrolytic coloring has much possibilities. For example, the pattern coloring on anodized aluminum is also possible[32].

References

1) V. Caboni; Italian patent 399,232 (1936)

2) L. Pfanhenser; German patent 741,753 (1940)

3) T. Asada; Japanese patent 310,401 (1960)

4) T. Asada; British patent 1,022,927 (1966)

5) T. Asada; U.S. patent 3,382,160 (1968)

6) T. Asada; British patent 1,121,228 (1966)

7) T. Asada; Canadian patent 662,063 (1963)

8) Sumitomo Chemical Co.; Japanese patent 49-48824 (1974)

9) Sumitomo Chemical Co.; German patent 2,112,927 (1970)

10) Sumitomo Chemical Co.; British patent 1,331,365 (1973)

11) S. Wernick, R. Pinner; "The surface treatment and finishing of aluminum and its alloys", Fourth Ed., Vol. 2, Robert Draper Lt (1972)

12) E. Hermann; Galvanotechnik, 63, 110 (1972)

13) P. G. Sheasby, W. E. Cooke; Transaction of the Institute of M Finishing, 52, 103 (1974)

14) S. John, V. Balasubramanium, B. A. Shenoi; Finishing Industri April, 32 (1978)

15) T. Sato, S. Sakai; The Journal of the Metal Finishing Societ Japan, 29, 361 (1978)

16) S. M. Ahmed; "Oxide and Oxide Films", Ed. by J. W. D. Diggl Vol. 1, p 319, Marcel Dekker Inc. (1972)

17) H. Nozaki, K. Honda, S. Hanya, M. Kobayashi; Seisan-Kenkyu, 23, 262 (1971)

3) T. Suzube, A. Akiyama, T. Saji; The Journal of the Metal Finishing Society of Japan, 27, 531 (1976)

9) T. Sato, T. Harizuka; ibid., 28, 119 (1977)

0) T. Sato, T. Harizuka; ibid., 28, 236 (1977)

1) T. Sato, H. Hineno; ibid., 28, 181 (1977)

) T. Sato, S. Sakai; ibid., 29, 409 (1978)

) J. P. O'Sullivan, G. C. Wood; Proceedings of Royal Society of London, A, 317, 511 (1970)

T. Sato, S. Sakai; The Journal of the Metal Finishing Society of Japan, 29, 595 (1978)

N. Baba; Journal of Metal Society of Japan, 15, 393 (1976)

T. Sato; The Journal of the Metal Finishing Society of Japan, 28, 41 (1977)

T. Asada; Japanese patent 51-1337 (1976)

T. Asada, ALCAN; U. S. patent 4,022,671 (1976)

Pilot Pen Co.; Japanese patent 52-94832 (1977)

Pilot Pen Co.; Japanese patent 52-135841 (1977)

Fuji Sash Co.; Japanese patent 51-138543 (1976)

T. Sato; Plating and Surface Finishing, March, 53 (1978)

. Keller; German patent 2164030 (1976)

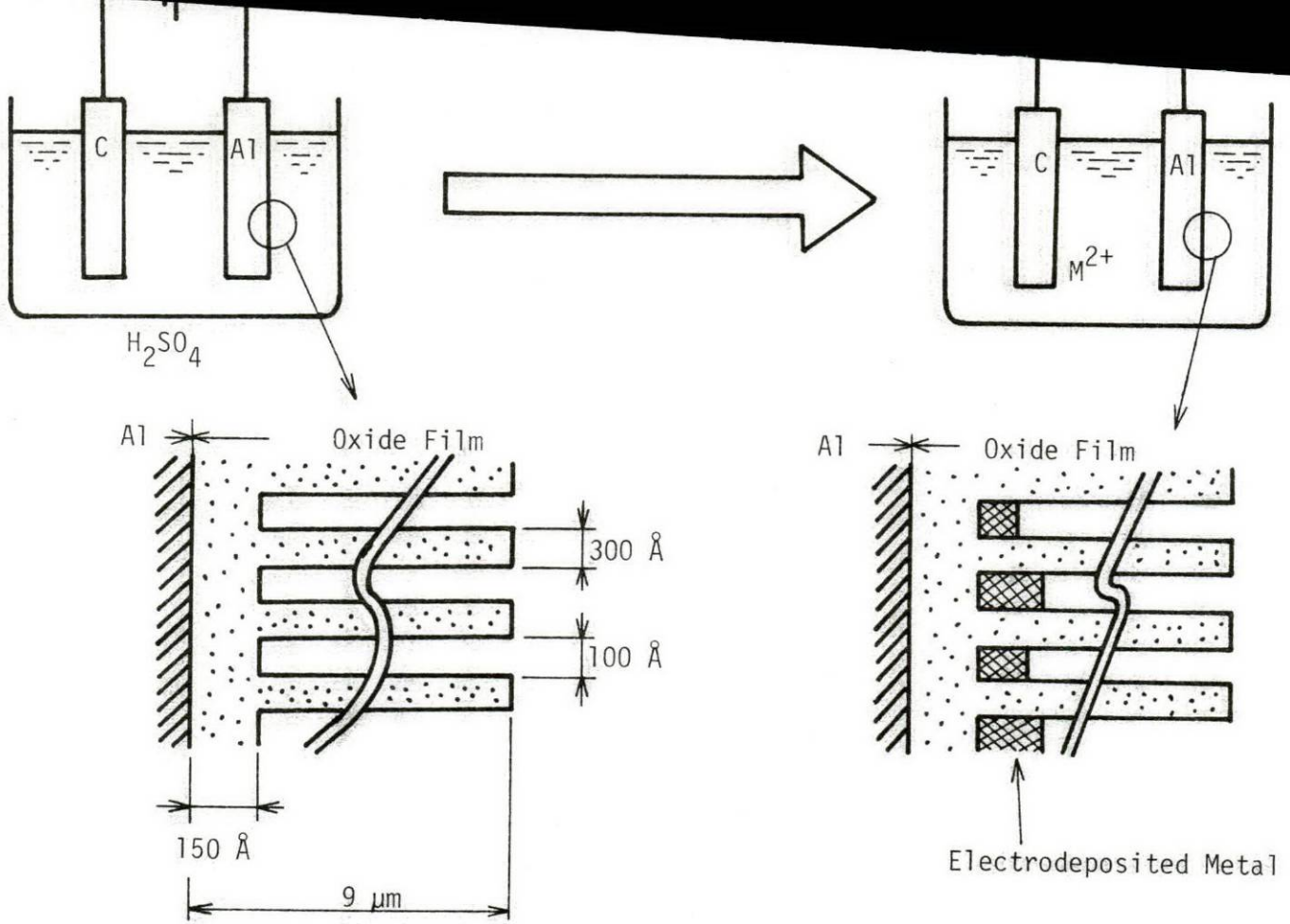


Fig.1 Electrolytic coloring process.

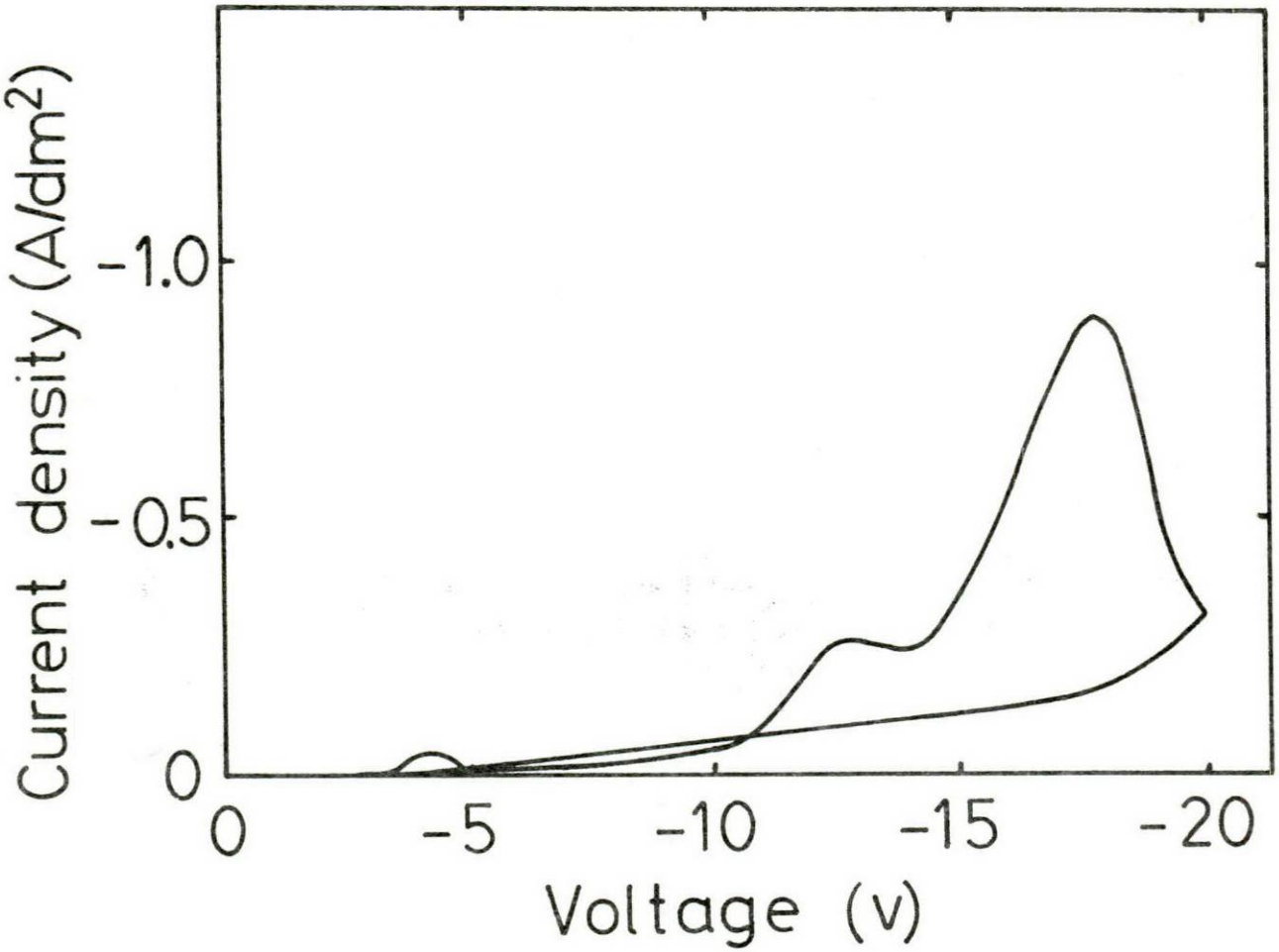


Fig 2 Cathodic polari

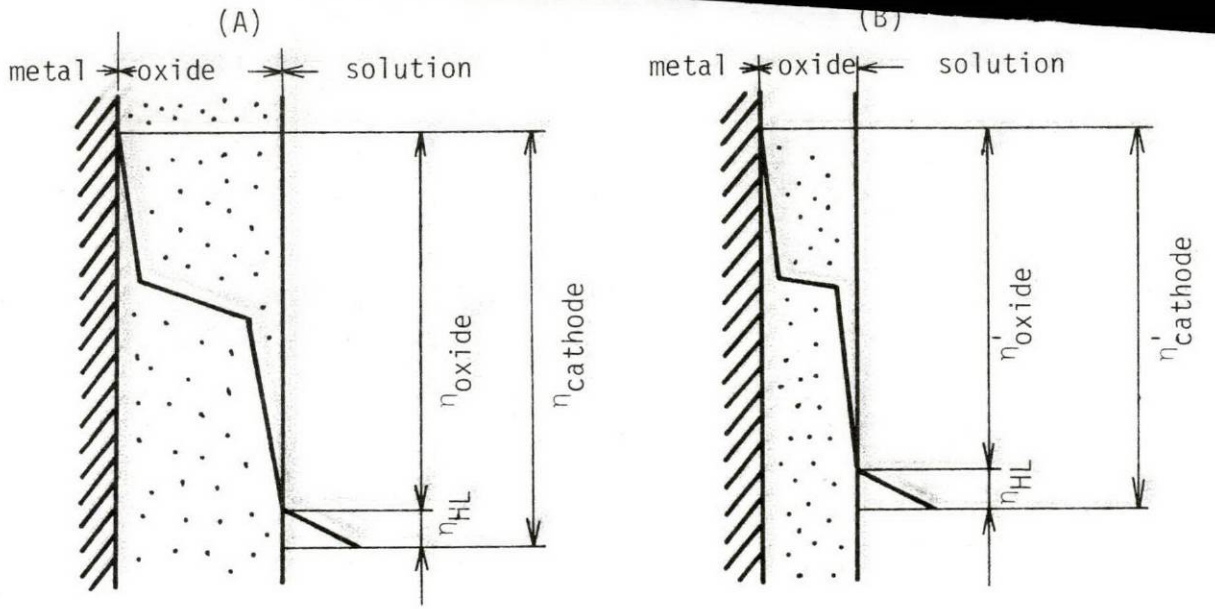
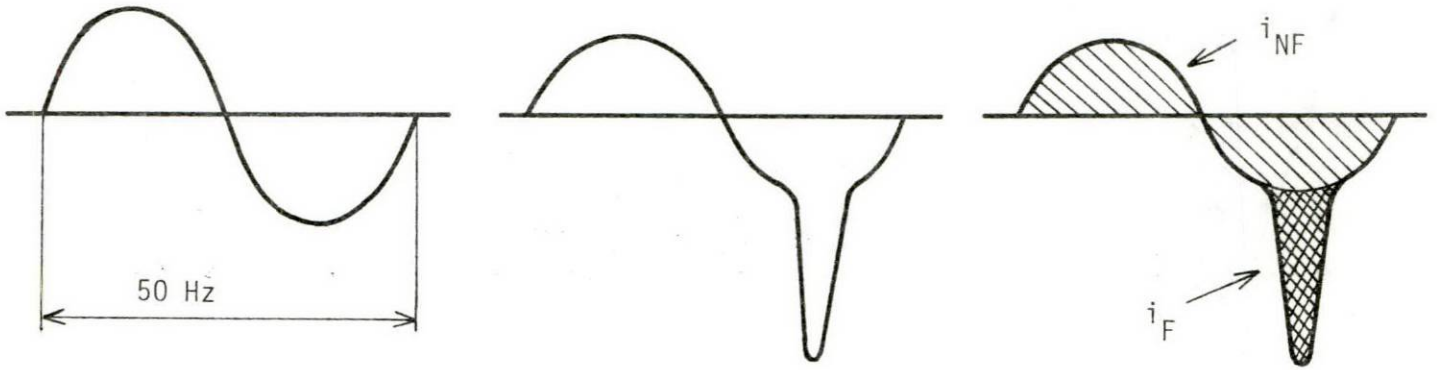


Fig.3 Voltage dropes in cathode electrode.



(A) Voltage (B) Current (B') Current

Fig.4 Voltage waveform and current waveforms (I).

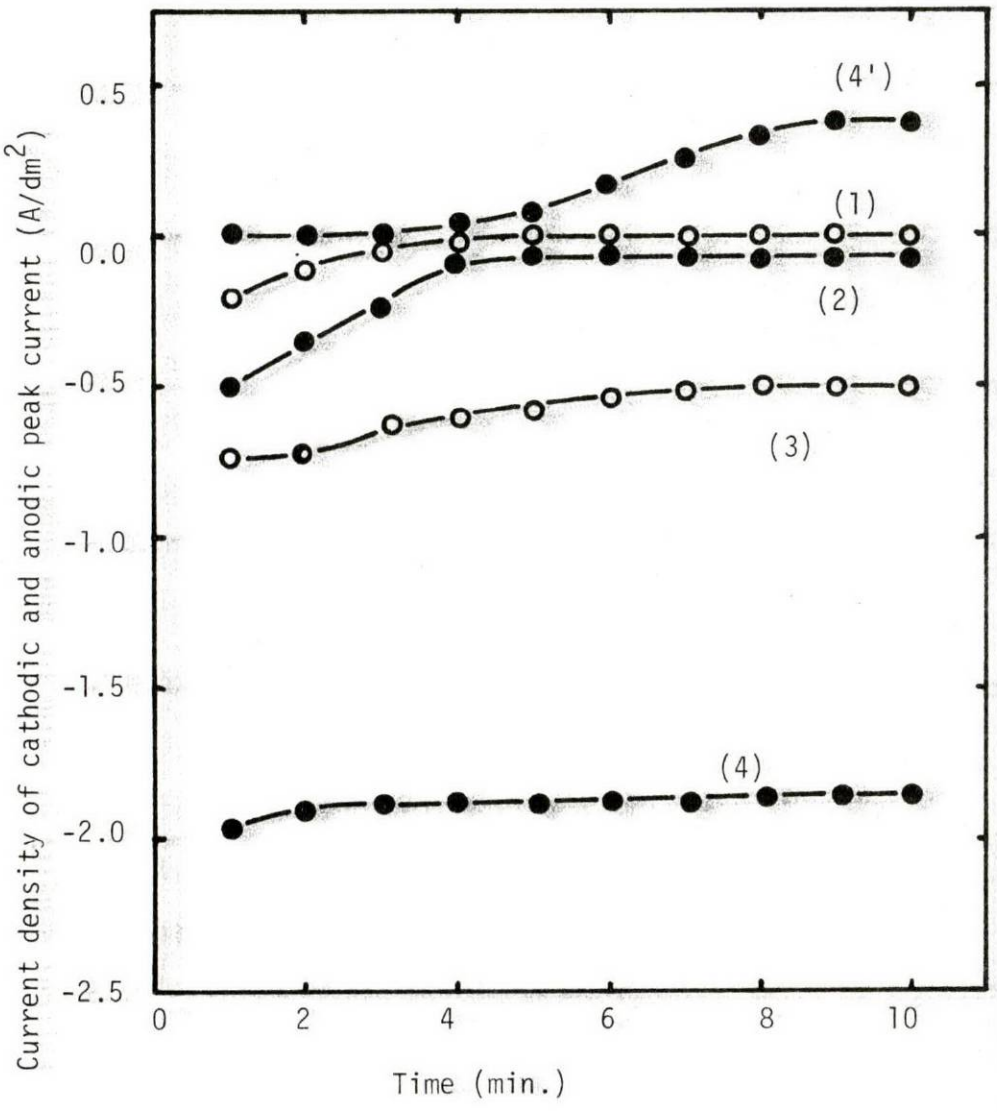


Fig.5 Peak current as a function of time.

(1) Cathodic peak current in $NiSO_4$.

(2) Cathodic peak current in $NiSO_4$-H_3BO_3.

(3) Cathodic peak current in $(NH_4)_2SO_4$-H_3BO_3.

(4) Cathodic peak current in Na_2SO_4-H_3BO_3.

(4') Anodic peak current in Na_2SO_4-H_3BO_3.

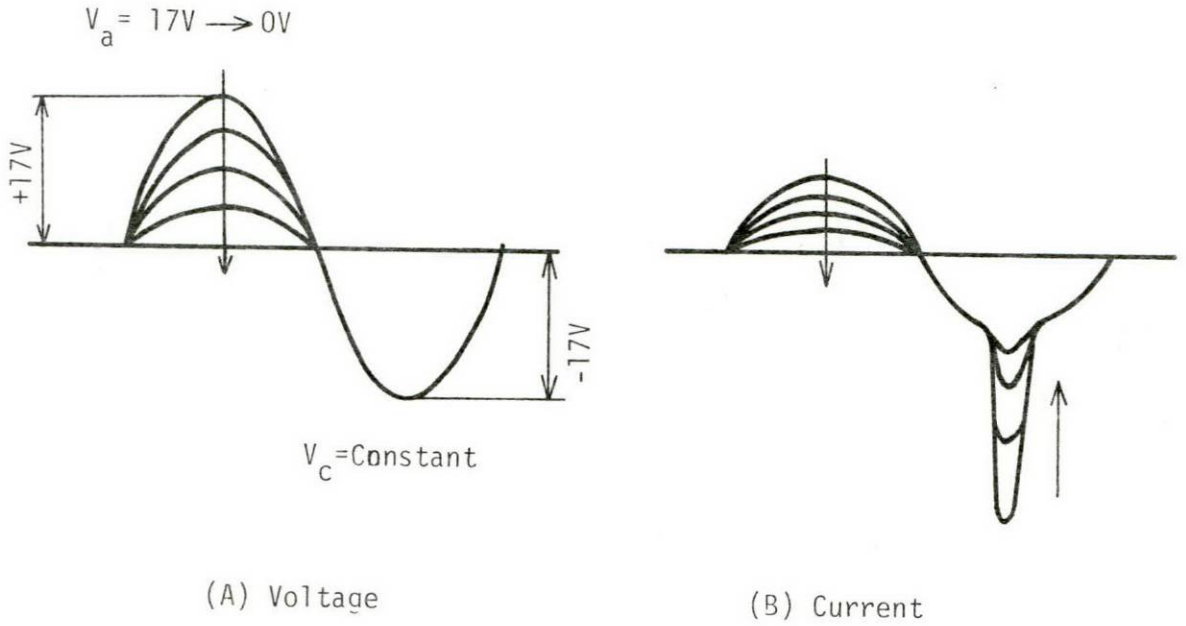


Fig. 6 Voltage waveforms and current waveforms (II).

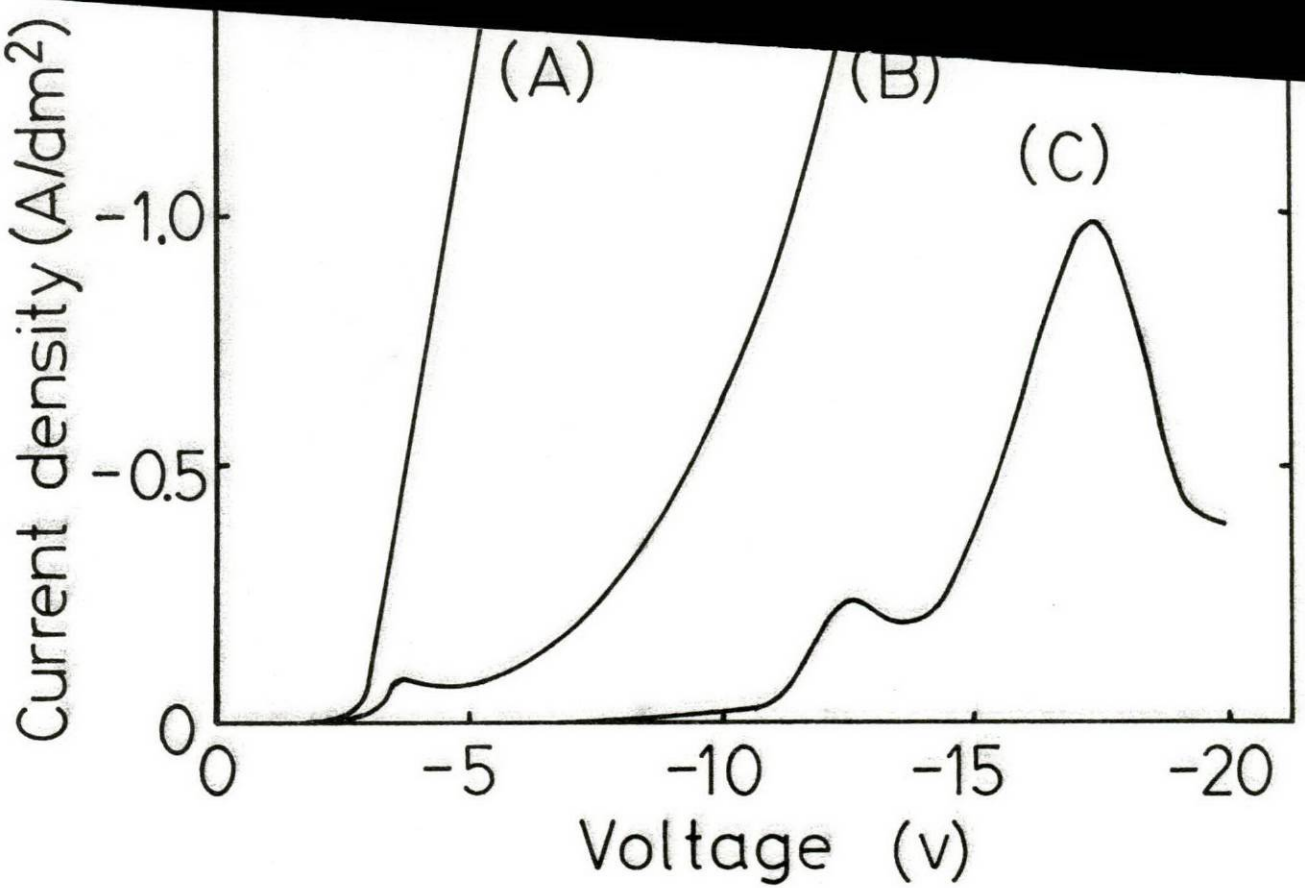


Fig.7 Cathodic porarization of anodic oxide film in a $NiSO_4$-H_3BO_3 mixed bath (Effects of the thickness of porous layer; Thickness of barrier is 150 Å). Thickness of porous layer ; (A) 2μm (B) 4μm (C) 9μm

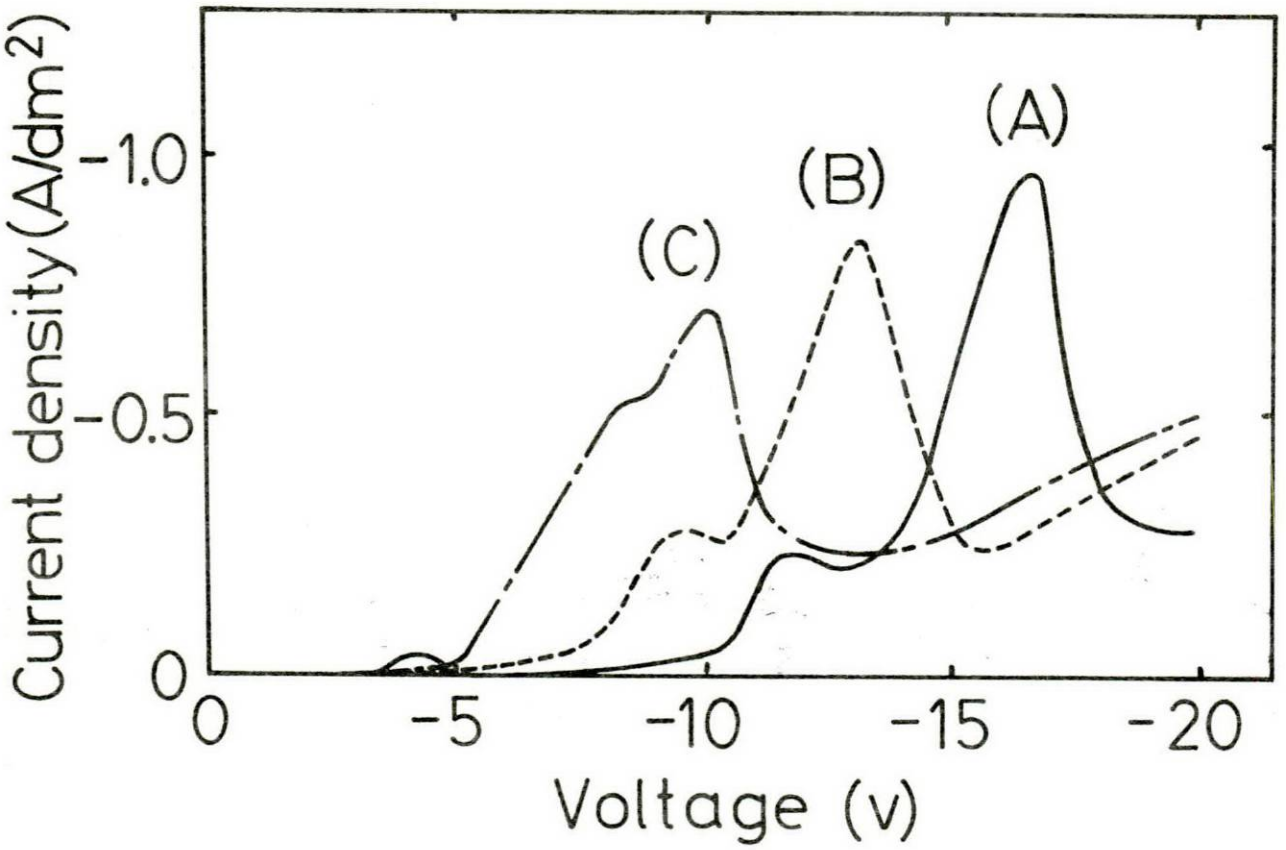


Fig.8 Cathodic polarization of anodic oxide film in a $NiSO_4$-H_3BO_3 mixed bath (Effects of the thickness of barrier layer; Thickness of porous layer is 9μm).

Thickness of barrier layer :

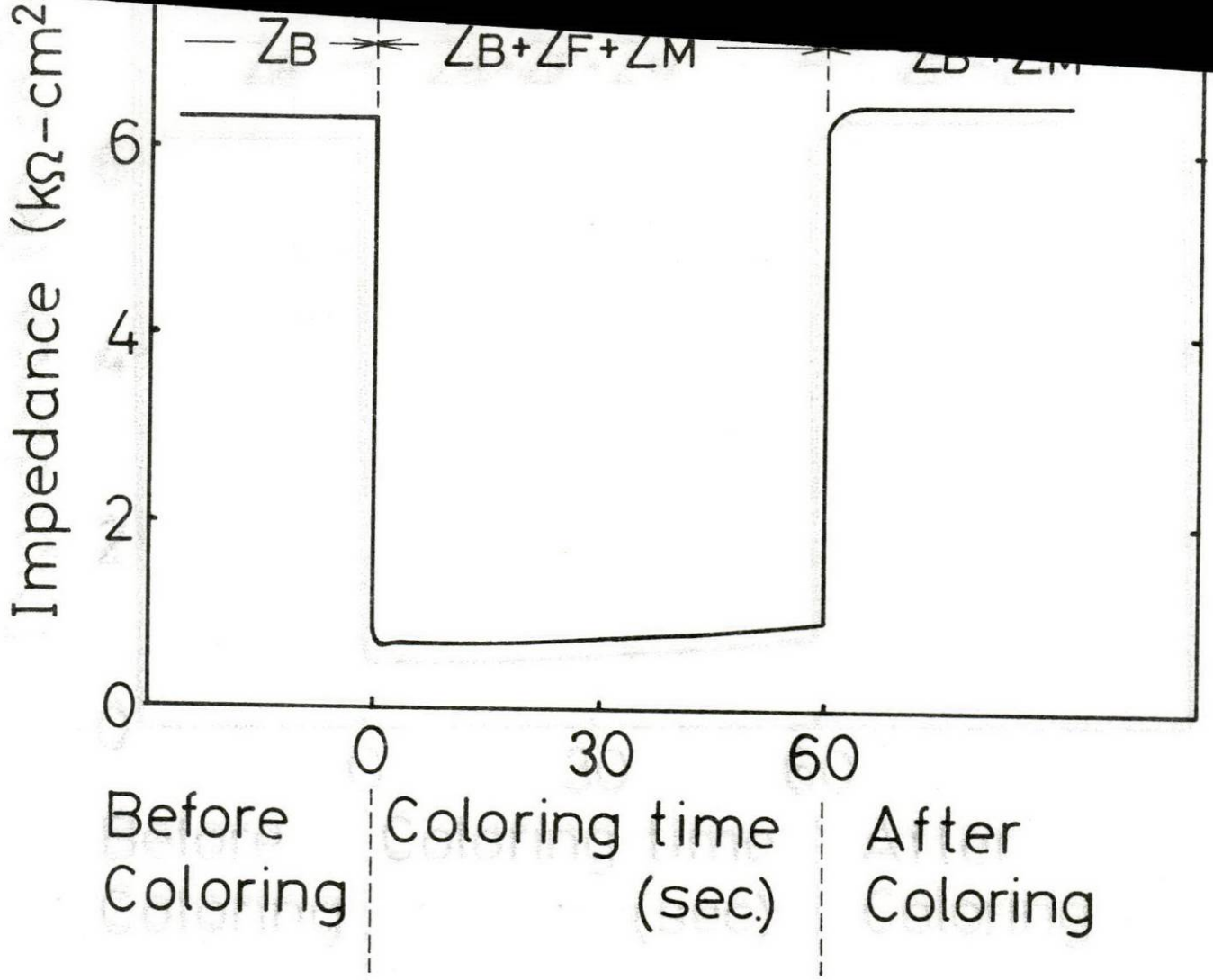


Fig.9 Impedance of anodic oxide film in a $NiSO_4$-H_3BO_3 mixed bath.

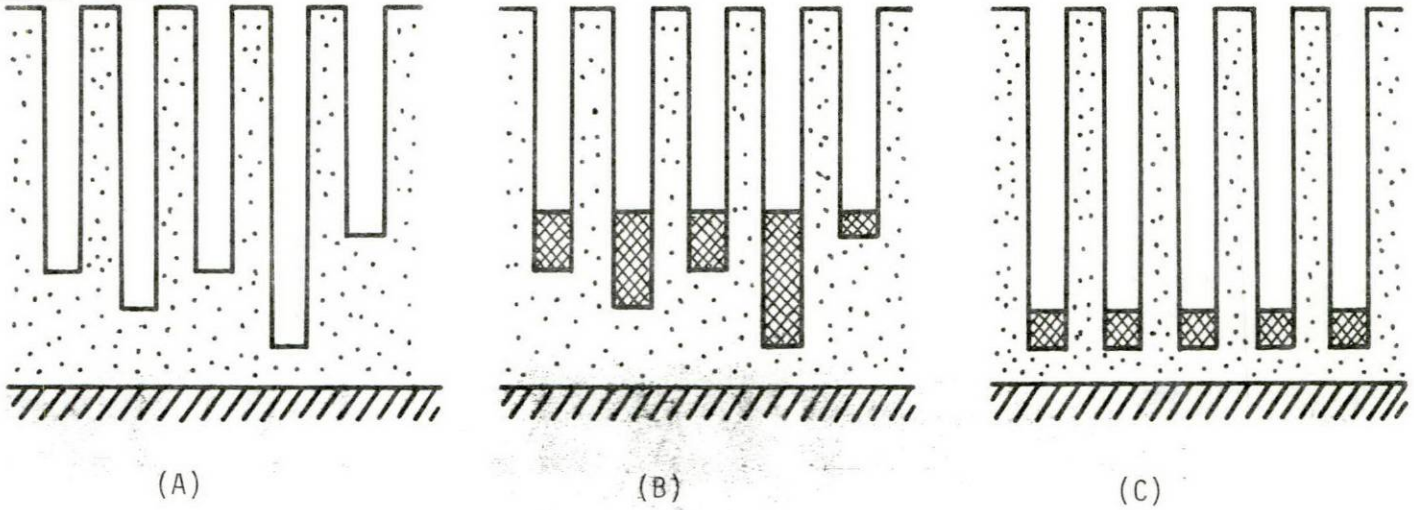


Fig.10 Electrodeposition of metal in the pores of oxide film (I) .

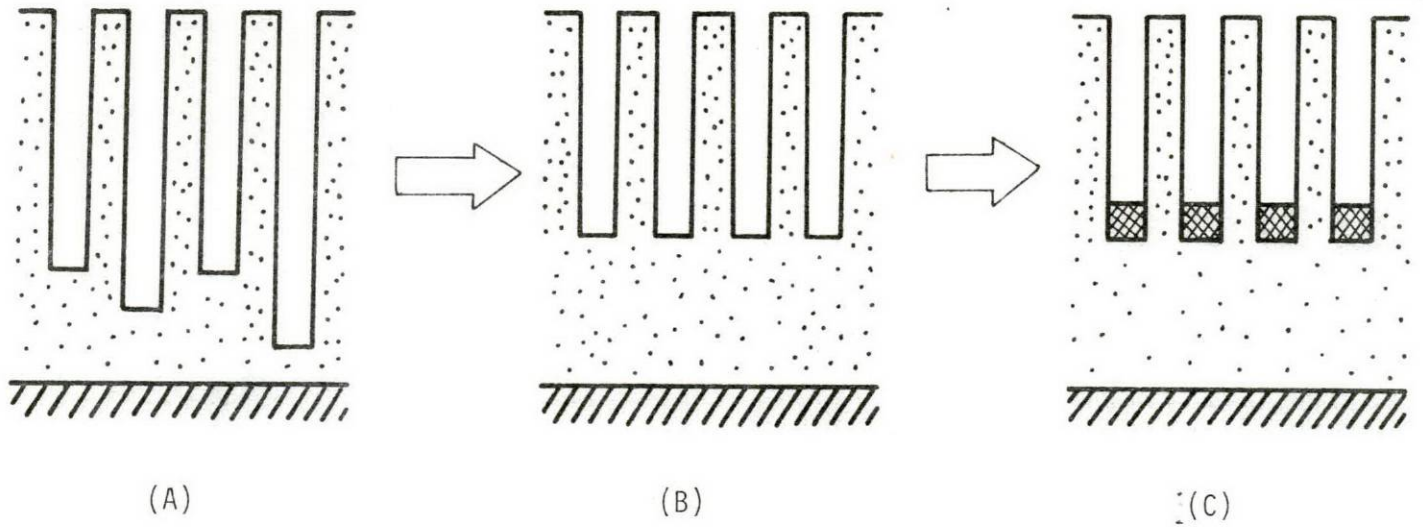


Fig.11 Electrodeposition of metal in the pores of oxide film (II).

Table 1 Electrolytic coloring of anodized oxide films on aluminum**.

		Anodizing voltage (D.C.volts)							
		0 V	4 V	6 V	8 V	10 V	12 V	13 V	15 V
Voltage of electrolytic coloring (A.C.volts)	4V	brown	non-colored						
	6V		pink	pink	pink				
	8V		gold	green	pink	pink			
	10V		gold	gold	redish green	pink	pink		
	12V		blue	green	redish green	pink	brown		
	14V		green	green	redish green	redish brown			
	16V		bluish green	yellowish green	redish brown	redish brown			
	18V		bluish violet	yellowish green	yellowish green	yellowish green			
	20V		pale green	pale red	pale green	pale red			
	22V		redish violet	pink	pale pink				

** Anodizing conditions ; 15 wt.% H_2SO_4, 20°C, 5 min.

Electrolytic coloring conditions ; 30 g/l $NiSO_4 \cdot 7H_2O$-30 g/l H_3BO_3, 20°C, 2 min.

I-3

Light Metals Finishing III
Session I

Automatic Buffing, Polishing, Satin-Finishing And Texturing of Aluminum

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AUTOMATIC BUFFING, POLISHING, SATIN-FINISHING AND TEXTURING OF ALUMINUM PRODUCTS

T. C. Andrew

With the tremendous growth of aluminum products in fields ranging from
tic cases to automobile bumpers, new processes and equipment have been
ned to meet the requirements. This paper will deal with equipment, buff
, polishing heads and processes specifically designed to finish aluminum
e various methods required.

utomatic buffing equipment comes in several sizes and types. For fairly
outputs, single station buffing machines and attachments for use with buff-
ads are particularly effective. With this type of equipment, articles
aded on a machine for a single buff operation. Equipment of this type is
versatile, and eliminates much of the manual effort involved in
onal hand buffing.

Figure 1

larger outputs and where a number of polishing stations are necessary,
tomatic equipment is available. The type of equipment employed depends
hape and size of the components, the output requirements, and the number
ning stages and the buffing techniques required. An automatic buffing
enerally consists of one or more buffing heads, together with a trans-
m on a carrier or track on which the work is mounted on jigs or fixtures.
carriers or jigs are usually provided with rotation or controlled
ion in order to ensure effective buffing on the article's surface.
ses, the whole of the surface may be buffed in a single operation
thers it is necessary to use a series of buffs that finish different
he surface, and a number of different type of conveyors are employed
include rotary table and rectilinear track designs.

e 2

Figure 3

There are normally two different types of buffing heads and they are classified as (1) fixed head designs, either mounted from the floor or fr an overhead suspension; and (2) follower-type heads, mounted in the same m that float along the contour of the part that they are finishing.

Figure 4 Figure 5

Buff heads incorporate the buffing wheel and its electric motor drive a provision for an electric head feed mechanism for adjusting the buff or in order to compensate for buff wear. The buff heads can be supplied wit speed suitable for mush buffing operations. In mush buffing, wide, up to feet long, large diameter bias buffs are operated at a very low rpm. The dividual buff sections are separated by spacers in order to provide flex so that the parts can be forced into the buff surface, thus enabling con areas to be buffed in a single stage.

For example, an aluminum surface can be buffed on one face and edge then turned over and buffed on the opposite face. Mush buffing is part applicable to rectangular machines on which extremely wide buffs can be

Figure 6

Another class of head used on buffing machines is the belt head. The belt, normally, is used for heavy cutting operations on aluminum and is used primarily for removal of the parting lines, etc., on aluminum parts. In many cases, very fine grit belts are used for deve final finishes as well.

It is very important to note that in most belting operations a l is necessary to eliminate belt loading.

Figure 7

The majority of indexing, straight line and rotary table machine fixed or follower type heads. The follower type buffing head is mou a pivoted arm and can therefore follow the contour of the surface be as the particular article passes by the buff. This type of head pro

emely sensitive control or buff pressure. The better systems are controlled and hydraulic devices.

For automatic buffing of aluminum, the use of bias type buffs is now ral. Buff sections are normally made up of sections approximately one-half wide and made concentric to the spindle by use of center plates. The od of construction assembly is such that air circulates through the center ol the buff surfaces and avoid build-up of heat at the surface of the buff ontact with the part.

The resillience of an air-flow buff section is controlled by varying the of folds of cloth in each section by the size of the center retaining and by the degree of pleating. Heavy buffing operations are usually done reater number of folds of cloth and greater number of pleats in the buff uction. The gathering of the pleats at the center of the buff maintains gressiveness of the buff as the wheel wears out and the surface feed es. There are two types of cloth pick: Cut wheels are made of cloth x 82 threads per square inch; lighter-duty wheels are made up of cloth threads per square inch.

Figure 8

purpose for buffing wheels is to carry the compound that is normally on the wheel with the use of an air-operated spray gun. At the present e are three types of guns in use: One is an air-operated spray gun ays the liquid compound in a stream of air at approximately 60 pounds e inch and drives the compound into the wheel. The other two systems ally airless spray systems which drive the compound into the wheel at up to 1200 psi. The importance of the compound is that it establishes removal in combination with the buff wheel.

er class of wheel used with buffing machines in conjunction with of aluminum parts is the nylon or synthetic fiber with bonded abrasive sing a tough resin to form a resillient non-woven, non-rusting,

non-loading and long-lasting material. Grit sizes range from coarse to ve fine, and the abrasive types used in aluminum finishing include aluminum oxide, silicon carbide, flint and garnet. A whole series of brushes using tampico and impregnated synthetic fibers are also employed. In most cases this type of wheel is used in preliminary operations on aluminum, and also used to establish a textured or satin-finished type finish, applicati of which we will be discussing later on in this paper.

Another class of wheel used in finishing aluminum parts is the flap w which is made up of flaps of abrasive material that extend radially from center hub and is extremely useful in finishing aluminum parts where no l is allowable due to painting operations after the finish has been establi

Spindle rpms in most finishing operations for aluminum range betwee and 1800. It should be noted that these slower rpms are normally requir aluminum finishing because the surface can be easily finished with belts and buffs without disturbing or distorting the original surface.

Figure 9

There are two basic cutting compounds used on aluminum products. a Tripoli compound; the other is calcined alumina. Both of these comp are mixed with fatty acids, preservatives, glycerides and other chemica that they can be easily sprayed on the buffing wheels in the several m discussed.

The viscosities of these materials are changed and are made suita either low pressure buff systems where fluid compounds are used, spec pressure tank applications where compounds must seek their own level introducing air to the systems.

A second class of low pressure viscosity compounds is made somew heavier for use in pump systems where the compound is pumped from ba the guns. This compound is normally made heavier because the pumpin breaks down the viscosity, creating a greater amount of fluidity or viscosity in the compound reaching the gun.

In standard low-pressure guns a lower viscosity compound is used. All of
se systems use timers for opening electrical solenoids and firing the guns.

In low-pressure/high-pressure systems, viscosity is not as important
use measured amounts of compound are fired from a chamber, dispensed from
gun or chamber each time it fires and viscosity therefore is not as much
factor.

Low viscosity compounds in standard low pressure systems will increase
volume from the gun per each firing cycle and can develop into uneconomical
of compound.

Compound viscosities in standard high pressure systems where the 1200 psi
m is throughout all of the system necessitate that the compound be wiped
the side of the barrel with a ram so the compound doesn't cavitate and
air to form in the manifold and compound systems.

he alumina compounds are normally used for cut-color and coloring
ions in aluminum. Color of course can be developed on aluminum surfaces
he alumina flours suspended in fatty acids and petro chemicals. The
oloring compound used is a chrome oxide which does impart very high
s to aluminum surfaces.

Figure 10

analysis of the term "cut" should be established. This term in the
trade is usually the surface acquired by using an 86 x 82 type cloth
el and Tripoli. Normally, this type surface is later prepared using
ch and followed by the usual anodizing process. Now, chrome-
an be applied to aluminum surfaces, and again, a very high finish
cessarily needed because the anodic etch in the case of anodizing
eveling type nickels and chemical processes take care of the very
ch that occurs when using Tripoli. The subsequent coloring opera-
ally follow the Tripoli cut operation and mechanically removes the
that occur on the surface of the aluminum, created by the Tripoli.

"Polishing" usually refers to belting and abrasive flap wheel type operation. It is this operation that imparts a rather heavy scratch to th surface that can be readily seen with the naked eye. Following are illust tions of buffing operations on aluminum products.

In the last few years, aluminum has been used extensively on automobi to cut down on the weight of the vehicle. One of the best examples of thi aluminum bumpers. These materials are high-strength aluminum and start as sions and form into different attitudes, depending on the design of the bu

A second class of material is the sheet material which is drawn and by the usual processes in presses. Normally, there are some basic pre-po operations done on bumpers where dies and the operations themselves creat mars on the surface of the material and do require a leveling normally as with belts and flap wheels. Some of these operations are done manually, others automatically, depending on the volume.

The most commonly used equipment is the rectilinear method which the bumper in a perpendicular attitude and,in conjunction with twelve-fo finishes the bumper in several stages. Ordinarily, a twelve-foot head w about 14 inches of bumper, and by using camming to articulate and posit bumper into its various attitudes, can be buffed completely at rates of 800 bumpers per hour. On the average, the spindle speeds for this oper approximate 1200 rpm. Treated buff wheels and Tripoli are used.

One experiment: A measured scratch of approximately a thousandth half to two thousandths was removed, using a twelve-foot head, angled 14 inches of surface, wheel speed approximately 1200 rpm, and buff whe a heavy treatment, with a wheel spacing of one inch, at a conveyor spe 10 feet per minute. Large stock removals can be acquired without dis roughing up the surface to a point where it is difficult to level for finish required in anodizing and plating, and of course, the first op to the coloring of the aluminum product.

Figure 11

Figure 12

Another item that has come to the forefront in automotive industry is the
inum wheel disc. Again, the weight reduction is of great importance and
ease of buffing and satin finishing the aluminum wheel disc and hub cap
it very economical as well as practical to use.

Machines, using seven and twelve-foot heads of the recti linear type on
ight line machines, and utilizing rotation under spaced treated and untreated
ls, buff wheel discs at rates up to 1500 per hour. Again, Tripoli only is
and the end of the last buff wheel is used to wipe the wheel disc clean.
ction rates on a rotary machine would be approximately 800 per hour
his equipment would be used only on very deep drawn aluminum wheel discs.
A new development on aluminum wheels: Utilizing again the broad wheel
t, buffing both the wheel and the aluminum spider assembled, widely
wheels up to 3 inches in diameter and wheel speeds of approximately
n, finish this type of wheel, regardless of the physical characteristics.
e of the benefits of using the "mush buffing" technique is of course
les used for cooling the brake system would normally pick out and
streaking, using the rotary method, whereas using the long buff method,
l is uniformly worn down because the wheel is being rotated unformly
he face of the wheel.

ure 13 Figure 14 Figure 15

ther example of the use of aluminum is the trim portion of the car
is case a satin finish operation, finishing applique trim for the
roof trim on many automobiles. Automation of this job makes use
ng belt type heads, using a nylon impregnated type material on a
backed belt. The heads are designed to float over the surface
rmally not flat, making use of a floating roll and automatic belt
to maintain the tracking of the belt and the uniform finish required.

This operation, previously done by hand prior to automation, now sav up to ten operators at production rates of up to 1200 per hour. These materials are heavily lubricated, using spray guns and a lubricant that keeps the belts from loading.

Unique type vacuum system is used to hold the parts without marking. A Venturi type system using small amount of air to create vacuum in conju tion with suction cups, hold the part to the fixture during the operation

Figure 16

Another use of aluminum is on sole plates for flat irons. The highl conductive characteristics of this alloy make for universal acceptance i the steam iron business. Normally, two machines are used to finish the sole plates.

The latest development, of course, is the die cast method of making sole plate followed by a four-head polishing machine, using grits from 8 through 320. The part is placed on a conveyor and transported through t four belt heads, spindle speeds of approximately 1200 rpm are used, and heads are oscillated to break up the scratch pattern, eliminate abrasive tracking and develop very uniform and smooth finish.

Again, the diecasting is normally in good condition coming to this polishing operation and the less material removed, the better. This el getting down into what is called in the diecast trade the "sponge" area Accuracy of fixtures is very important in this operation. Lubrication applied, using a soluble oil, and is flowed on with use of a small pump large reservoir for recirculating the soluble oil, making this a very e ical way of lubricating the belts. A sump area, using screens, collec abrasive and aluminum residue and the reservoir or sump can be emptied a day. All of these pumps have Teflon bearings to reduce any possibil rapid wear.

A second machine incorporates the use of floating belt heads and
ds using the slack of the belt in conjunction with camming for polishing
sides and beveling the edges of the flat iron.

Recent developments would utilize the flat polish and edge polish on
machine, saving extra handling.

Another application for aluminum is the racket ball racket and the tennis
racket. The racket frames are buffed by positioning the racket through
n or twelve-foot heads; the aluminum rackets are turned over after one side
ne and in the second operation, the racket is completely buffed, having
through the machine twice. Normally, operators are placed at each end of
urn type rectilinear machine so that the parts can be turned in the back
l as in the front, and production rates of up to 1,000 per hour are
ed. Wheel speeds of approximately 900 rpm are used; in some cases,
d wheels are used, but in most cases the standard 86 x 82 cloth is ample
tting down the surface prior to anodizing, and irridescent type dyeing
o anodizing. Again, it is important to have a uniform type finish for
dizing operation. Figure 17

other use for aluminum is the aerosol type case used in the cosmetic
Drawn shells are buffed, using either Tripoli or alumina for the cut-
ration, using treated 86 x 82 cloth, or untreated, followed by 64 x 68
eels for coloring, using alumina and chrome or pure chrome coloring
to acquire the high luster required for this type of jewelry finish.
tes of up to 90 per minute are easily attained, using the rectal linear
em, employing up to 5 heads, 30" in length, for the process. Smaller
rates make use of the continuous rotary machine, using the same
s and same type compounds. In some instances, bar applicators are used.
cases, it is important that all compounds are compatible to the
ocess being used.

Figure 18

Another example of the use of aluminum products is the outboard mo housings. The use of flap wheels in this operation was imperative beca the parts had to be painted after polish and there was no way to proper clean the surface. Belt heads of course could not be used without lubr and the flap wheel, as described earlier, was used. The wheels were ma and shaped for the different size outboard motors and production rates to 150 per hour were realized. Head feed controls were optimized by us micro timers so that the heads, particularly on the skeg area of the o motor, could be fed in micro seconds. This, in conjunction with a fla light determining when the circuits were on, made it easy for an opera control the head feed. Of course the flap wheel being used did not l because the wear was radial to the surface. Spindle speeds were 180 and oscillation on all of the flat areas was used so that the polish pattern was broken up. This again is an operation that had been done hand and as many as 8 to 10 operators were saved in this operation.

Another finishing operation: an aluminum sheet used for wing sk aircraft has become of great importance. Again, a high finish resis rosion and improves aero dynamic characteristics of the aircraft, th no need for painting, and of course cuts down on the weight of the a itself.

Two methods have been used for finishing these sheets:

(1) A table passes under a stationary head that oscillates. Sheets 12 feet wide are buffed in this manner, and the material is held, u vacuum system, and the part is passed under the wheel with the hea tion to break line pattern and finishes of 1 to 2 micro inches are attained.

(2) The other machine style is a traveling type head where the part
eld on a table and the head is transported back and forth across the
ace being finished.

Both methods are excellent for finishing aluminum products, and of
se Tripoli and alumina, along with the proper buffs, are used, depending
ype finish required.

With the advent of highly stressed parts in aircraft, the finishing
ng spars and wing skins has become of great importance. One style
ne is a pinch roll or billy roll machine that transports spars similar
e aluminum extrusions used in buildings, and a series of buff wheels,
both synthetic fabrics, buffs and compounds and other types of finish-
dia, radiuses and finishes aluminum spars so that they meet aircraft
ications regarding fatigue and corrosion resistance.

ircraft engine housings are radiused and deburred both inside and
on special equipment designed for selective radiusing and deburring
aluminum housing used to house the turbine engines. Again, all of
rk is high labor intensity and of course the savings and the uniformity
sh make the equipment a must in this particular industry.
heads are controlled by hydraulic mechanisms that position the
sing controls conveniently located at the operator's station.

Figure 20

iously aluminum usage has increased in all fields in recent years,
lly, the ease at which the material can be formed and finished
ably make the material more popular in the future. Of course
strength and light weight make it prime material for aircraft and
ilar applications.

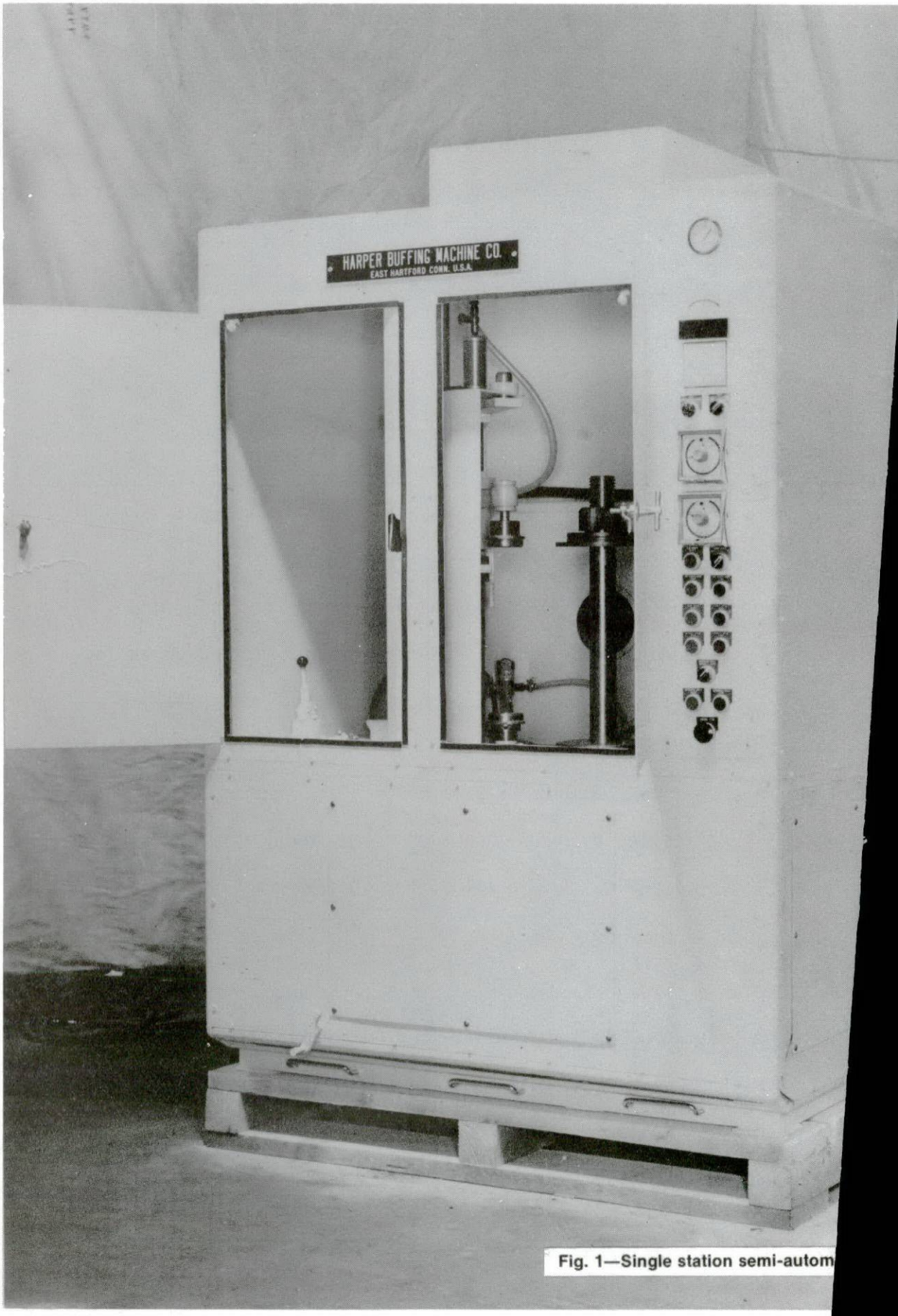

Fig. 1—Single station semi-autom

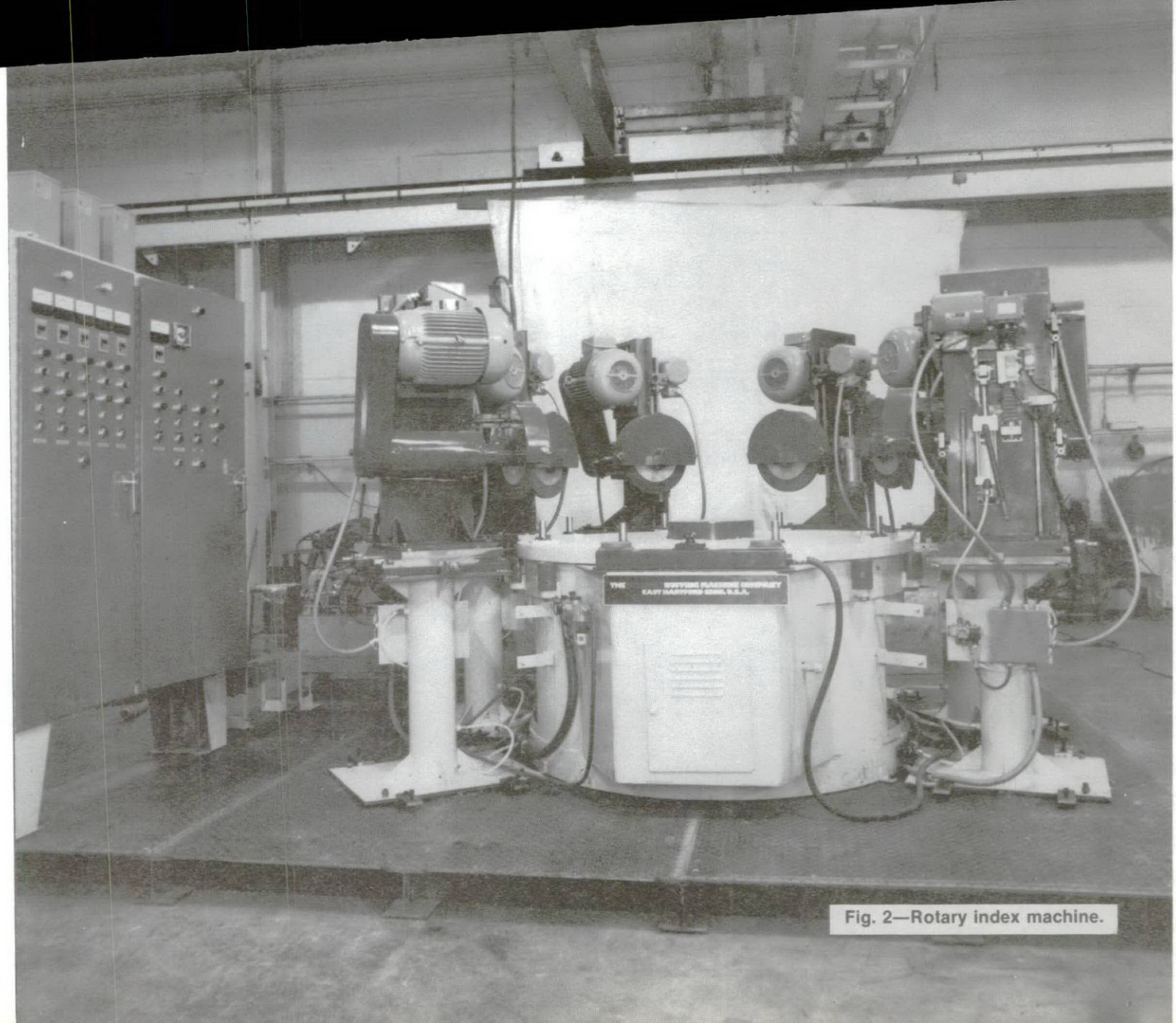

Fig. 2—Rotary index machine.

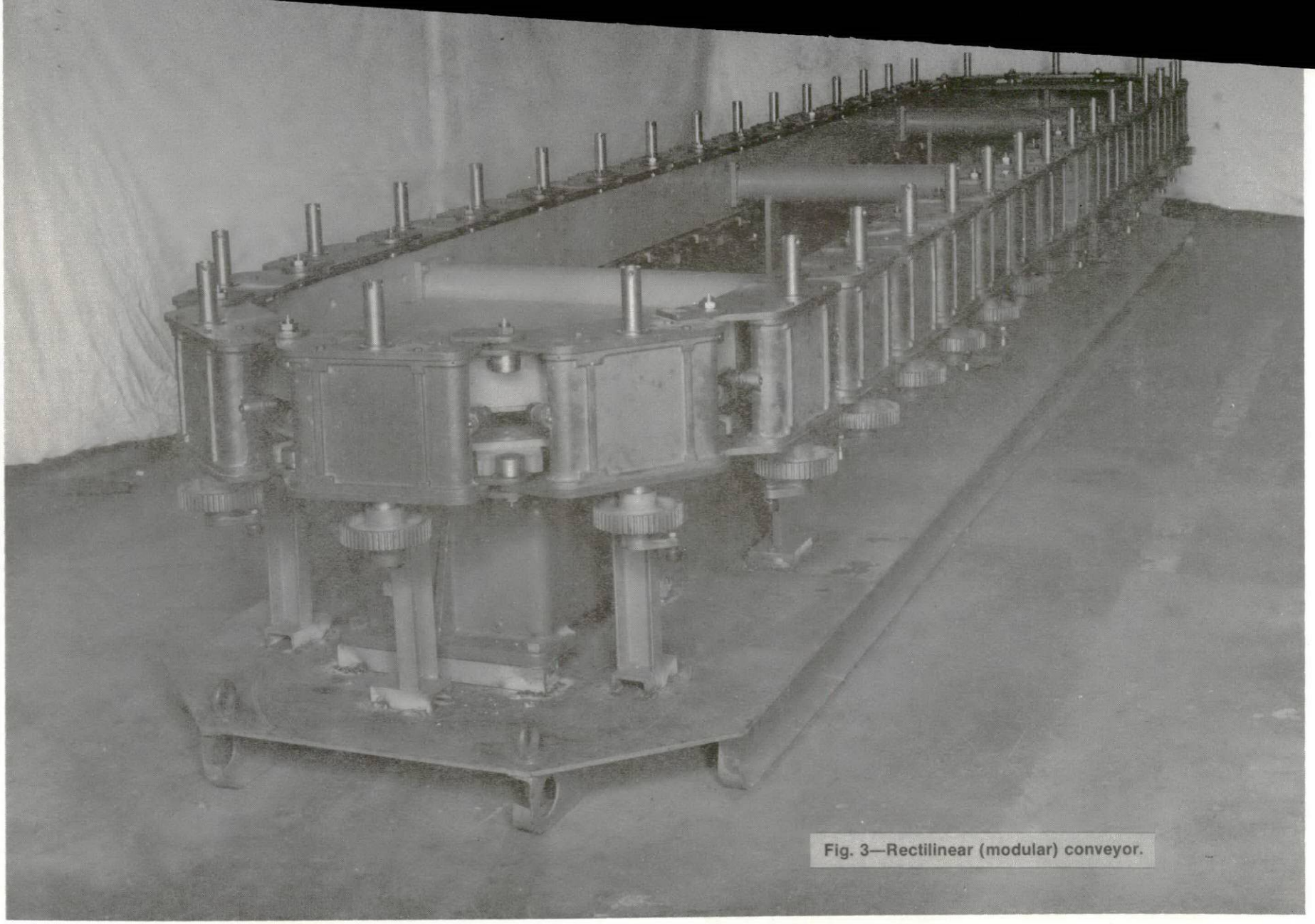

Fig. 3—Rectilinear (modular) conveyor.

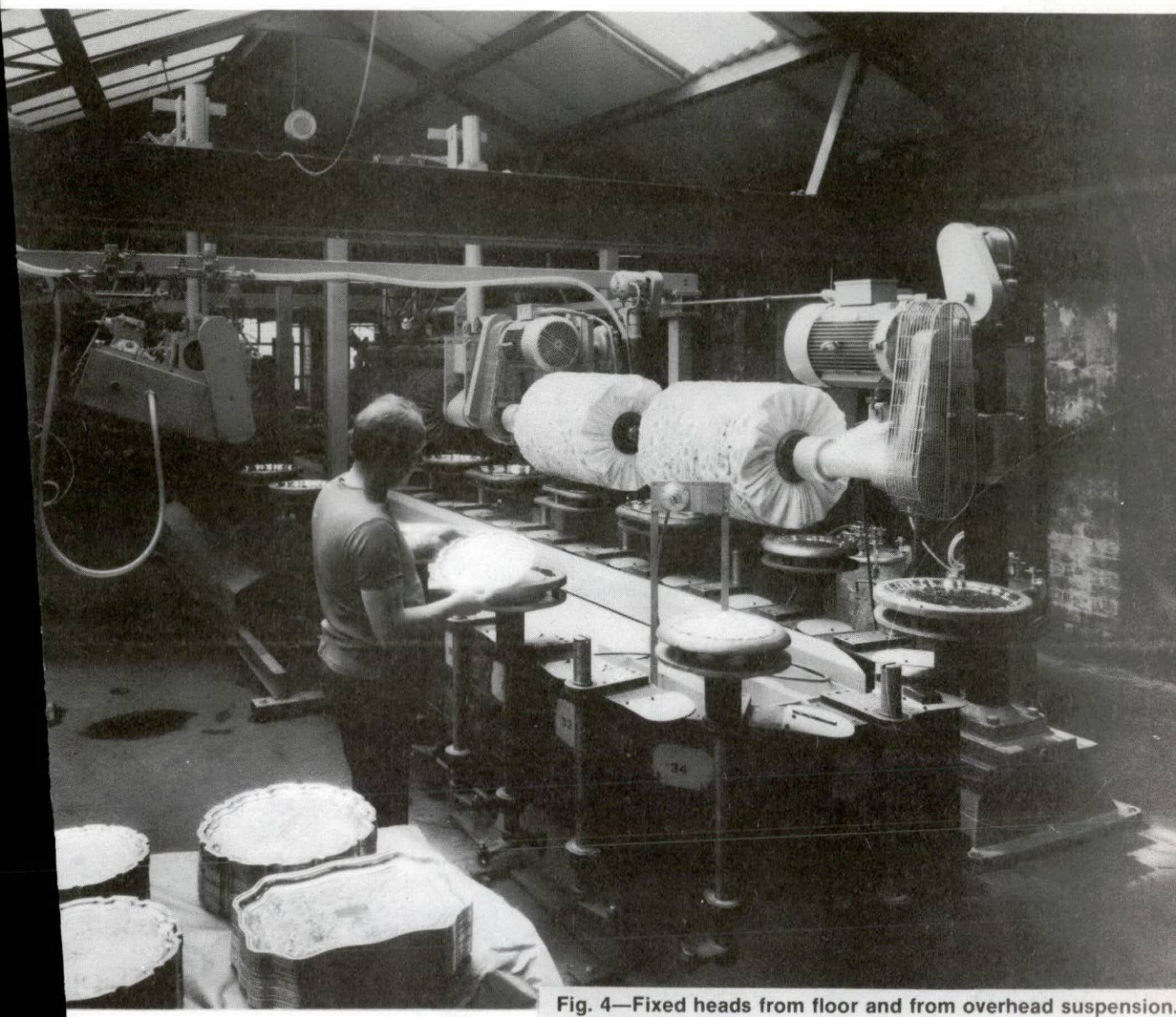

Fig. 4—Fixed heads from floor and from overhead suspension.

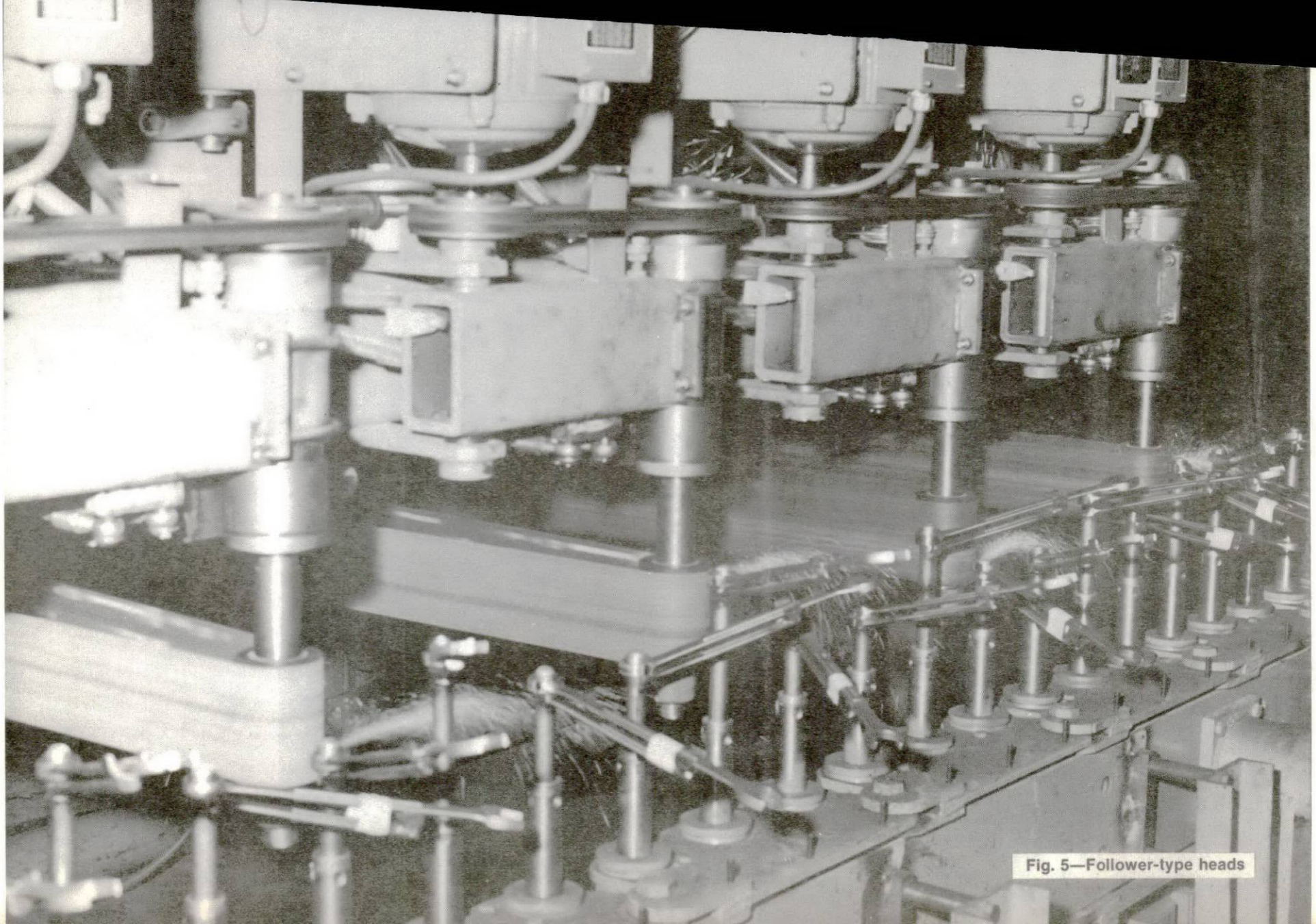

Fig. 5—Follower-type heads

Fig. 6—Buff head.

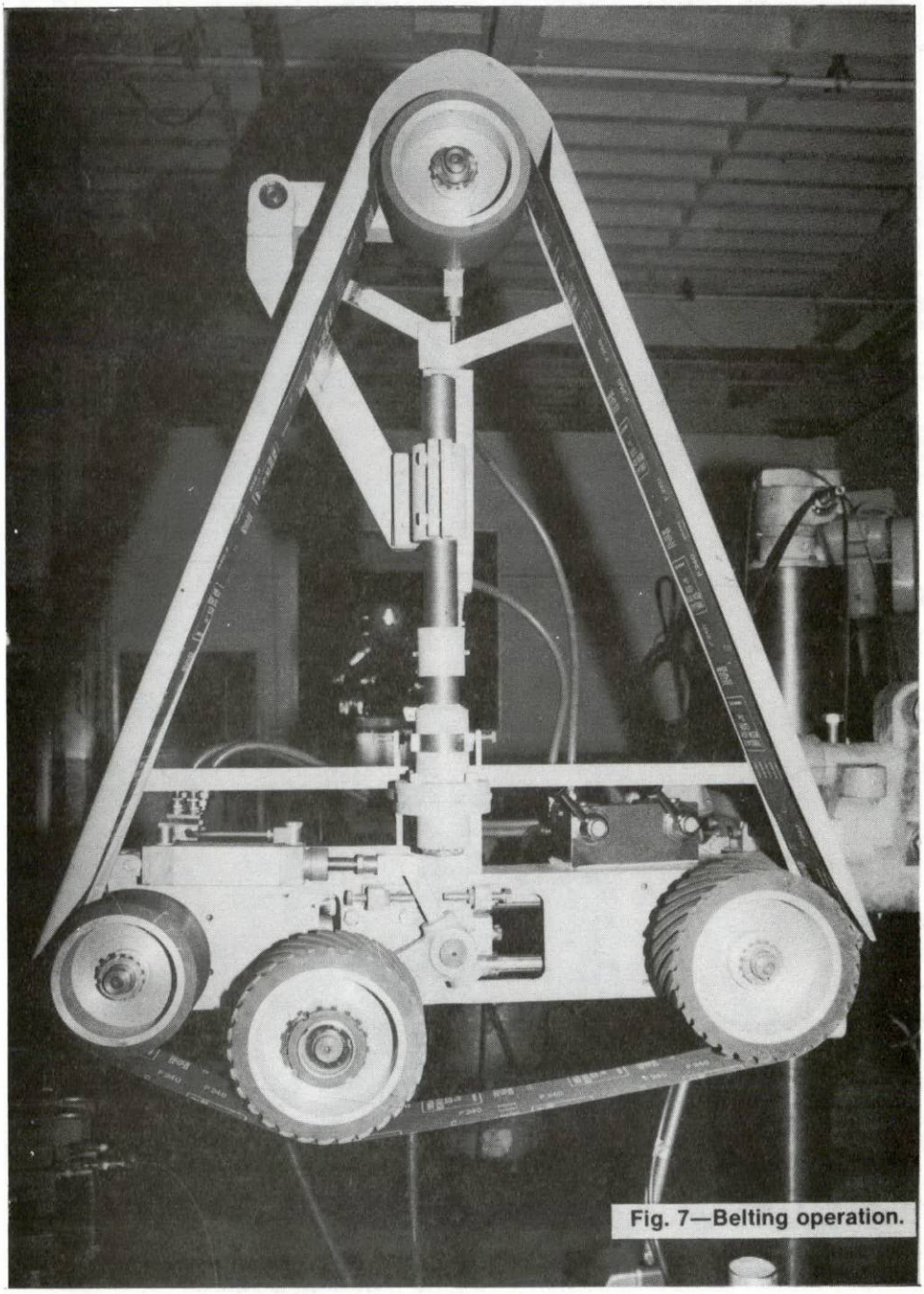

Fig. 7—Belting operation.

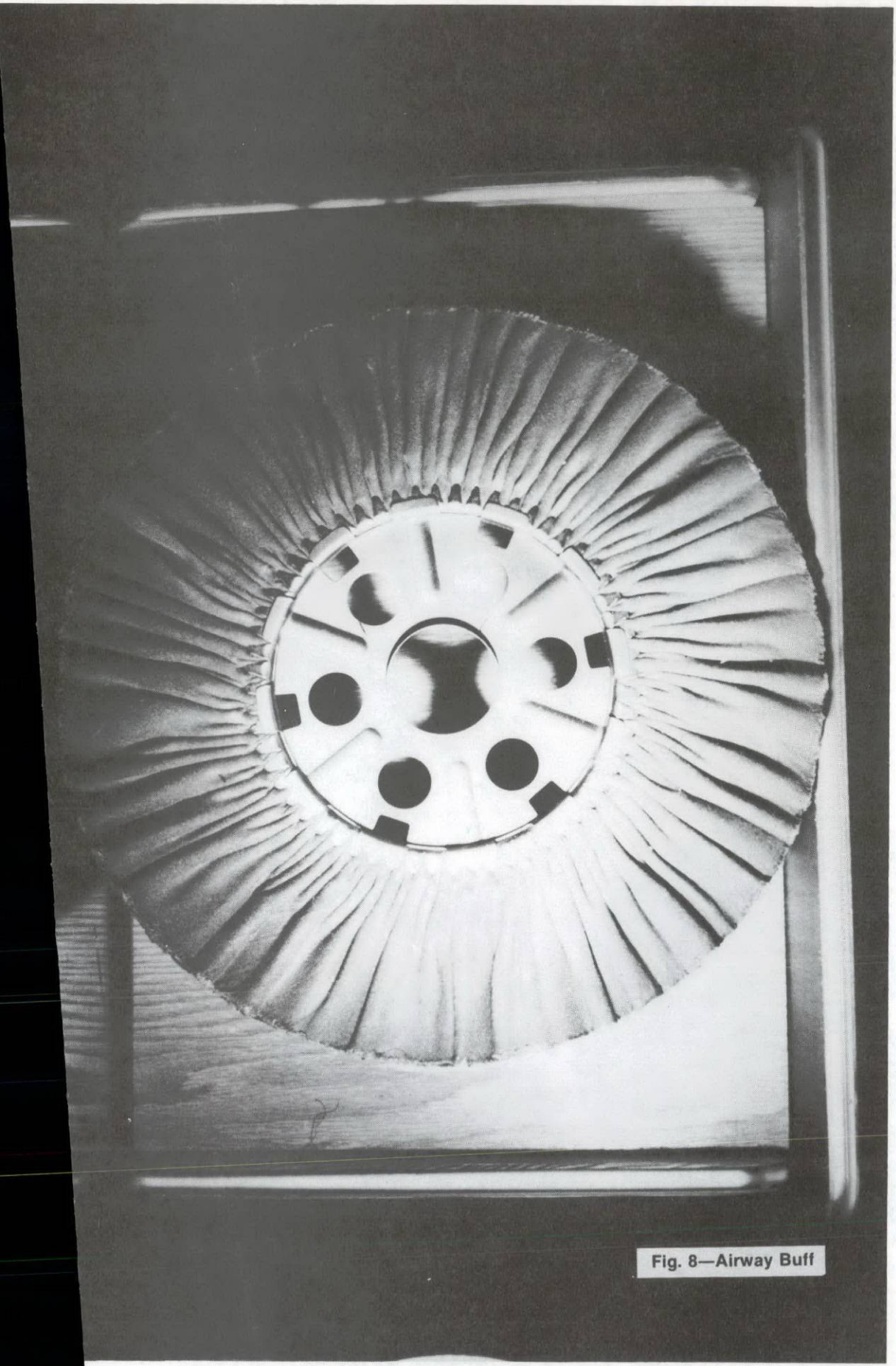

Fig. 8—Airway Buff

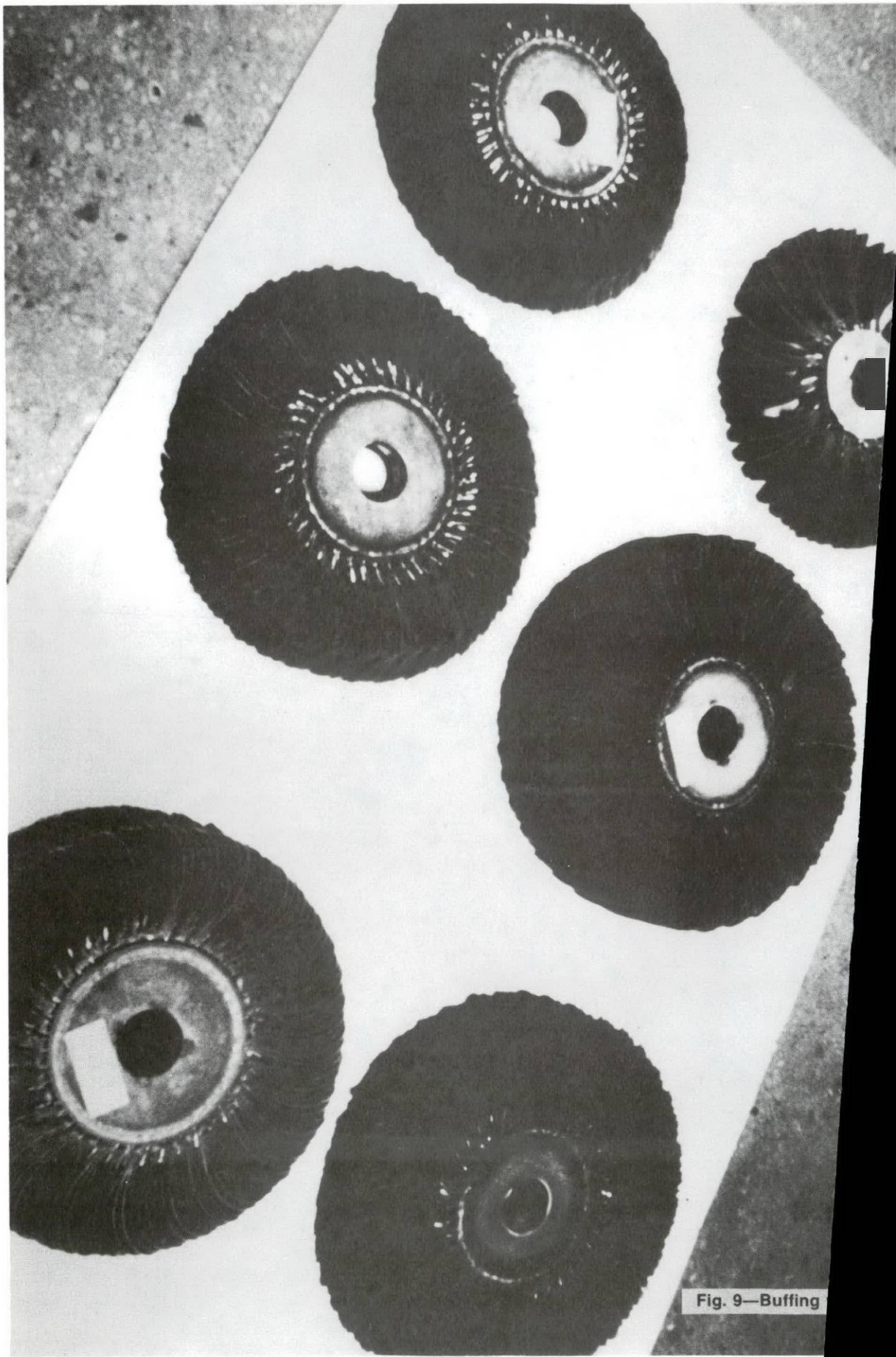

Fig. 9—Buffing

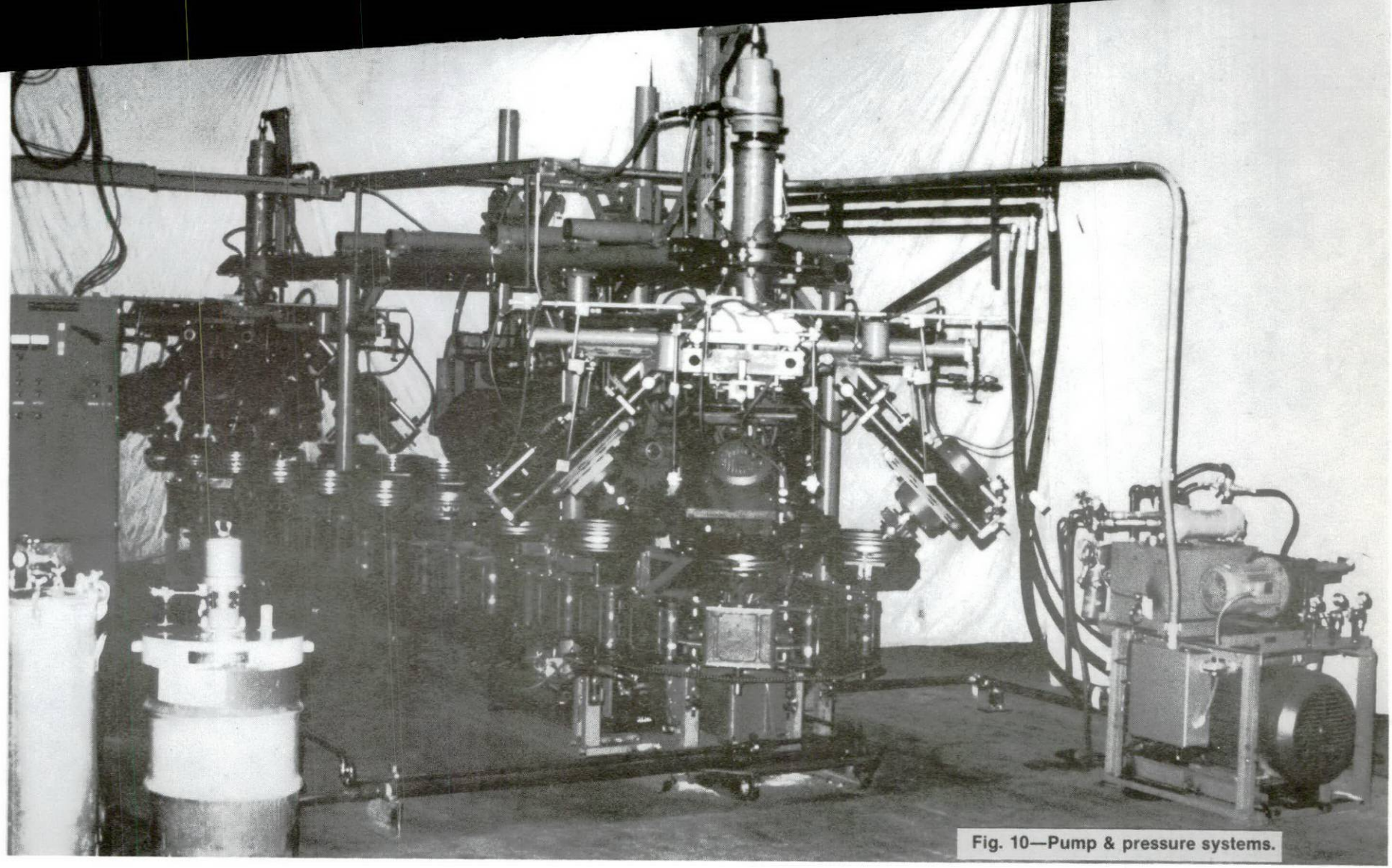

Fig. 10—Pump & pressure systems.

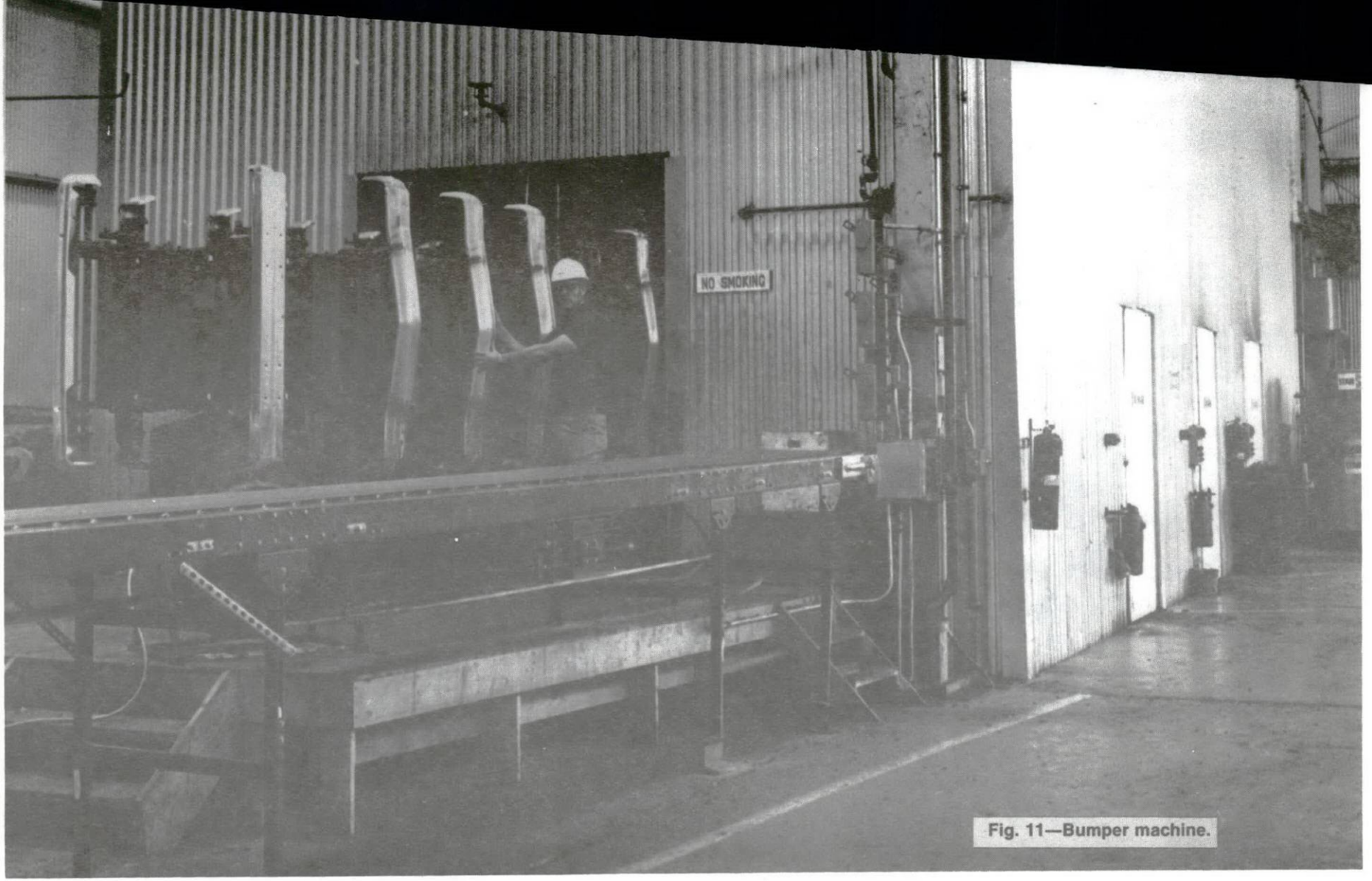

Fig. 11—Bumper machine.



Fig. 12—Bumper machine.

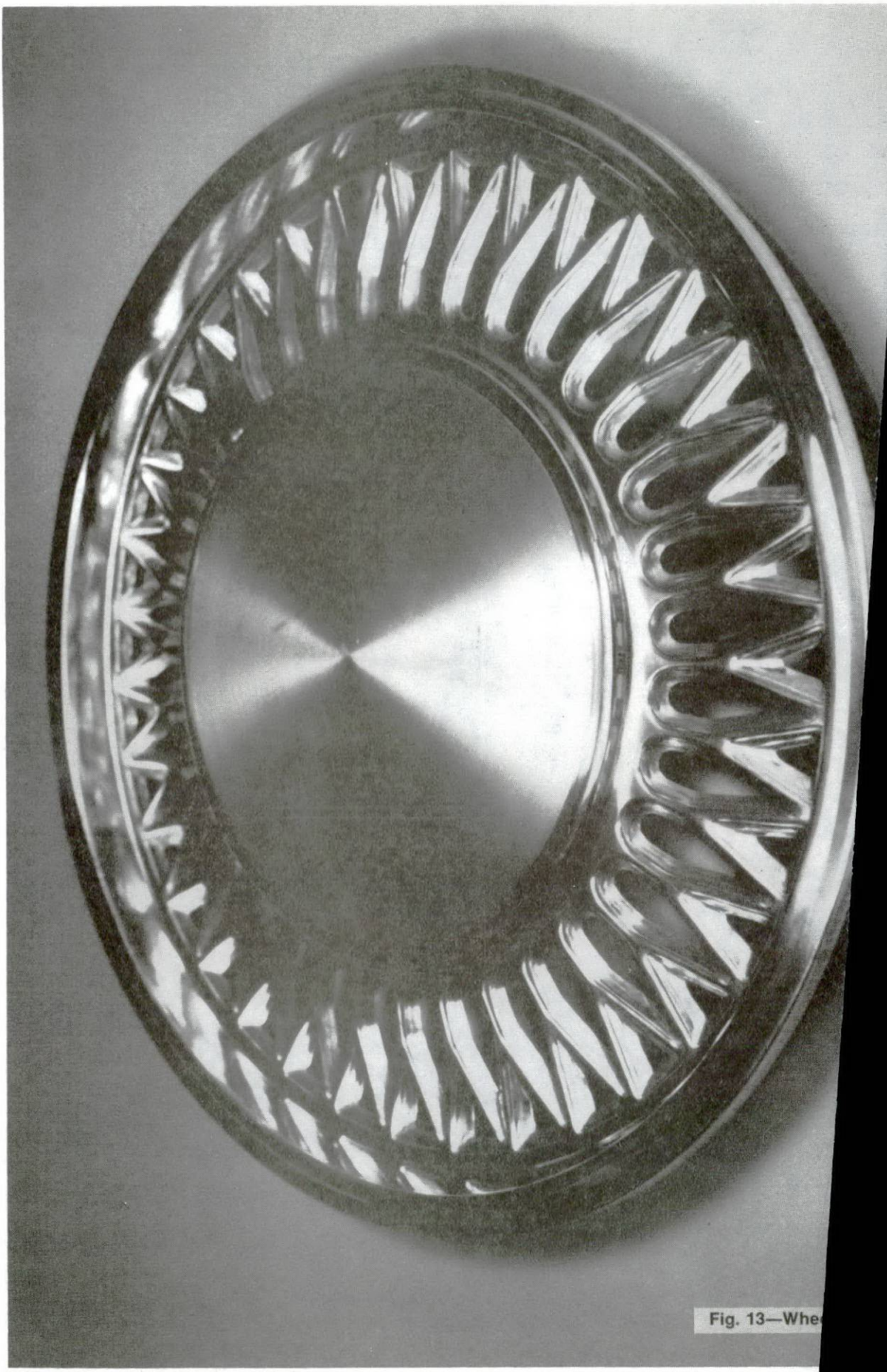

Fig. 13—Whe

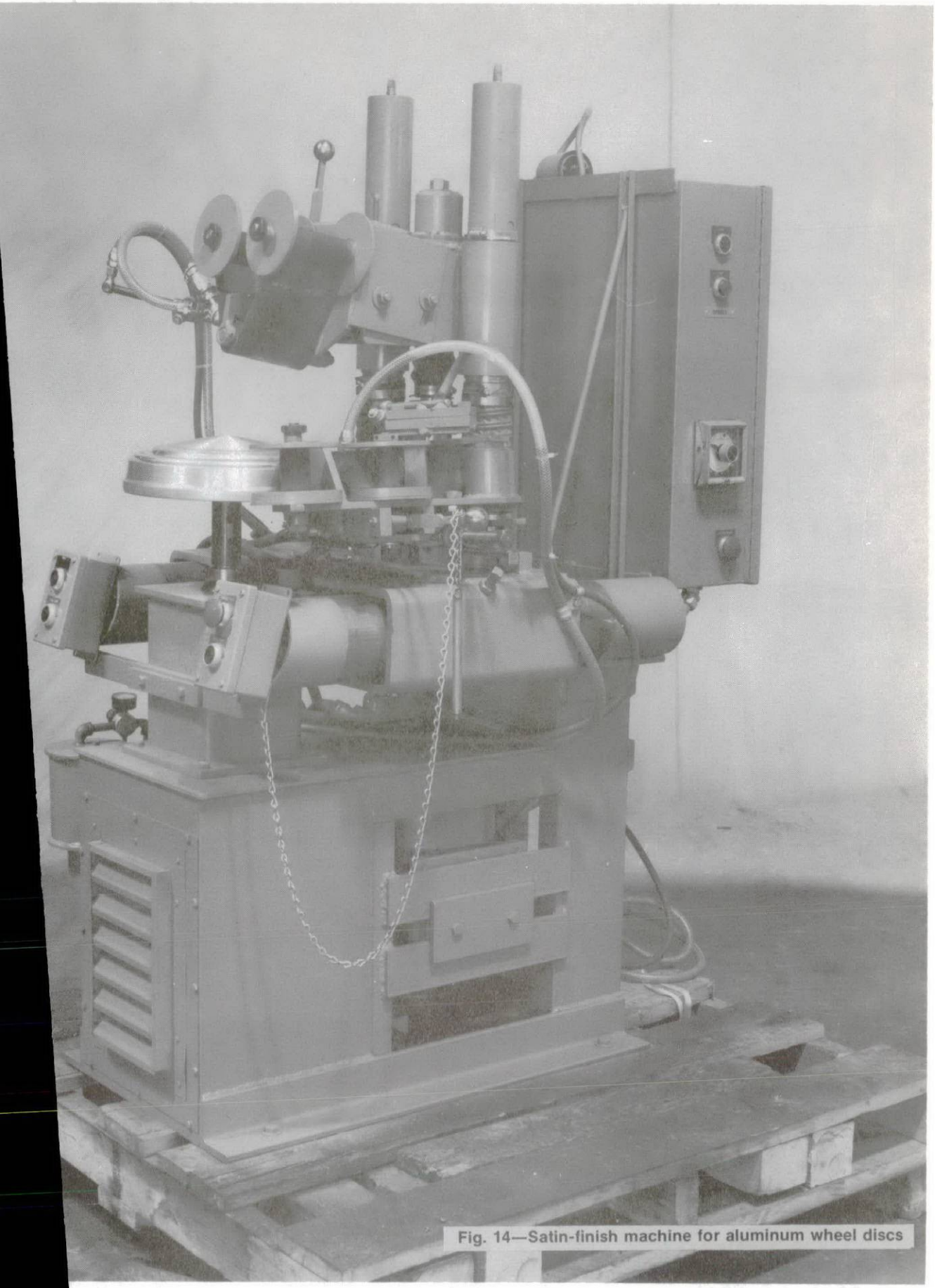

Fig. 14—Satin-finish machine for aluminum wheel discs

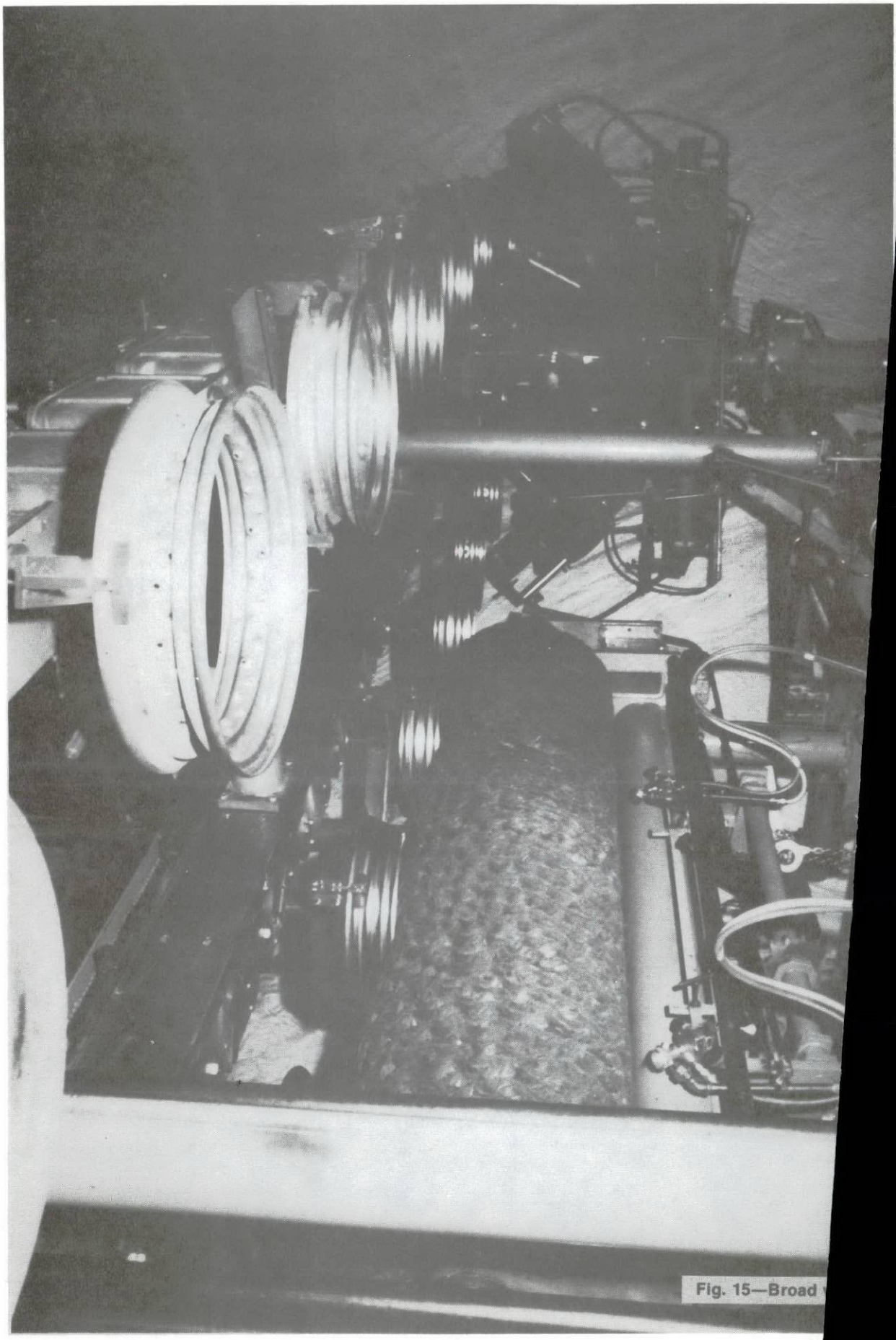

Fig. 15—Broad

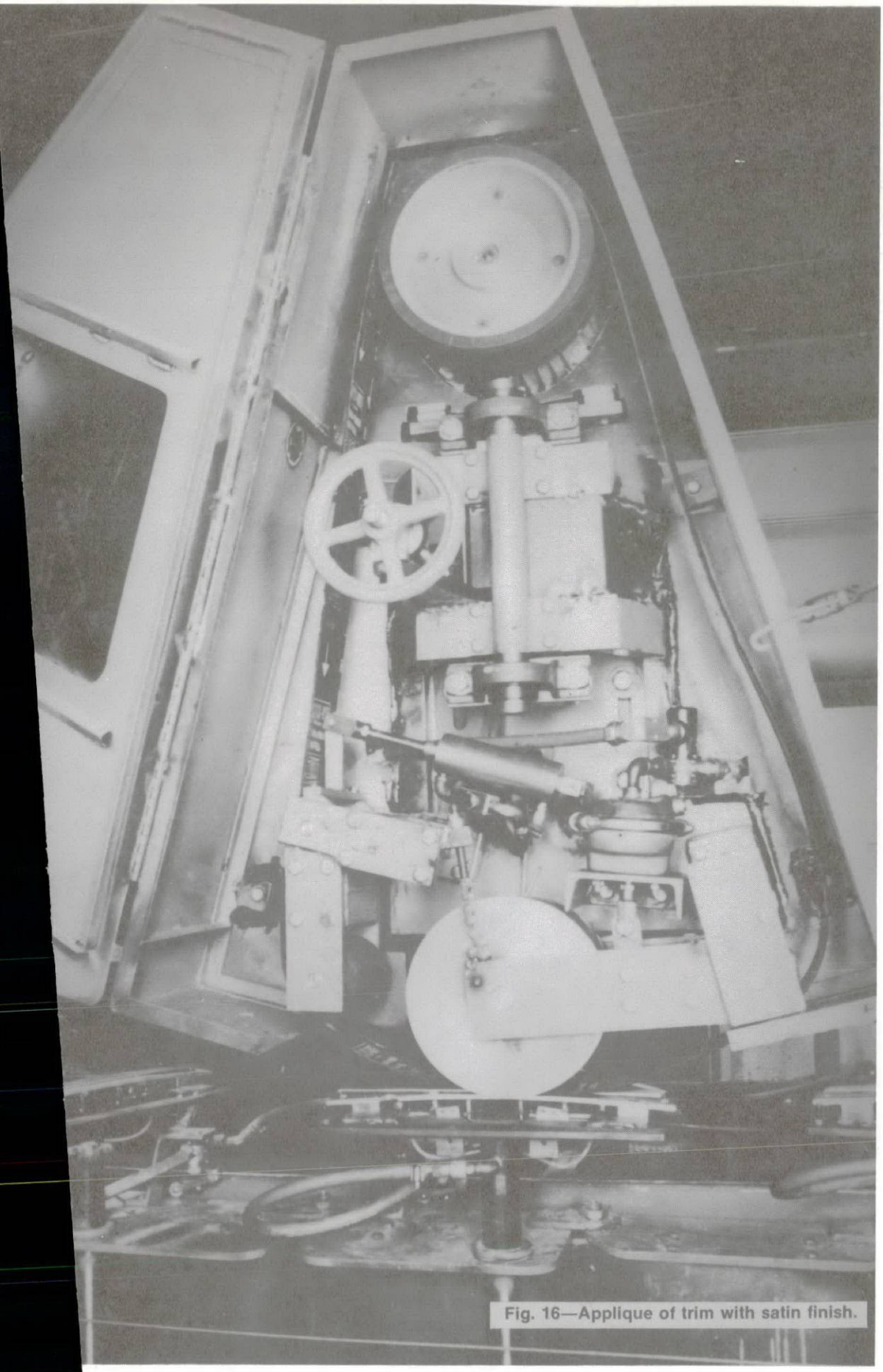

Fig. 16—Applique of trim with satin finish.

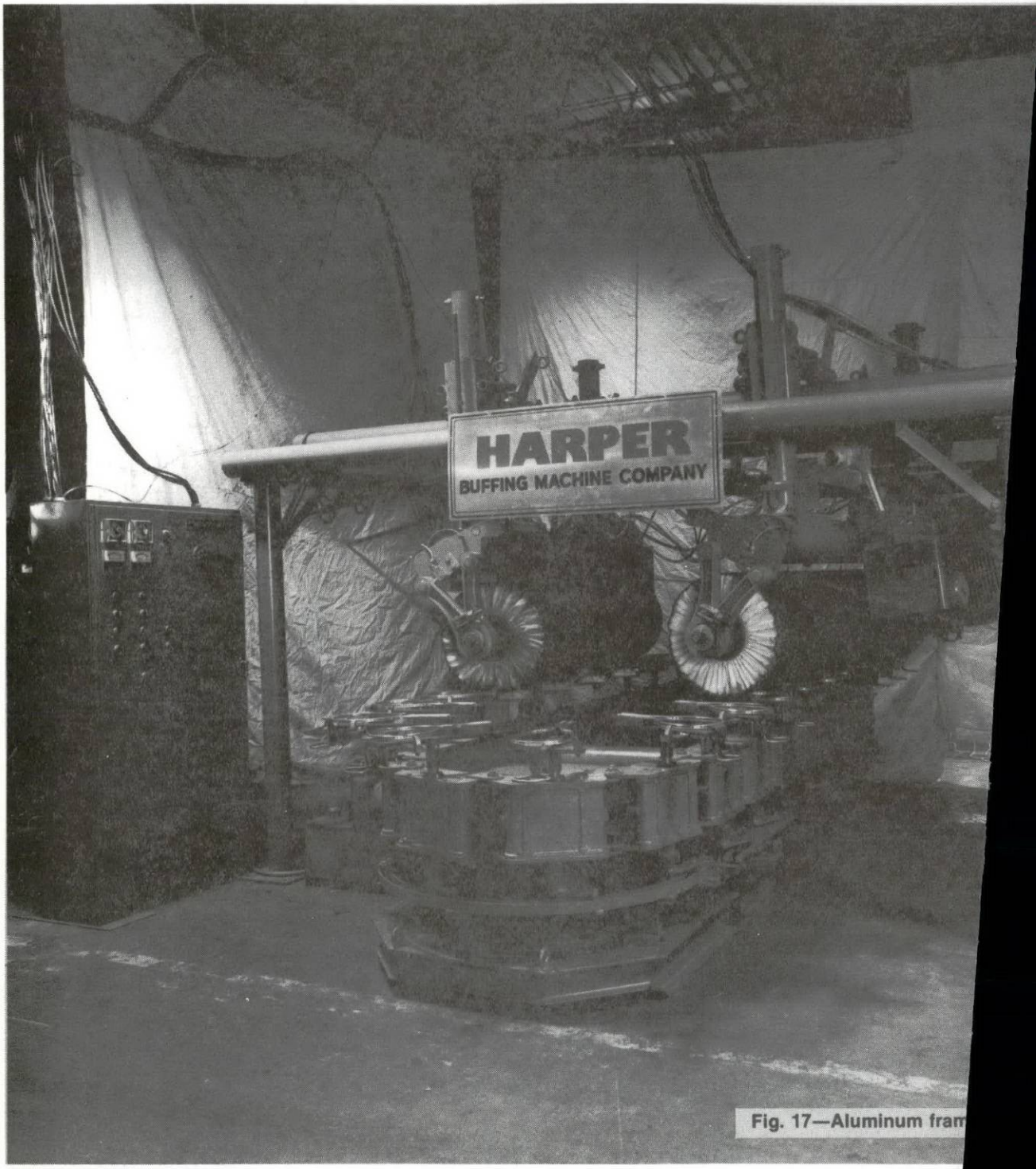

Fig. 17—Aluminum fram

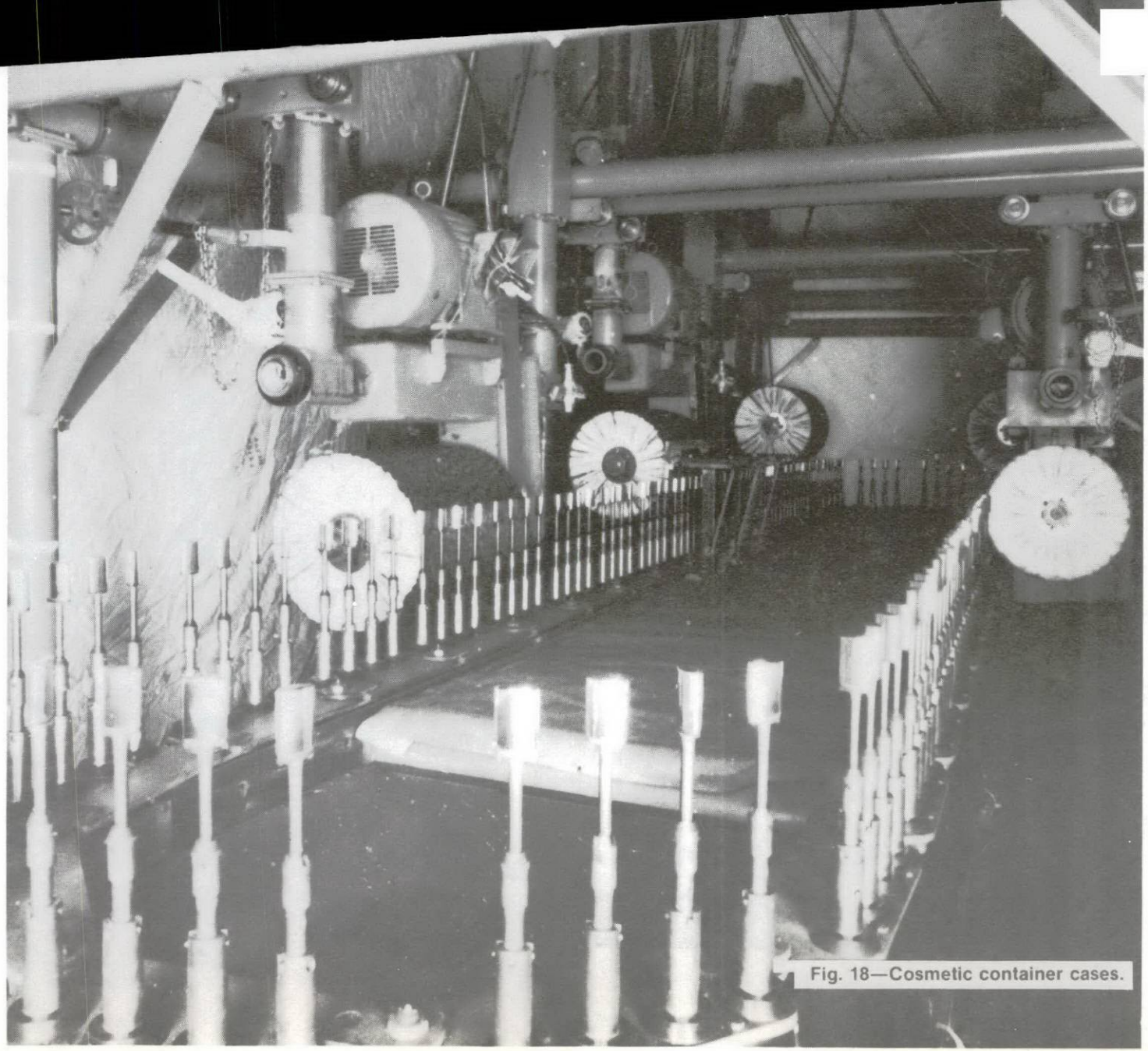

Fig. 18—Cosmetic container cases.

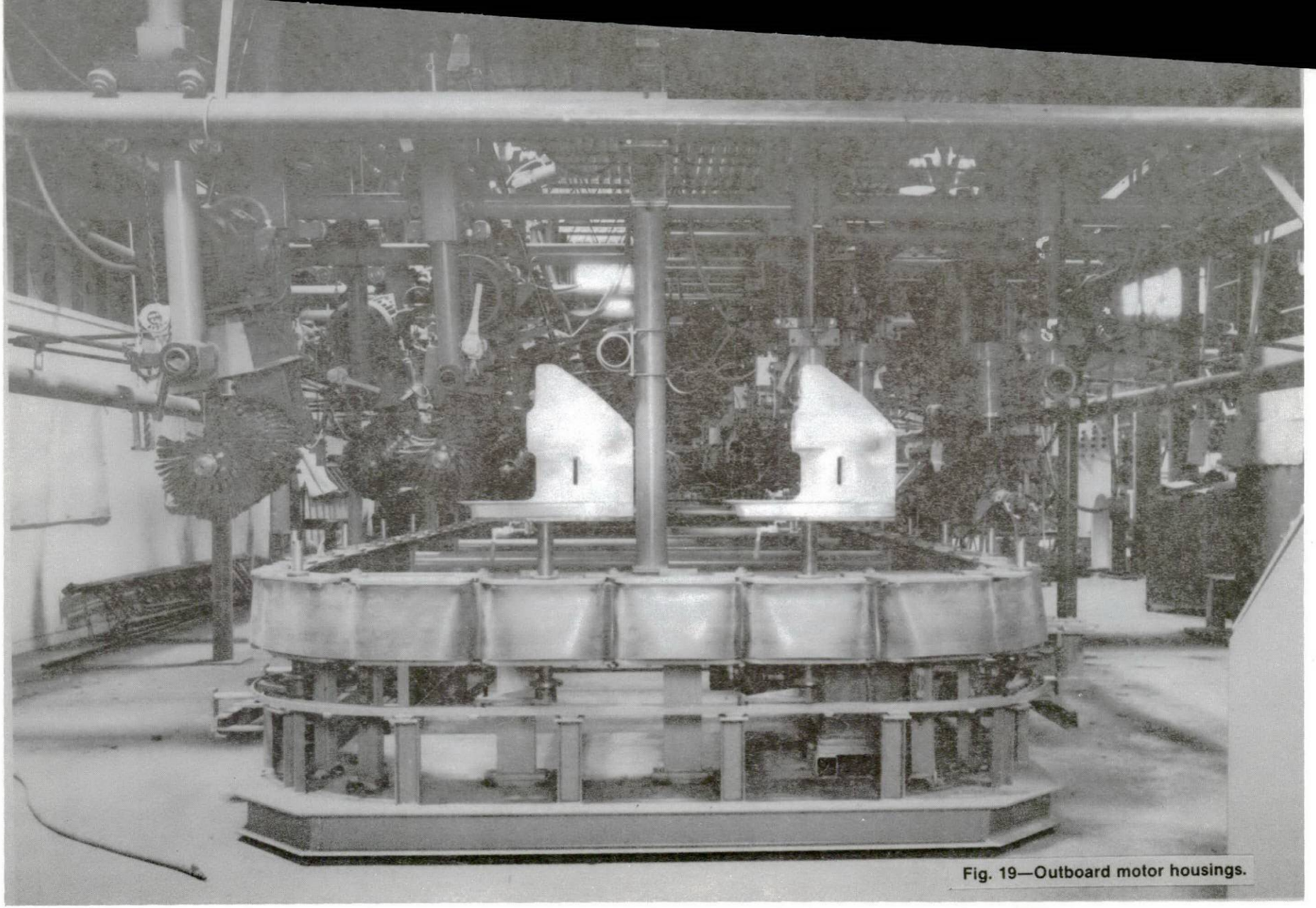

Fig. 19—Outboard motor housings.

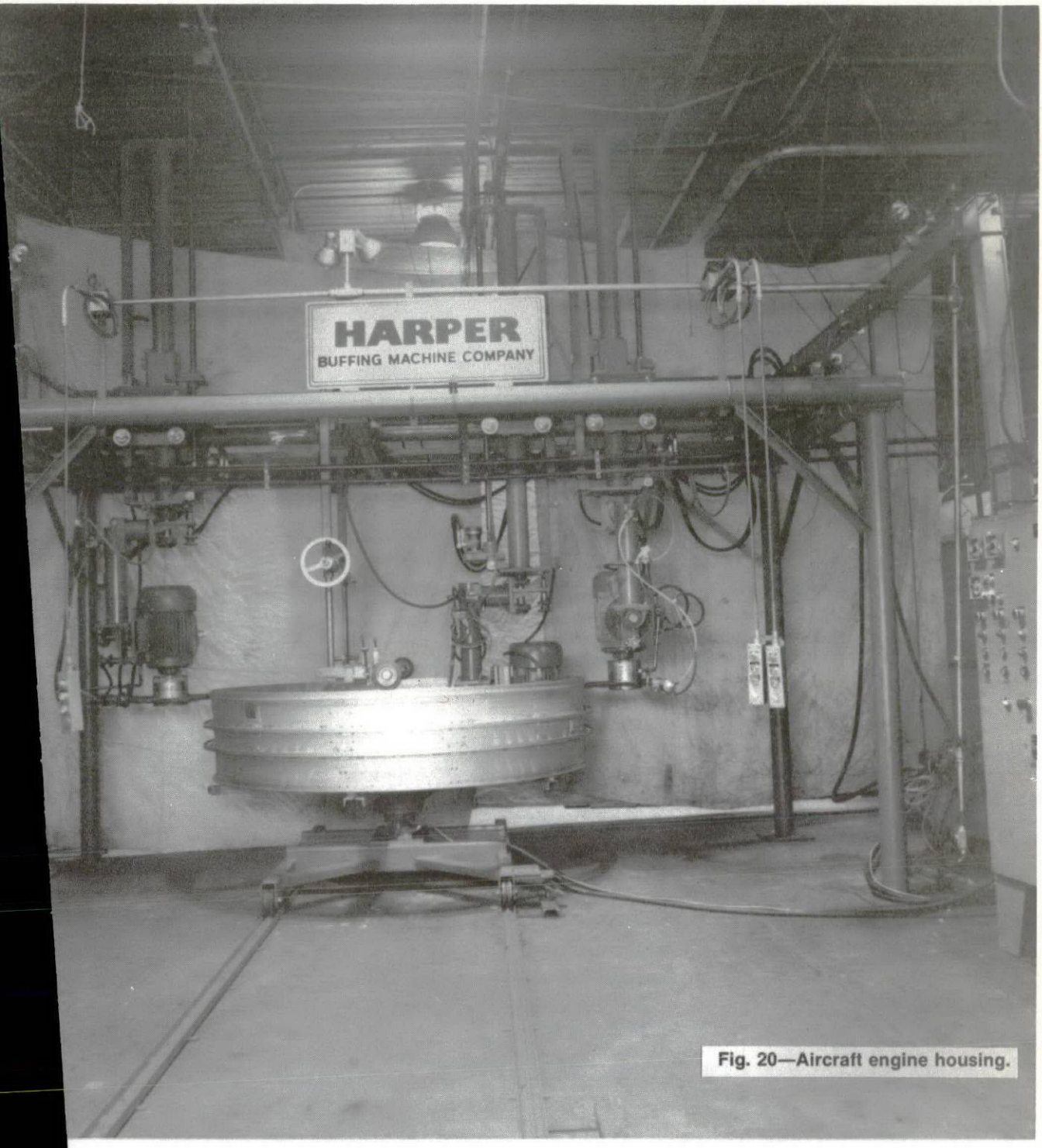

Fig. 20—Aircraft engine housing.

J-1

Chromium I
Session J

Anode Considerations for Chromium Plating

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Alpha Metals, Inc.
Jersey City, New Jersey

"ANODE CONSIDERATIONS FOR CHROMIUM PLATING"

by: James P. Langan
Alpha Metals, Inc.
January 25, 1979

mium plating is usually classified in two major categories and it is emely important that careful consideration in selecting and placing es be observed in each.

first category is called decorative chromium and chromium is applied thin non-tarnishing durable deposit usually over another electro- it such as nickel. The second is a heavy coating and is referred to dustrial or "hard" chromium. This type utilizes chromium's special rties which includes resistance to heat, wear, corrosion and errosion ow efficient of friction.

olution formulation and anodes employed in both types are essentially me. The difference is in the thickness of the deposit. Chromium deposited from a solution of chromium acid and water containing more acid radicals which act as catalyst to bring about or aid in thodic deposition of chromium. Those most commonly used are sulfate uoride.

rowing power of chromium plating solutions is relatively poor and attention must be paid to the placement of anodes. In many hard m plating operations, the use of auxilliary anodes is mandatory minimum thickness requirements. (1)

N COMPOSITION

nercial process of chromium plating started in 1923 principally g from the work of C. G. Fink and C. H. Eldridge. This solution osed of chromic acid, water and sulfuric acid. In 1949, self ng solutions using a double catalyst system, generally sulfate co fluoride, was introduced. This solution was easier to control ced plating time considerably by increasing cathode efficiency. (1)

t years a new solution employing an organic inorganic trivalent complex in a low valence chromium plating solution, has found ptance in decorative chromium but few applications in industrial cause of limitations in the thickness and hardness of the deposit. (2)

POSITION

ic acid catalyst solution almost always uses lead or lead alloys A film of lead peroxide is formed on the anode surface during using the trivalent chromium to be reoxidized continuously to chromium (chromic acid), thereby keeping trivalent chromium alue. Excessive trivalent chromium build up in the solution render the solution inoperable.

Initially lead was used for anodes but lead is a very soft material and is susceptible to warpage when used in long anodes. Alloying with antimony reduced many of the early problems with chemical lead. An alloy of between 4-10% antimony was normally used. With the introduction of the fluoride containing mixed catalyst, the presence of tin was required to reduce chemic attack during operation.

Anodes constructed of iron, steel, nickel and stainless steel can be used in special industrial chromium plating operations when higher strength and rigidity than are obtainable with lead alloys were required. However, use of this type of anode leads to iron contamination and an excessive build up of trivalent chromium. Because of this, steel or copper can be coated with a lead alloy when high strength, high conductivity, and rigidity are required for a particular application. Also, inserting a copper or steel rod in to a hollow lead anode and sealing with a lead alloy can be also employed.

In the vast majority of applications, the selection of a high strength lea alloy can eliminate the need for special construction. In the early 1950' it became apparent that lead and lead antimony were not acceptable anodes for the fluoride containing solutions. It then was recognized that tin was required to reduce chemical attack. Two alloys were developed at this tim which were proven to provide superior performance in both the standard and mixed catalyst solutions. One of these was 7% tin 93% lead. It was deter that 2% tin was required to reduce solution attack and the additional 5% provided the increased strength. The other alloy was 2% tin, 4% antimony and 94% lead which provided the same result.

Both alloys have been used for over 25 years with little or no problems. Attempts to use other alloys have often encountered problems so that at t present time the vast majority of anodes consist of either of these two a

From 1972 to 1978, the cost of tin increased from $1.50/lb. to over $8.0 This represents an increase of $0.46/lb. in the 7% tin anode while only a 0.13/lb. increase in the 2% anode. Since the performance of both alloys similar and the majority of anodes used are the tin antimony lead alloy, companies whose material specification requires the 7% tin 93% lead allo are rapidly changing to the less expensive tin/antimony/lead. This perm them to reduce anode costs without sacrificing quality.

Another alloying element that can improve performance is silver. Silver concentration of 0.5-2.5% increases anode life and provides increased s but because of the cost of silver ($90/lb.), the alloy cost offsets the advantages. Other alloying elements such as calcium and tellurium can used in conjunction with tin but must be carefully controlled to produc consistent results.

ANODE FABRICATION

Lead alloy anodes are almost exclusively extruded. The reason for this that extrusion provides a dense fine grain material that is less suscep to chemical attack.

e a chromium plating operation produces an extremely corrosive environ-
, it is important that hooks be homogeneously bonded to the anode. This
ides for maximum strength and efficiency in electrical conductivity.
Fig. 1)

best way to assure bonding during all manufacturing operations is to first
a copper alloy hook with a corrosive resistant lead alloy utilizing a
ng acid flux to assure good wetting. This assures an extremely solderable
ce for casting a bulb around the hook to provide a lead alloy of at
2" to protect the copper. The hook is then thoroughly cleaned to re-
all flux residues.

inal attachment to the anode is performed by a lead burning procedure
utilizes a reducing gas to provide fluxing. The finished anode is
neously bonded to the hook for maximum electrical conductivity, and free
rosive flux residues.

ELECTION

lection of the best hook design for a particular application should
nto consideration the following:

The size and shape of the conductor bar.

The maximum current the hook must carry.

The distance from conductor bar to solution.

The size and shape of the anode.

he type of lifting mechanism that may be used.

portant that the hook be designed for the conductor bar so that it
vide maximum contact. Hooks will carry current in direct proportion
ross sectional area of the copper. Most hooks will carry
00-400 amps. In most plating situations, a current exceeding 100
anode is rare. If there is a possibility that the current is over
per anode, it is advisable to check with your suppliers as to the
urrent carrying capacity. (See Fig. 2-3-4)

es in chromium plating will safely conduct 80 amps per square inch
sectional area provided there is good contact between hook and conductor
tact problems are usually the major cause of anodes running hot.

ead alloy anodes act as insoluble anodes in chromium plating, there
ich will eventually erode the anode. During plating, a film of lead
l be formed which is essential to reoxidize trivalent chromium.
urrent is off, this will be converted into lead chromate. This is
precipitate which is found on the bottom of all chromium plating
n current is again applied lead peroxide is reformed. This reaction

causes the anode to eventually wear to the point where it must be replaced The life of a lead alloy anode varies from six months to six years. The longest life will be in automatic plating installations where the current on continually.

AUXILLIARY ANODES

Since chromium plating solutions have extremely poor throwing power, it is often necessary to employ auxilliary anodes to meet minimum thickness requ ments. Figure 5 is an example of a 3/16 rolled sheet of 2%Sn 4%Sb 96%Pb that has ¼" square holes punched out. This can be easily cut out into the shape of the recess area for an auxilliary anode. The holes allow solutio to flow through and thus does not restrict the current flow from the main anode. (See Fig 5)

Often lead alloy wire is used for auxilliary anodes. It is best to use e 2%Sn 4%Sb 94%Pb or 7%Sn 93%Pb but these alloys are not available in wire The following common solder alloys can be utilized:

5Sn 95Pb	2.5Ag 97.5Pb
10Sn 90Pb	1.5Ag 1Sn 97.5Pb
10Sn 2Ag 88Pb	

These alloys are used in soldering in wire diameter between 0.032" and 0

ANODE SHAPE

The majority of anodes employed in chromium plating are round because th configuration is best for obtaining uniform current density all over the Flat anodes will usually produce a variation in anode current density be the side facing the cathode and side facing tank. This can be overcome punched flat anode to form an open basket weave. (See Fig. 6-7) This surface area by 100% and provides uniform current density throughout th A 3" x ¼" flat anode of this type is ½ the weight of a 1½" and ¼ the we of a 2" round anode. This flat anode, because of its reduced weight i in hard chromium applications where anodes must be constantly moved.

Another way to reduce weight is to use a hollow anode. (See Fig. 8) A weight can be reduced by 50%. In both cases, the cross sectional area be sufficient to conduct the current required.

SUMMARY

The alloys most often employed for anodes in chromium plating are 2%Sn 94%Pb and 7%Sn 93%Pb. The former is usually preferred because of its cost and equal performance. Most anodes are extruded since this provi dense fine grain structure that is less susceptible to chemical attac selection is very important and current carrying capacities of both h anode should be adequate to prevent overheating. Positioning of anod use of auxilliary anodes are often required to obtain maximum throwin

the lead alloy selected must be one that will reoxidize efficiently
lent chromium.

ENCES

. Dubpernell - Modern Electroplating 5, 80 (1966) 2nd. Edition John Wiley
nd Sons, Inc. New York City.

E. Bride - Plating, November 1972.

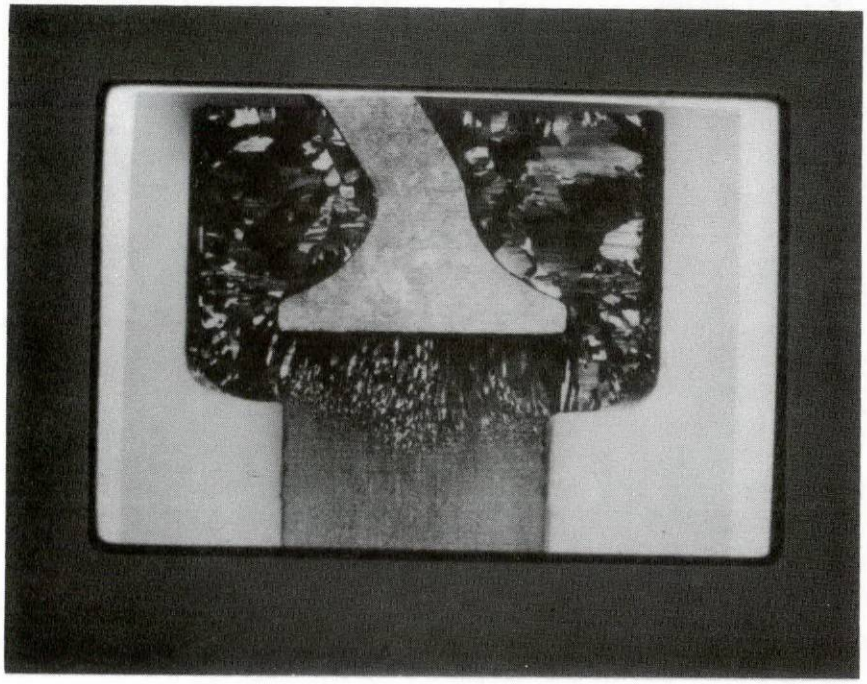
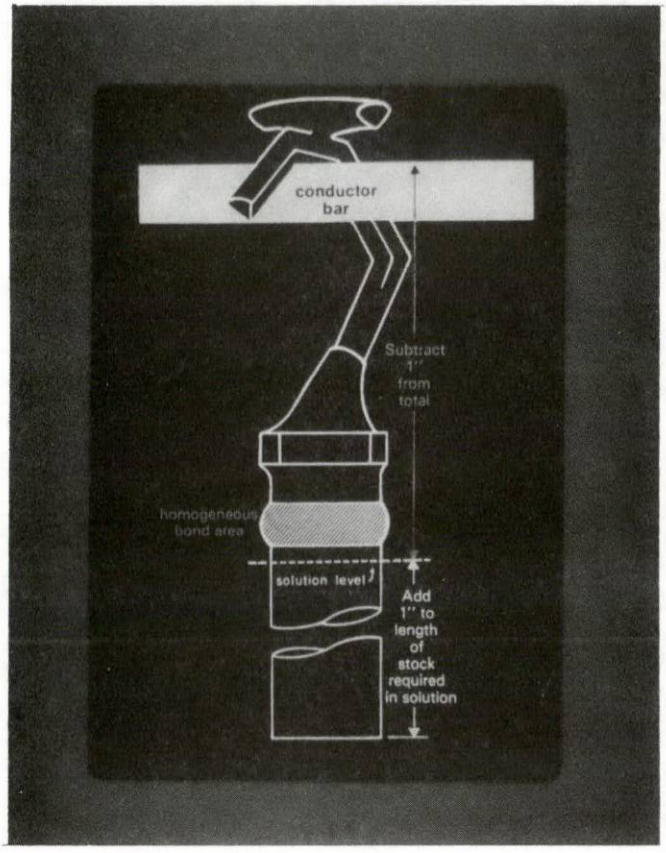


Fig. 1 Anode hook homogeneously bonded to extruded anode. Note: Fine g
structure of extruded alloy material in anode.



Hook selection depends on distance from conductor bar to solution level.



Fig. 3 Anode hooks designed for square and rectangle conductor bars. hook will conduct 350 amperes, while other 225 amps.



Anode hook for round conductor bar. Note: Differences in pickup arm and current carry capacity 350/225 amps.

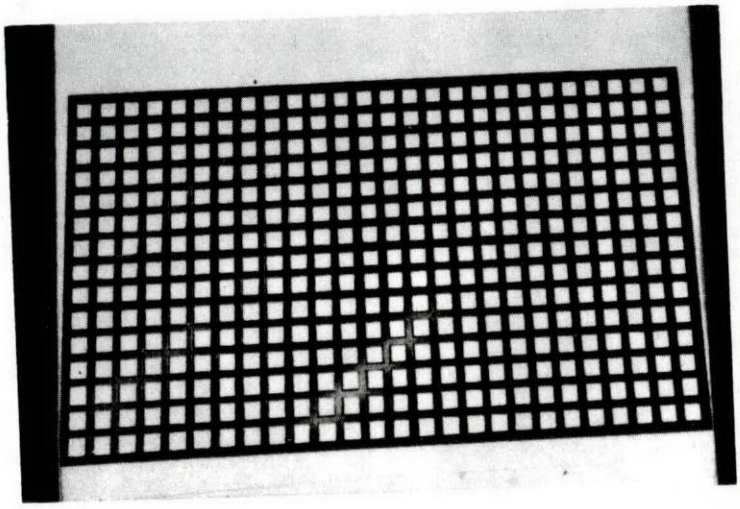
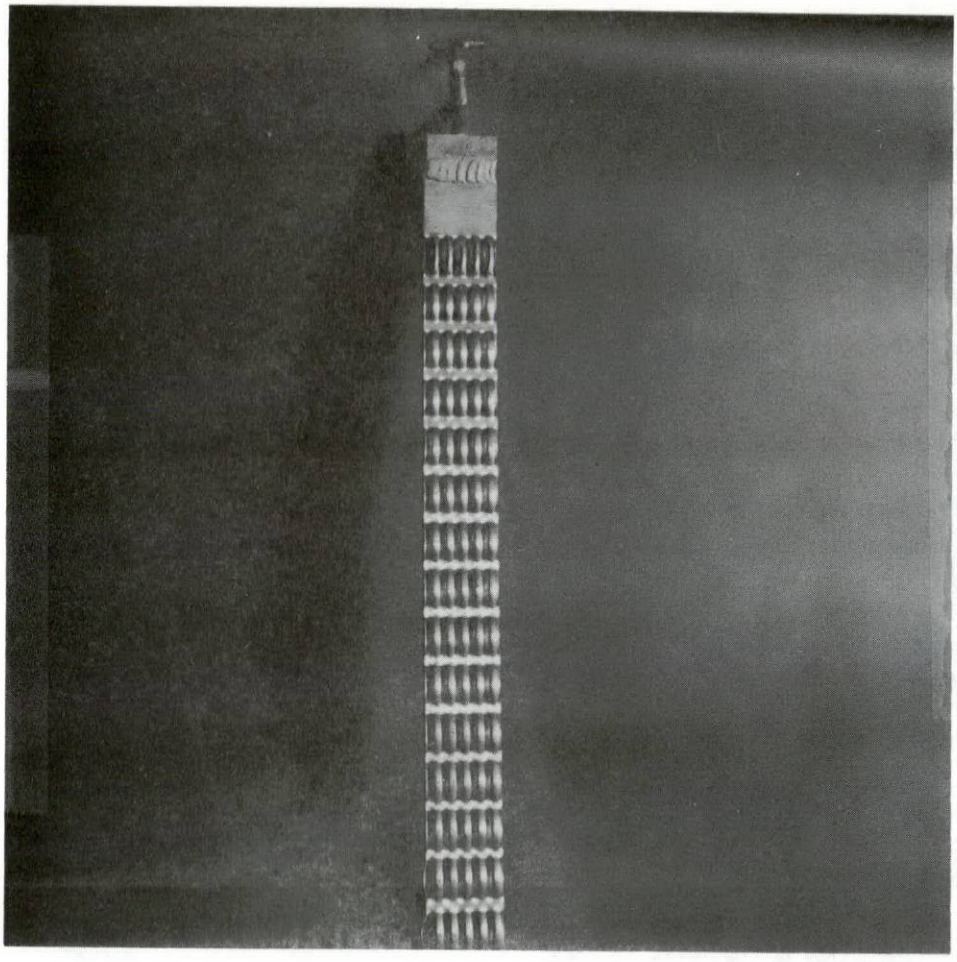


Fig. 5 For hard chromium platers

The 3/4" holes permit rapid circulation of plating solution. E
and formed into cylinders and other shapes for special applica



Special anode configuration to increase anode area and permit solution flow through anode.

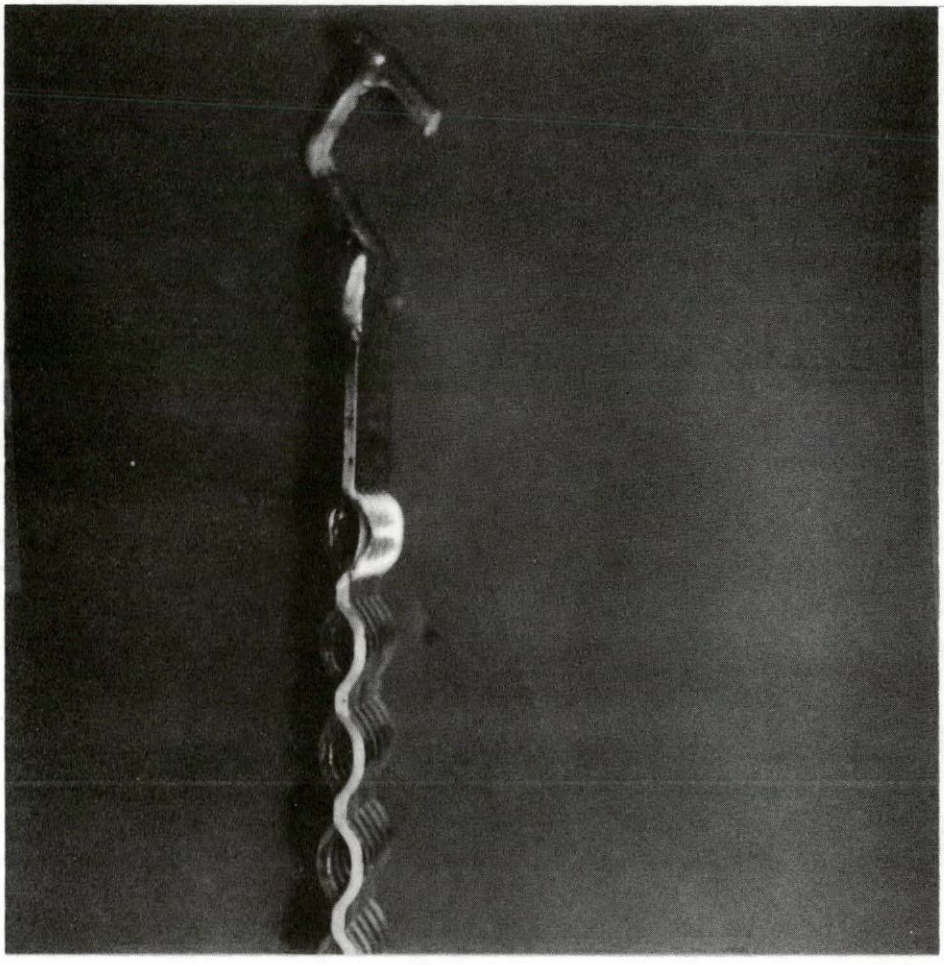
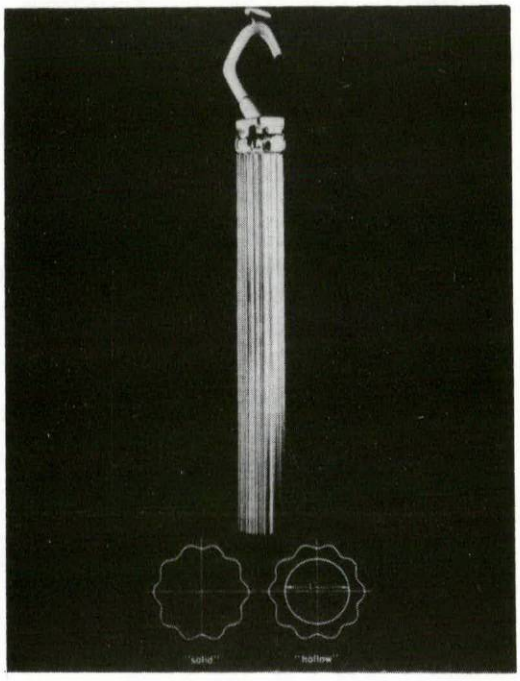


Fig. 7 Side angle view of Fig. 6.



Hollow ripple round to reduce weight and increase surface area. Note: Weight reduced from 1.2 to 0.62 lbs./inch. However, current carrying capacity reduced by 60%.

J-2

Chromium I
Session J

Low Concentration Hexavalent Chromium Electroplating Baths

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ABSTRACT

Two types of non-conventional low concentration hexavalent chromium electroplating baths have been investigated. One is a catalyst free CrO_3 bath of about 15-100 g/l CrO_3, the other a CrO_3/H_3BO_3 bath of 5-20 g/l CrO_3 and 20-60 g/l H_3BO_3. On electroplating, both baths produce a color film which can be removed by an acid treatment to expose the bright chromium underlayer. These baths are tolerant to interrupted current and non-filtered DC current.

Low Concentration Hexavalent Chromium Electroplating Baths

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mmercial decorative chromium electroplating relies on two pes of baths: the hexavalent chromium and the trivalent romium. The successful operation of the trivalent chromium ectroplating process is quite recent and will not be scribed here. On the other hand, hexavalent chromium ctroplating is an old process, the successful operation which can be dated back to 1923 or earlier.[1] The bath as d today usually contains chromic acid (CrO_3) and a sulfate $_4^=$) as the major ingredients. The presence of $SO_4^=$ or $_4$, called a catalyst, in the hexavalent chromium bath is ust, otherwise no chromium will be deposited. Another alyst frequently added to the bath with H_2SO_4 is fluosilicic (H_2SiF_6) or silico fluoride ($SiF_6^=$). Baths containing Cl^-, ClO_3, Br^-, NO_3^-, H_3BO_3, BO_3^-, Na^+, K^+, Mg^{+2}, Al^{+3}, have been investigated or formulated,[2] but the results either uncertain or unacceptable.

is paper, experimental results obtained in the laboratory the operation of two non-conventional low concentration alent chromium baths will be described.

IMENTAL PROCEDURE

um electroplating was carried out either in a modified ell or in a 1.5 litre beaker, both containing one of solution. The modified Hull Cell consists of a 267 l Cell placed in an 11.1 cm X 20.3 cm (4 3/8" x 8") op rectangular box (Fig. 1). The Hull Cell, made of , was modified by making three 1.1 cm (7/16") holes bottom and removing 5.1 cm (2") of the wall along the side of the cell and next to the anode. A magnetic g bar was placed in the rectangular box next to the section. Solution circulation as created by the stirring bar and

induced by the natural convection during electroplating helps maintain a uniform temperature throughout the rectangu box. A lead anode and a nickel electroplated cathode were placed in the typical Hull Cell positions for electroplating

Electroplating in the 1.5 litre beaker was conducted with a lead anode directly across from a flat 3.8 cm X 15.2 cm (1.5" x 6") nickel electroplated buffed brass cathode. For thickness measurement experiments, the nickel electroplated cathode was masked off with plater's tape to expose a 29 cm^2 (4.5 in^2) section. A magnetic stirrer on the bottom of the beaker was used to maintain a uniform bath temperature. Bath temperature in both the modified Hull Cell and the 1.5 litre beaker was maintained at 43.3°C (110°F). A thermisto sensor and a quartz heater were used for temperature contro

For each panel to be plated, the following cycle was employ (water rinses are not shown):

1) Electrolytic alkaline cleaning
   4.3 A/dm^2 (40 ASF) for 1 min., cathodic
2) Acid dip 20% HCl by volume
3) Bright nickel electroplating
   4.3 A/dm^2 (40 ASF) for 5 min.
4)* Experimental chromium electroplating
   Various conditions at 43.3°C (110°F)
5) Post-treatment to remove color film
6) Forced air drying

* Panels for thickness measurement were partially masked-off prior to chromium electroplating.

CATALYST FREE LOW CONCENTRATION CrO_3 BATHS

If one tries to electroplate something out of a CrO_3 bath with no catalyst in it, a rainbow colored film will be obtained instead of the chromium metal. The color film electroplated from a catalyst free 15 g/l CrO_3 bath has examined using the ESCA (Electron Spectroscopy for Chemi Analysis) technique, which indicated the presence of Cr^+ and $O^=$ in the film, and also the possibility

f chromium metal underneath the film.
ne color film from catalyst free CrO_3 baths was very inert.
oot testing for about an hour on panels electroplated with
ne film showed that the film did not dissolve in dilute or
oncentrated H_2SO_4 or HNO_3, but did dissolve in 30% by
olume or more concentrated HCl solutions. Only nickel was
etected after the film was dissolved. A decorative chromium
yer could be obtained if the panel containing the film was
mersed in a 20% by volume H_2SO_4 solution for several
nutes and then removed and rubbed hard with a paper towel.
e immersion and rubbing technique was repeated until the
m was completely removed from the panel.

was found that a longer immersion time was required for
ms which had been dried in air, also for films obtained
n longer electroplating time and from baths of higher
concentrations. Typical immersion times are given in
e I.

e II shows the approximate thickness of four chromium
sits from catalyst free CrO_3 baths. It is seen that the
troplating speed decreases with an increase in CrO_3
ntration, and also with an increase in electroplating
Although it is not known exactly what causes these
es, it is assumed that these changes have something to
th the process of the film formation during electroplating.
f the possibilities would be that the film gets thicker
electroplating and gets denser (i.e., more packed)
lectroplated in higher CrO_3 concentration baths. In
f the results shown in Table I, these assumptions are
o unrealistic.

mersion time required in post-treatment was drastically
when a hot H_2SO_4 solution was used, such as at 60°C
. Under this condition, an immersion time of 15
was long enough to remove the films obtained from
nt baths regardless of post-drying time such as
n Table I.

sed chromium deposit from the catalyst free CrO_3

bright. But its current efficiency was very low. It is estimated to be less than 1% even with the most efficient dilute bath (Table II). However, there are two interesting features about this bath: its tolerance toward current interruption during electroplating and its allowance of the use of non-filtered DC current for electroplating. These bath characteristics, it is believed, are related to the formation of the overlayer film, which works in such a way that the underlayer chromium is protected.

Current interruption was made by current stoppage of one second in each minute for a total of six minutes electroplat time. After removal of the film by post-treatment, the exposed chromium on the panel was clear and without haze or color. In another experiment, a full wave non-filtered DC current was applied to six minutes of electroplating and th electroplated panel was immersed while wet in the 20% H_2SO_4 solution at room temperature. In this case, a much longer immersion time of 90 minutes was necessary, indicating that the film was quite dense. The exposed chromium was as cle as others.

LOW CONCENTRATION CrO_3/H_3BO_3 BATHS

It was found that the addition of boric acid (H_3BO_3) to th catalyst free CrO_3 bath improves its current efficiency significantly (about 3 times greater), especially for long electroplating time (see Table III). In addition, the overlayer color film then became soluble in dilute acids 3 minutes in 5-10 H_2SO_4, HCl, or HNO_3 by volume at room temperature) with no need of rubbing.

Examination by ESCA revealed that the film contained Cr^{+3} $O^{=}$, and B^{+3}, but B^{+3} was not detected after the piece had been immersed in water for 24 hours. This indicated that the boron compound (probably H_3BO_3) can diffuse into the surrounding water. The interesting point here is: even though the boron compound is not inolved in the backbone structure of the film, yet it has great influence on the properties (chemical and/or physical) of the film to cau the latter to be soluble in dilute acids.

A wider range of CrO_3/H_3BO_3 baths have been briefly test

arting with a low CrO_3 concentration of 1.25 g/l. Results from me of the low concentration baths are given in Table IV, together th those from 100:1 CrO_3/H_2SO_4 baths. (Higher concentration baths e not described here because they have somewhat different character- tics and testings for these baths are not finished yet.) As mpared to 100:1 CrO_3/H_2SO_4 baths of equivalent CrO_3 concentrations, w concentration CrO_3/H_3BO_3 baths can electroplate a brighter deposit th better chromium coverage in a wider range of CrO_3 concentration arting from as low as 1.25 g/l CrO_3. The best chromium deposit nes from baths with 5-20 g/l CrO_3.

lowing are some interesting features about the low concentration $_3/H_3BO_3$ bath:

1. The bath can tolerate current interruption during plating. Or, the electroplated piece may be taken out of the bath, inspected, and put back again for further electroplating without ill effects on the deposit. In fact, the electroplated piece may be kept in water overnight and transferred to the same bath to be electroplated again the next day without producing any whitewash or marks on the plate.
2. The bath is not affected much by the use of non-filtered DC current. The deposit produced has a very slight haze which is unnoticeable except under a bright light such as the tungsten halogen light.
3. Thicker chromium deposits from low concentration CrO_3/H_3BO_3 baths are microdiscontinuous. A deposit of .625μ (.025 mil) in thickness from a 15 g/l CrO_3 bath showed microporosity of 1,500,000 pores/in^2. Deposit of 1μ (.040 mil) thick showed microcracking of 1,750 cracks/in.
4. Low concentration CrO_3/H_3BO_3 baths cannot tolerate the presence of sulfate ion. As low as .01 g/l $SO^{=}_4$ will cause a frosty-milky deposit. In our practice, to safeguard against the possible presence of $SO^{=}_4$, a small amount of barium carbonate ($BaCO_3$) is always added to the bath before its use.

CONCLUSION

Two types of dilute hexavalent chromium baths have been described. One is the catalyst free CrO_3 bath, the other the CrO_3/H_3BO_3 bath. Special features common to both baths and their deposits are:

1. The formation of overlayer color film during electroplating and its removal by certain dilute acid treatment.
2. Tolerance to current interruption.
3. Allowance of the use of non-filtered DC current.

Additional features about the CrO_3/H_3BO_3 bath and its depos are:

1. Chromium deposit from a bath with as low as 1.25
2. Microporous and microcracking properties of thick deposits.

References

1. G. Dubpernell, Plating, 47, 35 (1960)
2. P. Morisset, J. W. Oswald, C. R. Draper & R. Pinner, "Chromium Plating", Middlesex, England, Robert Draper

TABLE I

Post-Treatment By Immersion and Rubbing
Using 20% H_2SO_4 at Room Temperature

Catalyst Free Baths: 15 g/l CrO_3 and 100 g/l CrO_3
Current Density: 13 A/dm^2 (120 ASF)
Bath Temperature: 43.3°C (110°F)

ating Time Min.	CrO_3 Conc. g/l	Immersion Time, Minutes Wet Film	Film 2½ Min. in Air	Film 30 Min. in Air
6	15	10	35	90
6	100	>10	60	150
3	15	5	--	---
3	100	<10	--	---

TABLE II

Deposition of Chromium From Catalyst Free CrO_3 Baths
(43.3°C or 110°F)

Bath osition CrO_3 g/l	Current Density A/dm^2	Approx. Deposit Thickness (µm) and Current Efficiency (%) 3 Min. µm	C.E.,%	6 Min. µm	C.E.,%
15	13	.022	.76	---	---
40	13	.022	.76	.028	.48
00	13	.020	.69	---	---
50	13	.012	.41	.018	.31

Fig. 1 THE MODIFIED HULL CELL

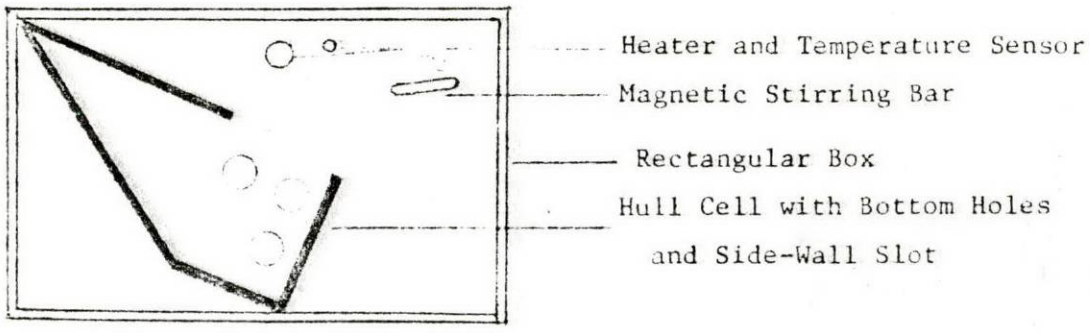

TABLE III

Deposition of Chromium From CrO_3/H_3BO_3 Baths
($43.3^{o}C$ or $110^{o}F$)

Bath Composition CrO_3 (g/l)/H_3BO_3 (g/l)	Current Density A/dm^2	Approx. Deposit Thickness (µm) and Current Efficiency (%)			
		3 Min.		6 Min.	
		µm	C.E.,%	µm	C.E.,%
15/30	13	.063	2.2	----	---
40/30	13	.053	1.8	.098	1.7
100/30	13	.053	1.8	----	---
250/30	13	.050	1.7	.088	1.5

CrO_3/H_2SO_4 Baths

in Modified Hull Cell (43.3°C or 110°F)

	CrO_3/H_3BO_3 Baths			100:1 CrO_3/H_2SO_4 Baths		
	Bath Composition	Chromium Coverage	Deposit	CrO_3 Conc.	Chromium Coverage	Deposit
A x Min.	CrO_3(g/l)/H_3BO_3(g/l)	mm	Appearance	g/l	mm	Appearance
0.5 x 3	1.25/2.5	25	Bright	1.25	0	No Plate
2 x 3	5/10	75	Bright	5	72	Bright
2 x 3	5/20	80	Bright			
3.5 x 3	15/30	79	Bright	15	81	HCD* Frosty
3.5 x 3	15/60	84	Bright			and Milky
3.5 x 3	40/30	77	HCD* Greyness	40	74	HCD Brown
3.5 x 3	40/60	84	HCD Greyness			Spots

*HCD = High Current Density Area

CrO_3/H_2SO_4 Baths
in Modified Hull Cell (43.3°C or 110°F)

	CrO_3/H_3BO_3 Baths			100:1 CrO_3/H_2SO_4 Baths		
	Bath Composition	Chromium Coverage	Deposit	CrO_3 Conc.	Chromium Coverage	Deposit
A x Min.	CrO_3(g/l)/H_3BO_3(g/l)	mm	Appearance	g/l	mm	Appearance
0.5 x 3	1.25/2.5	25	Bright	1.25	0	No Plate
2 x 3	5/10	75	Bright	5	72	Bright
2 x 3	5/20	80	Bright			
3.5 x 3	15/30	79	Bright	15	81	HCD* Frosty
3.5 x 3	15/60	84	Bright			and Milky
3.5 x 3	40/30	77	HCD* Greyness	40	74	HCD Brown
3.5 x 3	40/60	84	HCD Greyness			Spots

*HCD = High Current Density Area

J-3

Chromium I
Session J

High Speed Plating of Chromium

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HIGH SPEED PLATING OF CHROMIUM

By

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ABSTRACT

A high speed plating (HSP) system for chromium has been developed
d on a narrow gap between electrodes and high volume flow of electro-
. Electrodeposition of bright chromium was readily obtained at a
of 5 μm/min (0.0002 in./min) at a current density of 11 A/cm^2
$/in.^2$). The plating conditions and the device used for HSP are
ssed. Restricted longevity of the electrolyte pumping system
rs to be a future problem to be addressed.

HIGH SPEED PLATING OF CHROMIUM

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INTRODUCTION

In normal electrodeposition, the part to be plated is immersed in a table electrolyte in a plating tank and a low DC voltage is applied ween the part as cathode and a suitable anode. As current flows, metal sition results. Depending on the metal deposited, on the electrolyte on adjustment of variables, the current density may vary from 0.02 to A/cm^2 and the plating rate may vary from 10 to 100 μm/h. In most cases is a satisfactory system, since it provides the required coatings and nesses at reasonable costs.

The plating of chromium, one of the more useful engineering electro- its, is usually performed at higher current densities, 0.16 to 0.3 however, plating rates thus achieved are relatively low, 10 to 25 s a result of poor cathode current efficiency.

he use of proprietary electrolytes and systems, under some circum- , can permit the doubling or tripling of plating rates, but even ting periods can be measured in hours to obtain the desired thicknesses. esirable, therefore, to find a method to improve the efficiency and osition of chromium.

A number of characteristics of the chromium plating bath, and its operation, pose particular difficulties in attempting high rate deposition The more important of these are:

- Deposition occurs from a hexavalent chromium bath requiring six electrons to reduce the ion to the metallic state.
- Bath efficiency is usually low, ranging from 10 to 16%.
- The deposition requires a catalyst which must be controlled within a narrow range of concentration.
- The bath is a strong oxidant and is very corrosive.
- Semi-inert anodes (lead alloys) are used in deposition.

As a result of these unattractive features, it is one of the most c and most difficult plating processes in use and any improved system must come the problems.

Recently two methods have been publicized which purport to overcom problems and claim to be improved, high-rate processes. The first of t (1) plates at high rates compared to ordinary tank procedures. It is a to do so by abrading the cathode surface during plating with inert, har particles. This rapidly removes the cation-depleted electrolyte layer the cathodic surface and replaces it with fresh solution, thus raising limiting current density. The abrasion may also serve as an activatin smoothing operation while the plating proceeds.

The second publicized method (2) for high-rate deposition of chro combines electroplating and honing. The honing in this case provides removal of the cation-depleted electrolyte layer much as in the other and it is further claimed to provide size control and surface conditi concurrent with electrodeposition.

Another method that holds promise to accomplish improvement in chromium deposition is referred to as high speed plating (HSP). Development of a device based on narrow gap spacing and rapid electrolyte flow between anode and cathode, and some of the results obtained using this system are the subjects of this paper.

EXPERIMENTAL

The device developed for HSP consisted of an upright machine base, a fixture, pumping system, a rectifier and the necessary associated controls. This assemblage is shown in Fig. 1. The plating fixture employed in this work is shown in Fig. 2 in the plating position. Figure 3 shows the same fixture open and ready for sample removal. This is also the loading position of the fixture. The samples employed in this work are shown in close-up in Fig. 4.

achine Base

All plating was done in the machine base shown in Fig. 1. It nsists of a stainless steel frame, a traveling head carrying the work ece on a push rod, a variable speed drive unit and provision for gidly mounting the plating fixture. The drive unit speed was variable tween 0.33-2.44 cm/s. An air cylinder was used for fixture closure.

ting Fixture

The plating fixture, open for access, with the plating sample in ition is shown if Fig. 3. It is made of stainless steel lined with on. The fixture was made in three sections, upper, anode ring and r, all three insulated from each other by two Teflon separators, 3. All sections were made to pilot on one another for proper nment. Flexible, bottom outlet lines were 12.5 mm Teflon tube, less steel braid reinforced. The fixture was opened for access at oint between the anode and the top section of the fixture for nment or removal of the sample from the push rod.

Anode

A very satisfactory anode was made by inserting a lead-tin alloy (95%
plug inside a stainless steel ring, swaging the plug into the ring and bor
to the desired size. In this instance, lead-tin wall thickness of 3.1 mm
produced.

Plating Samples

Plating substrates were steel (SAE 1030) or copper tubes, 38 mm in d
meter, 76 mm long with a nominal wall thickness of 1.7 mm. The outer tub
surfaces were polished, buffed, electrocleaned, acid dipped and dried pri
to use.

Pump

A gear pump was used for electrolyte movement in the experiments.
pump body material was Hastelloy "C"; the shaft bushings and wear plates
made of compacted carbon rod and plate. The pump was equipped with a c
carbon-faced, mechanical internal seal. Both the pump shaft and the dr
gear were made of Hastelloy "C" and the driven gear was made of glass r
forced Teflon. Powered with a 2.25 kW, 1750 rpm motor, this pump provi
flow rate of 90 L/min of water at a discharge pressure of 0.7×10^2 kPa
diameters, inlet and outlet, were 32 mm. Electrolyte flow rate throug
plating fixture was 78 L/min at a pressure of 2.1×10^2 kPa. Under th
conditions, the linear flow velocity through the cell was calculated t
3.9 m/s.

Electrolyte System

The electrolyte tank contained 55 liters. Stainless steel pipe,
diameter, was used for most of the system, changing to 12.5 mm diamet
fixture inlet. The electrolyte was heated by two electrical immersi
heaters, 1000 W, 120 V.

ectrolyte

A CrO_3 electrolyte was employed in all experiments. The concentration ged from 225 to 450 g/L with most experiments employing 300 g/L electro-e. The ratio of CrO_3 to sulfuric acid was maintained at a nominal 100:1.

ting Operation

Plating in the HSP system employed the following procedure:

1. Attach dry sample to machine push rod.
2. Assemble and close fixture.
3. Pump electrolyte through fixture.
4. Activate push rod up-down movement.
5. Plate by turning on rectifier.
6. Reverse push rod movement at fixed point.
7. Reverse push rod movement at fixed point.
8. Repeat 6-7 until required thickness obtained.
9. Turn off rectifier.
10. Turn off traversing mechanism.
11. Turn off pump.
12. Drain fixture.
13. Open fixture and removal sample.
14. Rinse and dry.

e anode-cathode gap was 2.5 mm. Electrolyte temperature ranged from The anodic area was 16 cm^2. Most of the experiments were carried the cathode moving at a linear velocity of 6 mm/s relative to the ry anode. Some work was done with other cathode velocities, 3.3 24 mm/s. The rectifier remained on during the processing cycle, 6, 7 and 8 above so that the plating was not interrupted. es of plating voltage were selected in the range from 5 to 8 V; nts were between 80 and 215 A.

RESULTS AND DISCUSSION

From experience in another high rate electrochemical process--electrochemical machining, ECM,--it was shown that high metal removal rates could be obtained (3,4). The high metal removal rate was the result of application of an external voltage to a cell with a narrow gap between anode-cathode and with a neutral salt electrolyte pumped between the two at high velocity. If the electrolyte was correctly chosen, it was conceivable that plating could be obtained in a similar setup and it was assumed that the speed of reaction would approach that encountered in the ECM process. From results of these experiments it appears that, indeed, HSP, is obtained.

The speed of chromium deposition has been increased by a factor of 25: for HSP compared to conventional plating.

Plating Results

The most interesting result of the work herein described was the plati of bright chromium deposits at rates up to 5 μm/min using current densitie to 11 A/cm^2; the normal still-tank plating rate is usually about 0.3 μm/mi current densities of about 0.2 A/cm^2. Bright deposits were obtained at th plating bath temperatures, Table I. Efficiency measurements yielded an i result of 31-36%, more than double the efficiency of the usual tank plati

System Concept

The machine for holding the plating cell was based on the electrolyt broach from an electrochemical machining application (5). This type of m was necessary for alignment and stability to perform precise work in ECM inlet electrolyte pressures of 1.4 x 10^3 kPa generate large total end-pl pressures. Based on the intended use of similar electrolyte pressures, adapted for HSP. In addition, it appeared advantageous to use a limite anode and to employ cathode traversing to limit the current requirement factors did provide the advantages sought and led to the initial succes HSP of chromium.

ll and Electrolyte System

There were several exercises in the design of HSP cells and in the oices of materials of construction to evolve a stable fixture.

The most critical part of the HSP system was the pump providing the ctrolyte flow. Gear pumps were chosen for their self-priming ability, s offering good operating convenience. Due to the corrosive, oxidizing ctrolyte, pump performance was degraded when dissolution of the Hastelloy occurred. The electrolyte also slowly attacked the compacted carbon rial used for internal parts. The pump internal workings, such as bush- and end plates, were replaced periodically and the mechanical seal was lt at fairly short intervals. Experiments were performed with confi- , but it became apparent that no chemical process pump could survive enough to be process-viable. From the data gathered, it is apparent increased electrolyte flow rates will increase HSP capabilities; to his requirement much larger pumps or sophisticated systems are required.

SUMMARY

ating of bright adherent chromium deposits at a rate of 5 μm/min was d at current densities of 11 A/cm^2. This result was obtained from a eed plating (HSP) system based on a narrow gap between the electrodes gh volume flow of electrolyte. The results presented were exploratory, ppears that further development will improve the deposition rate. A pposedly adequate for the purpose, proved inadequate in capacity and resistance. It was concluded that larger and more sophisticated ems will be necessary for further advances in HSP.

REFERENCES

1. S. Eisner, "Electroplating Accompanied by Controlled Abrasion of the Plate. 1. Plating at Very High Rates.," Plating, 993 (1971).
2. D. Reichard, "New Process Simultaneously Plates and Hones Parts Quic and Economically," Machinery, 37-41, September, 1972.
3. L. A. Williams, Aircraft Production, 22, 389 (1960).
4. J. Bayer, M. A. Cummings, and A. U. Jollis, DDC Rept. AD 450199, Sept. 1964.
5. J. P. Hoare and M. A. LaBoda, Techniques of Electrochemistry, E. Y and A. J. Salkind, ed., Wiley, New York, Vol 3, 1978, p. 130.

Trial No.	Voltage (V)	Current (A)	Current Density (A/cm^2)	Temp. (°C)	Time (Min)	Deposit Thickness (μm)	Rate (μm/min)	Remarks
1	5	100	6	55	5	17	3.4	Smooth, white deposit; efficiency = 31.3%
2	6	130	7.7	55	5	23	4.6	Smooth, semi-bright deposit; efficiency = 35.9%
3	5	95	5.9	59	5	14	2.8	Bright deposit
4	6	125	7.8	59	5	19	3.8	Smooth, semi-bright deposit
5	5	85	5.3	68	10	14	1.4	Bright deposit; ratio 115:1
6	5	80	5.0	71	30	53	1.8	Near bright, good deposit; ratio 115:1
7	5	90	5.6	71	10	15	1.5	On steel substrate; bright, excellent deposit
8	6	125	7.8	77	5	14	2.8	Bright deposit
9	7	160	10.0	85	5	20	4	Bright deposit
10	8	215	12.8	85	5	25	5	Bright deposit

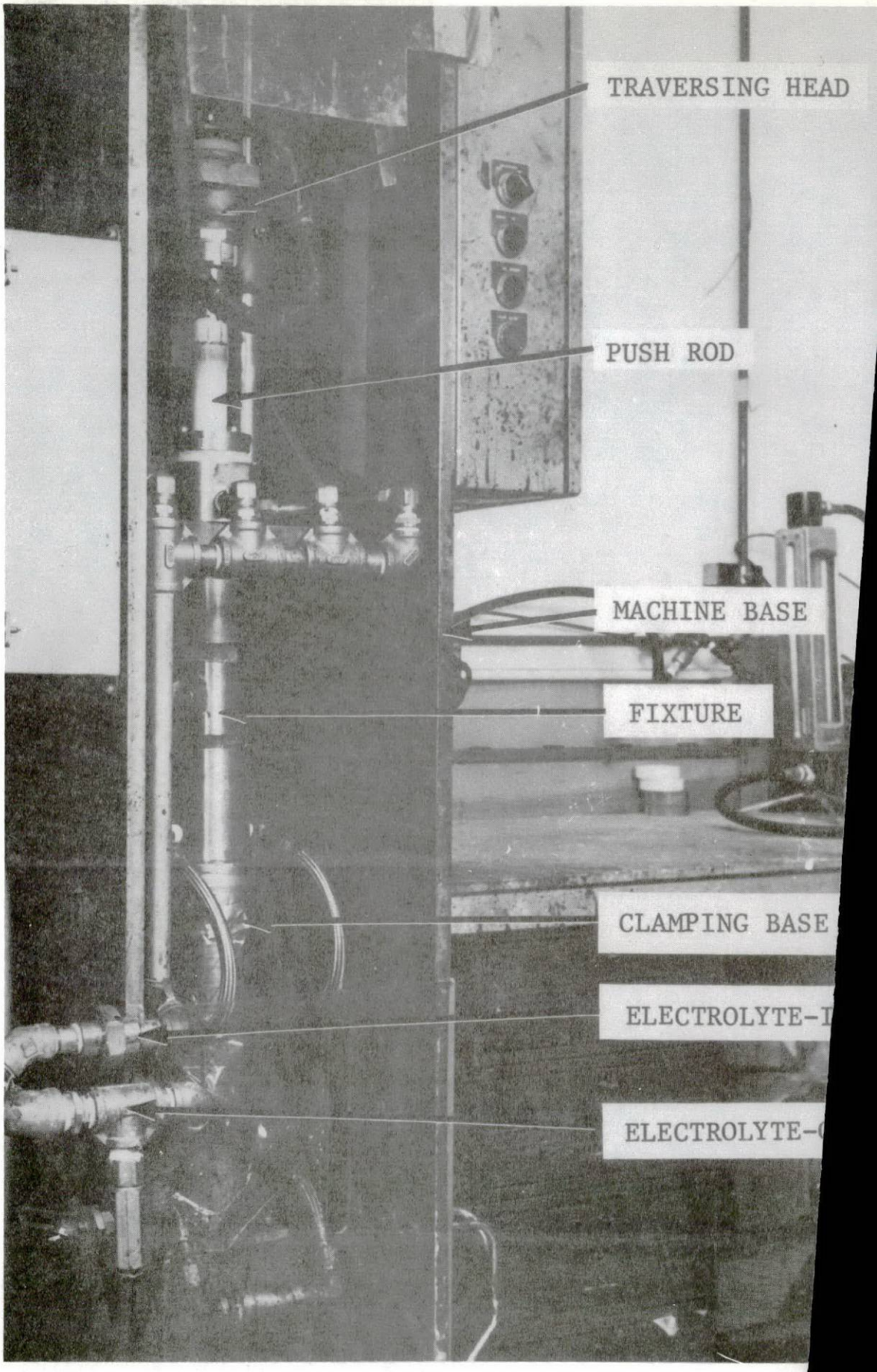

Fig. 1. High speed plating machine base and fixture assembly.

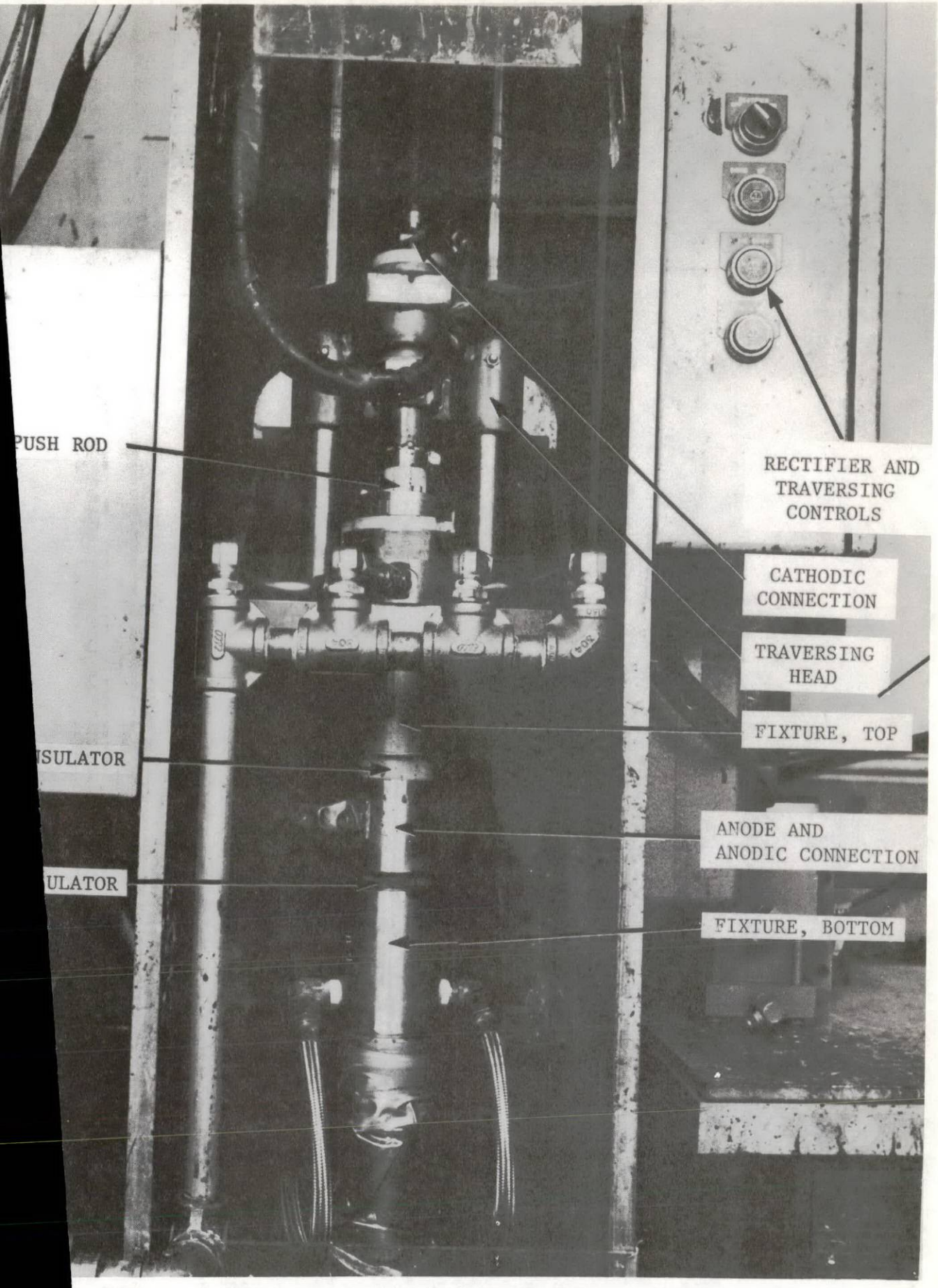

Fig. 2. High speed plating fixture in closed position with sample in plating position.

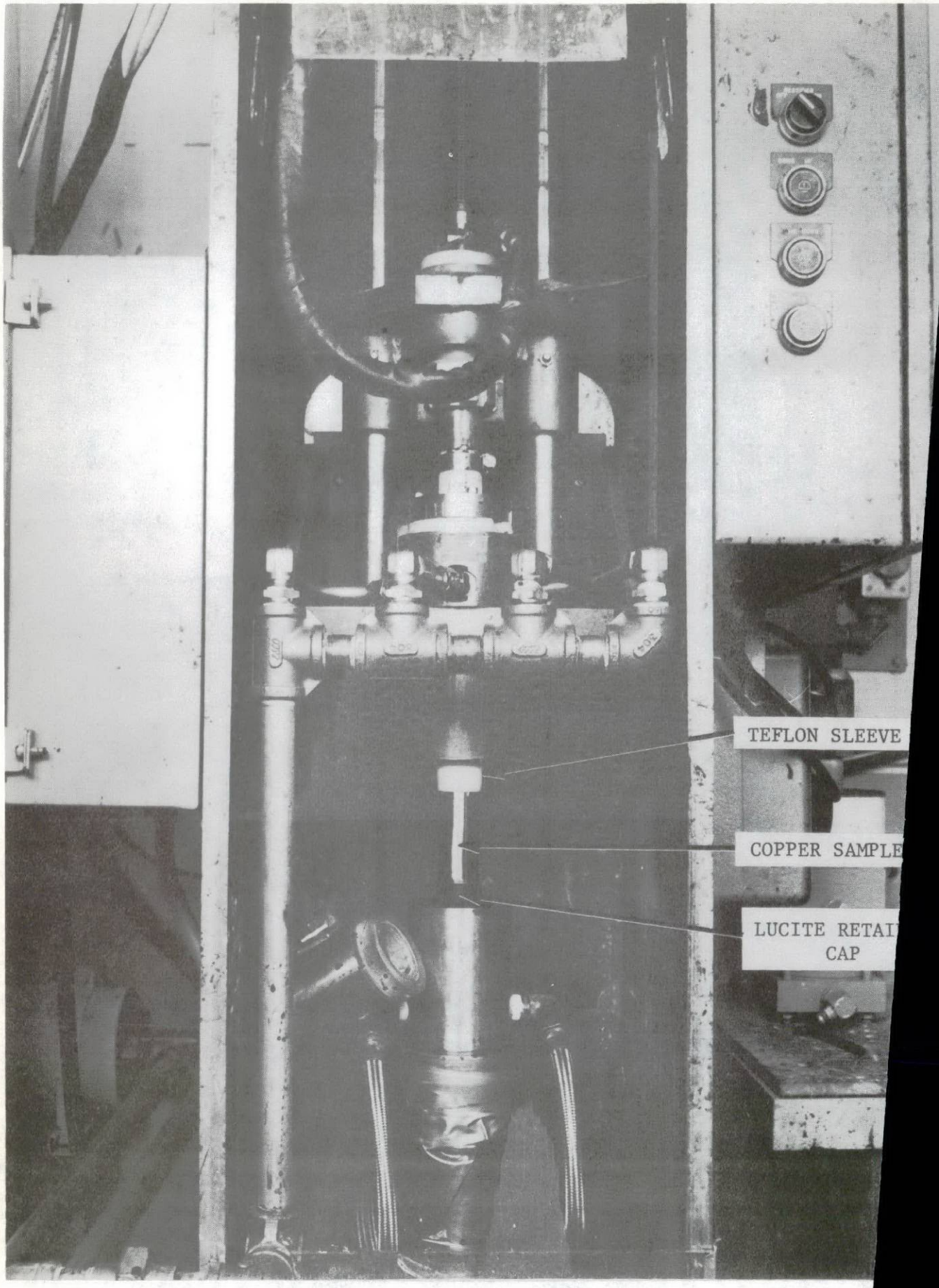

Fig. 3. Fixture open to load-unload position.

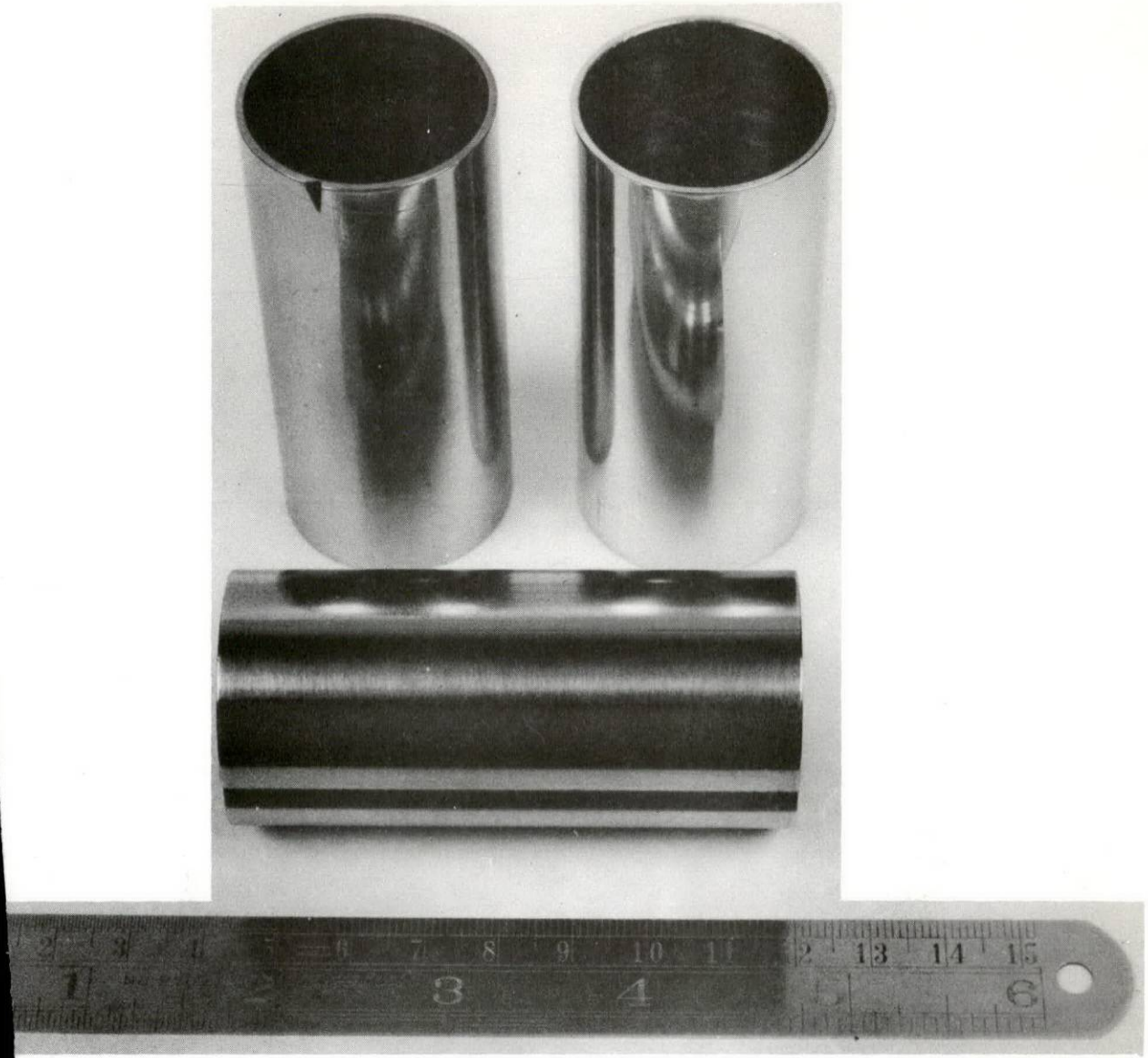

Fig. 4. Plating samples, copper and steel.

J-4

Chromium I
Session J

On the Kinetics of High Speed Plating Of Chromium

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ABSTRACT

A working model of the kinetics of the electrodeposition of metallic chromium (Cr) from conventional chromic acid/sulfuric acid plating baths is presented. In a high-rate flow system, mild steel samples were plated with Cr at high speeds, 20 μm (0.8 mil)/min at 32% coulombic efficiency at 68°C, 6 V and 15.5 A/cm^2 (100 A/in.^{2}). The kinetics of the high speed plating process were interpreted in terms of the proposed model for conventional Cr plating.

ON THE KINETICS OF HIGH SPEED PLATING OF CHROMIUM

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INTRODUCTION

Since the electrodeposition of industrial chromium is a very slow (∿25 μm/h or 1 mil/h) and inefficient (∿12-15%) process, it is highly desirable to develop a high speed plating system that can deposit chromium at a rate at least an order of magnitude greater than the conventional operation. Such a process has been developed (1), but to understand the mechanisms underlying this operation it was necessary to formulate the kinetics of chromium deposition from a conventional sulfate-catalyzed, chromic acid bath (2). It is the purpose of this report to describe an attempt to understand the kinetics of the high speed chromium plating process from an analysis of the model for conventional chromium plating.

THEORY

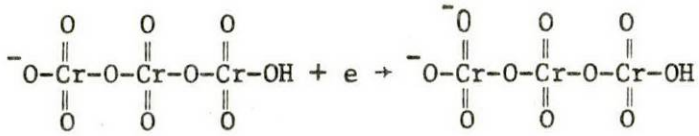
From an analysis of steady state polarization curves obtained on small Pt bead microcathodes in nitrogen-stirred solutions of various chromates, it was determined (2) that a deposit of metallic Cr is obtained only if a cathodic film is present; that a cathodic film is present only if a solution of a polychromate is employed; and that a low pH is required to decompose the cathodic film. Solutions of the

trichromate ion ($HCr_3O_{10}^-$) are red (3), and since the conventional plating bath is deep red, it is assumed that the active species is the trichromate ion. It was also concluded (2) that sulfate plays the dual role of both a catalyst and a blocking agent. In strongly acid solutions the $SO_4^=$ ion is nearly completely converted to the HSO_4^- ion. Consequently, it is the HSO_4^- ion that is the active catalyst, and it catalyzes the discharge of a decomposition product of the cathodic film. The HSO_4^- ion also makes complexes with the polychromate ions to form a distribution of trichromateoxybisulfate complexes in the cathodic film.

With these concepts in mind, one may now write down a working mechanism for the deposition of metallic Cr from a chromic acid solution. One begins with the discharge of the $HCr_3O_{10}^-$ ion. Since this ion is negatively charged, its closest approach to the cathode is in the vicinity of the outer plane of the Helmholtz double layer (4,5), as sketched in Fig. 1, because most of the potential drop be the electrode and bulk solution appears across this electrical doub layer. With a double layer thickness of about 3 to $6x10^{-8}$ cm (6), electron transfer takes place by quantum mechanical tunnelling thro the potential energy barrier of the double layer.

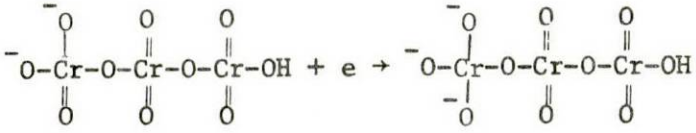
In the first step, a Cr(VI) atom is reduced to Cr(V) by elect tunnel transfer across the double layer to one end of a trichromat ion. The chromate ion is known (7-10) to have its metal-oxygen bo directed toward the corners of a regular tetrahedron and the tetra hedra are linked together to form polymers by sharing corner oxyg atoms, as shown in Fig. 2, after splitting off water molecules.

tetrahedra are symbolized for the sake of simplicity by the following structures.



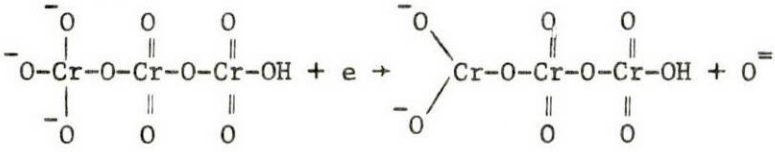
[1]

With the second electron transfer, Cr(V) is reduced to Cr(IV)



[2]

and finally to Cr(III) with the transfer of the third electron and the loss of oxygen



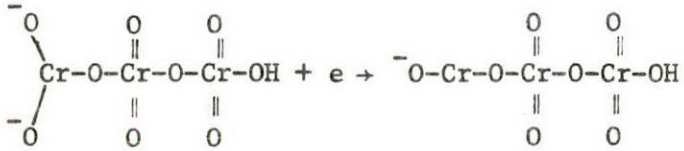
[3]

which reacts immediately with H^+ ions to form water

$$O^{=} + 2H^{+} \rightarrow H_2O \qquad [4]$$

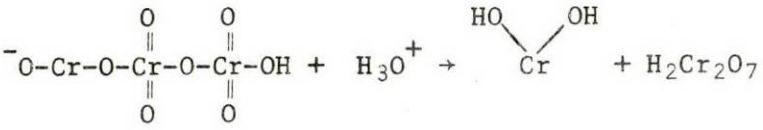
The chromic dichromate complex formed on the right side of eq. 3 protects the Cr(III) from reacting with water to form the very stable hexaaquo complex, $Cr(H_2O)_6^{+3}$ ion. It is for this reason that metallic Cr cannot be deposited from a simple Cr(III) bath because of the formation of this aquo complex from which Cr cannot be separated.

Chromous dichromate is formed by the transfer of a fourth electron followed by eq. 4.



[5)

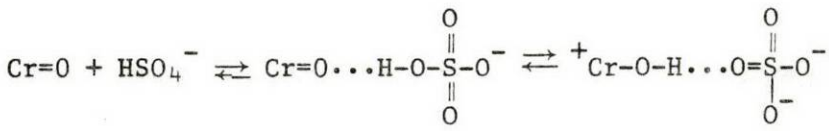
strong acid solutions, the chromous dichromate may decompose to omous hydroxide and a dichromate which can polymerize back to a chromate by condensation with other chromates



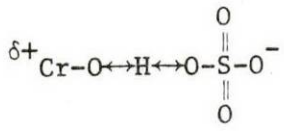
Equation 6 may be considered an acid-catalyzed hydrolysis reaction.

At this point in the mechanism, the HSO_4^- ion can exert its catalytic activity by forming a chromousoxybisulfate complex throug hydrogen bonding.

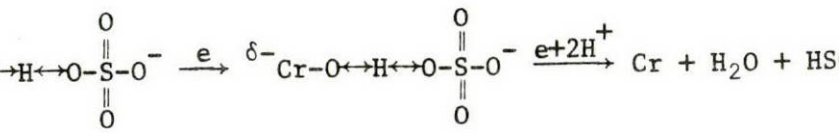
$$Cr(OH)_2 \rightleftarrows Cr{=}O + H_2O$$



For the sake of simplicity, the resonance forms of the complex wi be represented by

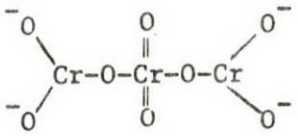


where the double headed arrows represent the hydrogen bond and t δ^+, a partial positive charge appearing on the Cr. By rotating dipole in the outer Helmholtz plane, the positive end of the com can be specifically adsorbed on the cathode surface with the dis placement of an adsorbed H_2O molecule and with the sulfate tetr extending into solution. With the successive transfer of two e to the specifically adsorbed Cr(II) species, Cr(I) and finally Cr along with the regenerated HSO_4^- ion are obtained.

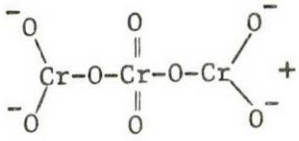


Without the HSO_4^- ion present, the $Cr(OH)_2$ discharges to form which is a mixture of chromium oxides and metallic Cr (11-13)

To account for the blocking agent role played by the HSO_4^- ion, one must refine the above mechanism. In eq. 1 it is possible to transfer electrons to both ends of the trichromate ion, and if this should occur, the complex formed by eq. 3 would be the di-chromic chromate



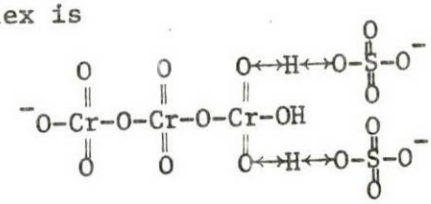
complex instead of the chromic dichromate complex. Dichromic chromates, it is proposed, decompose in strong acid solutions to form chromates and chromic ions which react immediately to form the stable aquo complex.



$$+ 9H^+ \rightarrow 2Cr^{+3} + HCrO_4^- + 4H_2O \qquad [10]$$

$$Cr^{+3} + 6H_2O \rightarrow Cr(H_2O)_6^{+3} \qquad [11]$$

However, the HSO_4^- ion can complex with any of the double bonded oxygens through hydrogen bonding, and it is assumed that electron transfer to a Cr atom for which both double bonded oxygens have been complexed is severely inhibited. As a result, the ideal trichromate-oxybisulfate complex is



[12]

Since one end of the trichromate ion is blocked so that electron transfer takes place only at the other end. It does not matter whether the Cr=O bonds of the middle Cr atom are complexed or not because electron transfer is considered to take place only at the terminal Cr atoms.

There is no reason why the HSO_4^- ion may not complex with any one or more of the Cr=O bonds. So one considers a distribution of trichromateoxybisulfate complexes embracing all permutations, and it is assumed that all of these complexes are in equilibrium with one another.

$$HCr_3O_{10}^- + n\ HSO_4^- \rightleftarrows [HCr_3O_{10} \cdot n\ HSO_4]^{(n+1)-} \qquad [13]$$

where n can have all values from 0 to 6. Since the complexes can rotate in solution, the 24 distinguishable complexes are represented in Fig. 3 with the trichromate spine as a horizontal line and the six Cr=O bonds as perpendicular branches. A complexed Cr=O bond is depicted as a circle at the end of the branch.

Those complexes which have both ends of the trichromate ion un blocked (Group A in Fig. 3) reduce to a dichromic chromate, and the products of cathodization are H_2 evolution and $Cr(H_2O)_6^{+3}$ ions. If both ends of the $HCr_3O_{10}^-$ ion are blocked (Group C in Fig. 3) elec transfer is severely inhibited and only H_2 evolution is the result cathodization. For those complexes in Group B of Fig. 3 where onl one end of the trichromate is blocked, cathodization results in th deposition of metallic Cr along with H_2 evolution as a side react

By varying the ratio of chromic acid to sulfuric acid in mak up the solution, the composition of the distribution of complexes be altered. In Fig. 4 is sketched the distribution functions fo special cases. Curve A represents the case where the bath is hi undercatalyzed and the most probable complexes are those in Grou of Fig. 3. Here Cr metal is not deposited and only H_2 evolution reduction of Cr(VI) to Cr(III) takes place. At the other extre

Curve C in Fig. 4, the bath is overcatalyzed and the distribution favors complexes with both ends blocked from group C in Fig. 3. Here only H_2 is evolved. For a bath which is properly catalyzed at a CrO_3/H_2SO_4 ratio of 100/1, the probability of the presence of complexes from Group B is the greatest as shown by Curve B. If one deviates significantly from the 100/1 ratio, the distribution of complexes is shifted to less favorable conditions for Cr deposition which accounts for the great sensitivity of the process to the 100/1 ratio. It is believed that the other complexes not included in these special groups will behave in an intermediate way between the special cases.

Because of the tail on the distribution curve, even in properly catalyzed baths there will be some complexes of Group A present and Cr(III) will appear in the bath as generally observed. The Cr(III) species may diffuse to the PbO_2 anode where they are oxidized back to Cr(VI).

According to this model, the chromic acid solution is viewed as an equilibrium distribution of H_3O^+ ions, H_2O molecules, HSO_4^- ions, $CrO_4^=$ ions, $Cr_2O_7^=$ ions, $Cr_3O_{10}^=$ ions, and all possible complexes of the chromates and polychromates with bisulfate through hydrogen bonding. It is unlikely that the negative ions are solvated as are the H^+ ions. Since the solution is deep red, most of the chromate-content of the solution exists as the trichromate ion. It is suggested that the cathodic film, which may be identified with the blocking film of Müller (14), the colloidal film of the Russian workers (15-17) and the viscous film of Saiddington and Hoey (18,19) is a mixture of chromic dichromate (see eq. 5) and dichromic chromate (see eq. 10) ions complexed with HSO_4^- ions to various degrees.

Accordingly, these Cr(III)-Cr(VI) complexes are less soluble than the Cr(VI) complexes of Fig. 3 and precipitate out in the Nernst diffusion layer next to the cathode surface to form the dark film which is seen to stream off the cathode after the current had been interrupted. As the Group B complexes are removed from solution by the electrodeposition process, they are replaced by shifts in the equilibrium established between the complexes in solution so that the given rate of Cr deposition is maintained under a given set of experimental conditions.

EXPERIMENTAL

The preparation of the samples to be plated and the plating pro cedure have been described in detail before (1). As before, a high speed plating machine was used through which the electrolyte moved at high flow rates (up to 120 L/min). Mild steel (Type 1020) tubes (7.62 cm long and 3.83 cm in diam) served as the test samples. Th outside surface of the tubes were plated with Cr from a chromic acid solution (300 g/L) composed of a CrO_3/H_2SO_4 ratio of 100/1 at an applied voltage of 6 V between the steel-tube cathode and the concentric toroid lead anode. Data were obtained at two temperat 68°C and 79°C, and at solution flow rates between 36.4 and 120 L/ The samples were plated for one minute at a current density of a 15.5 A/cm^2 (100 $A/in.^2$).

Deposit thicknesses were obtained from gain-in-weight measu ments of the sample and corrections for the corrosion of the sa in chromic acid determined from blank runs were found to be neg

small. From integration of the current-time traces recorded on a strip-chart recorder, coulombic efficiencies for Cr deposition were calculated.

Samples of the plated surfaces were analyzed by Auger (AES) and x-ray photoelectron (XPS) spectroscopy and scanning electron microscopy (SEM). Oxygen was detected from AES depth profiles in the Cr deposits but fell off rapidly with depth of deposit. At 68°C, oxygen content fell from about 15 atomic percent (at. %) at 30 nm to zero at 450 nm; but more rapidly at 79°C, from 15 at. % at 10 nm to zero at 50 nm. Sulfur was also present but at very low concentrations (∿0.5 at. %) and dropped rapidly with depth (zero at 100 nm for 68°C and 10 nm for 79°C)

RESULTS

The seven tube samples plated at seven flow rates at 68°C are shown in Fig. 5 and those at 79°C are shown in Fig. 6. It can be seen that a frosty deposit is obtained at the lower temperature whereas a bright deposit is obtained at the higher temperatures. For a closer look, the SEM micrographs in Fig. 7 show that the frosty surface is pebbly whereas the bright surface is very smooth with a slight scattering of hillocks and with microcracking of the surface. In each case the current density was the same within experimental error.

Plotted in Fig. 8 are the coulombic efficiency (circles) as well as the deposit thickness (triangles) as a function of the solution flow rate for the deposition of metallic Cr on mild steel

at 68°C, 6 V and 15.5 A/cm^2 (100 A/in.^{2}). Similar data obtained at 79°C, 6 V and 15.5 A/cm^2 (100 A/in.^{2}) are presented in Fig. 9.

DISCUSSION

From the SEM micrograph in Fig. 7b, one observes that the brigh chromium deposit from the high speed process is the same as that fro the conventional process. Both show the occasional hillocks on a flat plane of microcracked Cr. Note that the cracks do not go arou the hillocks but through them. It appears, then, that high speed plating is an extension of conventional plating.

From Fig. 1, the closest approach of trichromate ions to the cathode is the outer Helmholtz plane (about 6 x 10^{-8} cm from the c ode surface). One may think of the cathode surface as being cover by a layer of specifically adsorbed water molecules as shown in th first diagram of Fig. 10a. Certainly the H^+ ion in water solutio is hydrated, H_3O^+, and may become specifically adsorbed on the ca surface without replacing a water molecule by a mechanism repres by the first three diagrams of Fig. 10a.

Beyond the double layer exists a layer of solution known as Nernst diffusion layer and ranges in thickness up to 0.05 cm in stirred solutions (20-22). Across this layer there is a concent tion gradient of the electroactive species since the bulk of so is a reservoir of constant concentration of the species of inte At the electrode side of the diffusion layer, the concentration very low because the species of interest are removed by the ele reaction. In the present case, the species of interest are Gr trichromate-bisulfate complexes of Fig. 3 which diffuse to the

Helmholtz layer to be discharged. During the reduction process, chromic dichromate and dichromic chromate complexes with HSO_4^- ions are formed which can hydrogen-bond through water molecules to one another. The result is a formation of a highly viscous, cathodic film which greatly inhibits the diffusion of the trichromate ions toward the cathode. This behavior may be observed in actual plating. If a part is plated under known preset conditions, the initial current decays slightly to a steady state value reflecting the buildup of the cathodic film.

When the solution is stirred, the diffusion layer thickness is diminished allowing a higher rate of diffusion of the electroactive species and a higher deposition rate. However, even with the most efficient stirring, the deposition current is limited by the internal resistance of the plating cell. To increase the plating current still further, the cathode and anode must be brought closer together until in the high speed plating process the interelectrode gap is only 0.25 cm. With such a small amount of solution between the electrodes, the electroactive species is depleted quickly and the plating process comes to a halt. Consequently, the solution must be forced through the interelectrode gap at high rates of flow to bring in fresh solution to the cathode, to sweep out spent solution, to reduce the cathodic film thickness, and to prevent overheating or vaporization of the solution in the gap space. The data in Fig. 8 and 9 show that the rate of Cr deposition and the coulombic efficiency increase with flow rate up to a maximum value where the effect levels off. At this point, the trichromate ions diffuse to the cathode reaction zone as fast as they are discharged at the anode.

If the process is carried out at the higher temperature in Fig. 9, the efficiency and deposition rate are reduced because competing, parallel cathodic reactions are present. Since the solvated H^+ ion can be specifically adsorbed on the cathode without displacing water as in Fig. 10a, electrons can be transferred directly to the H^+ ion without tunnelling during the reduction of H^+ ions. This is not the case for the reduction of Cr(VI) to metallic Cr where three times the number of electrons are transferred (two-thirds by tunnelling) and the chromousoxybisulfate complex must displace a water molecule to become specifically adsorbed as in Fig. 10b. Consequently, the reduction of H^+ ion to H_2 can take place more easily than the reduction of Cr(VI) to metallic Cr which is one of the chief reasons why the coulombic efficiency is so low for conventional Cr plating. For high speed plating, however, the high solution flow reduces the diffusion path for the trichromate ions by lowering the thickness of the diffusion layer and by sweeping the cathodic film out of the gap space. As a result, that part of the current consumed in the reduction of Cr(VI) to metallic Cr, and hence the coulombic efficiency for Cr deposition are increased.

When the temperature is increased, the rates of both H^+ ion and Cr(VI) reduction are increased, but for a given temperature increase the velocity of the H^+ ion reduction process rises faster than that of the Cr(VI) reduction process. This behavior results in a larger part of the current being consumed in H_2 production with the resultant decrease in the efficiency for Cr deposition.

In conclusion, then, we see that an analysis of the model proposed (2) for the deposition of metallic Cr from a conventional chromic acid bath can account for the dependency of the plating rate on the rate of solution flow in the high speed process. The flow effect is described in terms of shortening the diffusion path over which trichromate complex ions must travel to the cathode, and the temperature effect in terms of the rates of reaction of the two competing processes of H_2 evolution and Cr deposition.

ACKNOWLEDGMENTS

The authors are grateful to D. W. Hardesty and S. M. Dobrash of the Electrochemistry Department of GMR for their helpful advice.

REFERENCES

1. M. A. LaBoda, Plating and Surface Finishing, submitted for publication.
2. J. P. Hoare, J. Electrochem. Soc., 126, 190 (1979).
3. A. R. Middleton, J. Chem. Ed., 10, 726 (1933).
4. D. C. Graham, Chem. Rev., 41, 441 (1947).
5. K. J. Vetter, Elektrochemische Kinetik, Springer-Verlag, Berli 1961, p. 73.
6. P. Delahay, Double Layer and Electrode Kinetics, Interscience New York, 1965, p. 44.
7. H. J. Emeleus and A. G. Sharpe, Modern Aspects of Inorganic Chemistry, Wiley, New York, 4th ed., 1973, p. 430.
8. J. S. Stephens and D. W. J. Cruickshank, Acta Cryst, B26, 22 (1970).
9. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry Interscience, New York, 1966, p. 841.
10. T. Moeller, Inorganic Chemistry, Wiley, New York, 1952, p.
11. E. A. Ollard, J. Electrodepositers Tech. Soc., 12, 33 (193
12. A. K. Graham, Proc. Am. Electroplaters Soc., 46, 61 (1959)
13. M. F. Qualey, Plating, 40, 982 (1953).
14. E. Müller, et al., Z. Elektrochem., 32, 399 (1926); 38, 2 43, 361 (1937); Trans. Faraday Soc., 31, 1194 (1935).
15. M. A. Shluger and V. A. Kasakov, Zhur. Priklad. Khim., 33 (1960).
16. A. T. Vagramyan and D. N. Usachev., Zhur, Priklad. Khim. 1900 (1958).

17. A. T. Vagramyan and M. K. Zhamagortsyants, Electrodeposition of Metals and Inhibiting Adsorption, Nauka, Moscow, USSR, 1969; NBS Translation, 1974, p. 194.

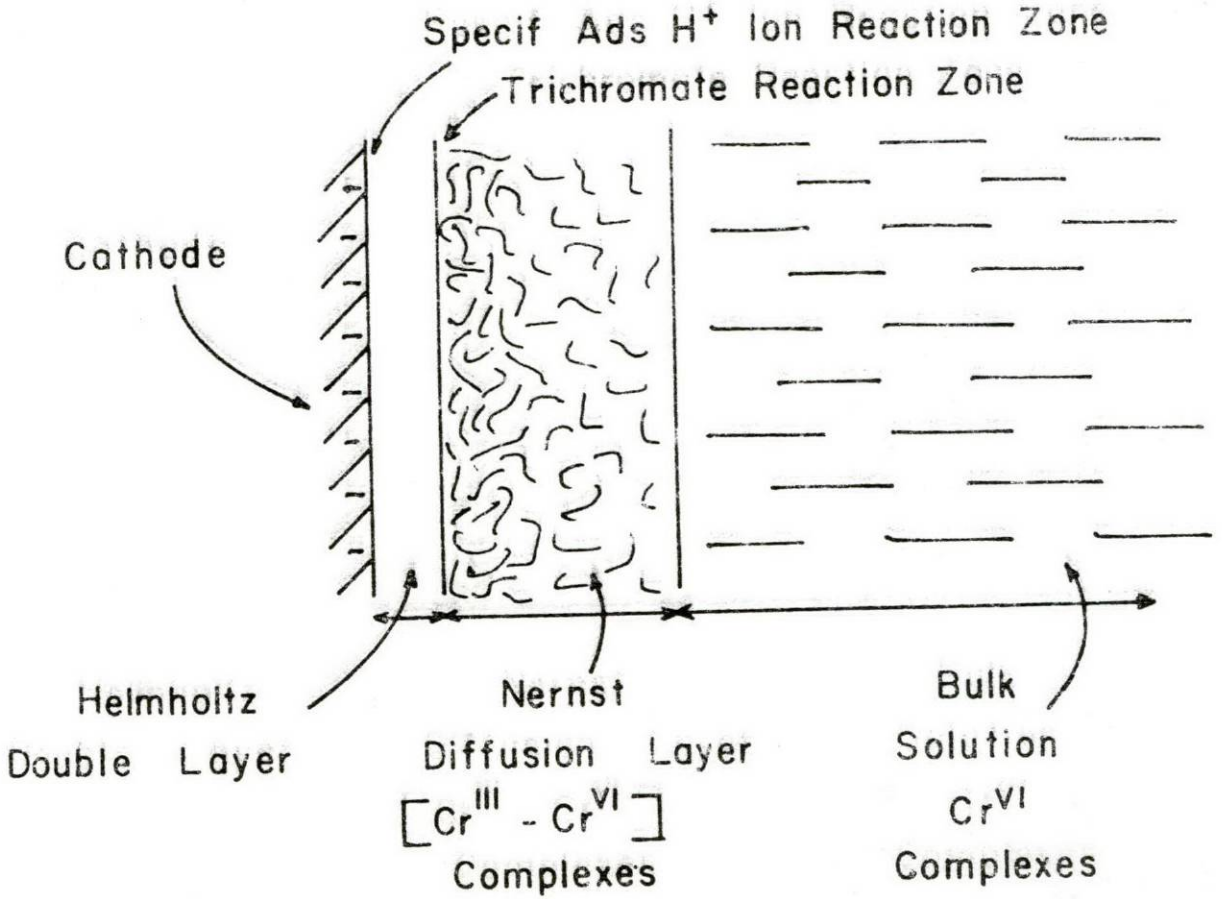
18. J. C. Saiddington and G. R. Hoey, J. Electrochem. Soc., 117, 1011 (1970); 120, 1475 (1973).

19. M. H. Jones and J. C. Saiddington, Plating, 52, 39 (1956).

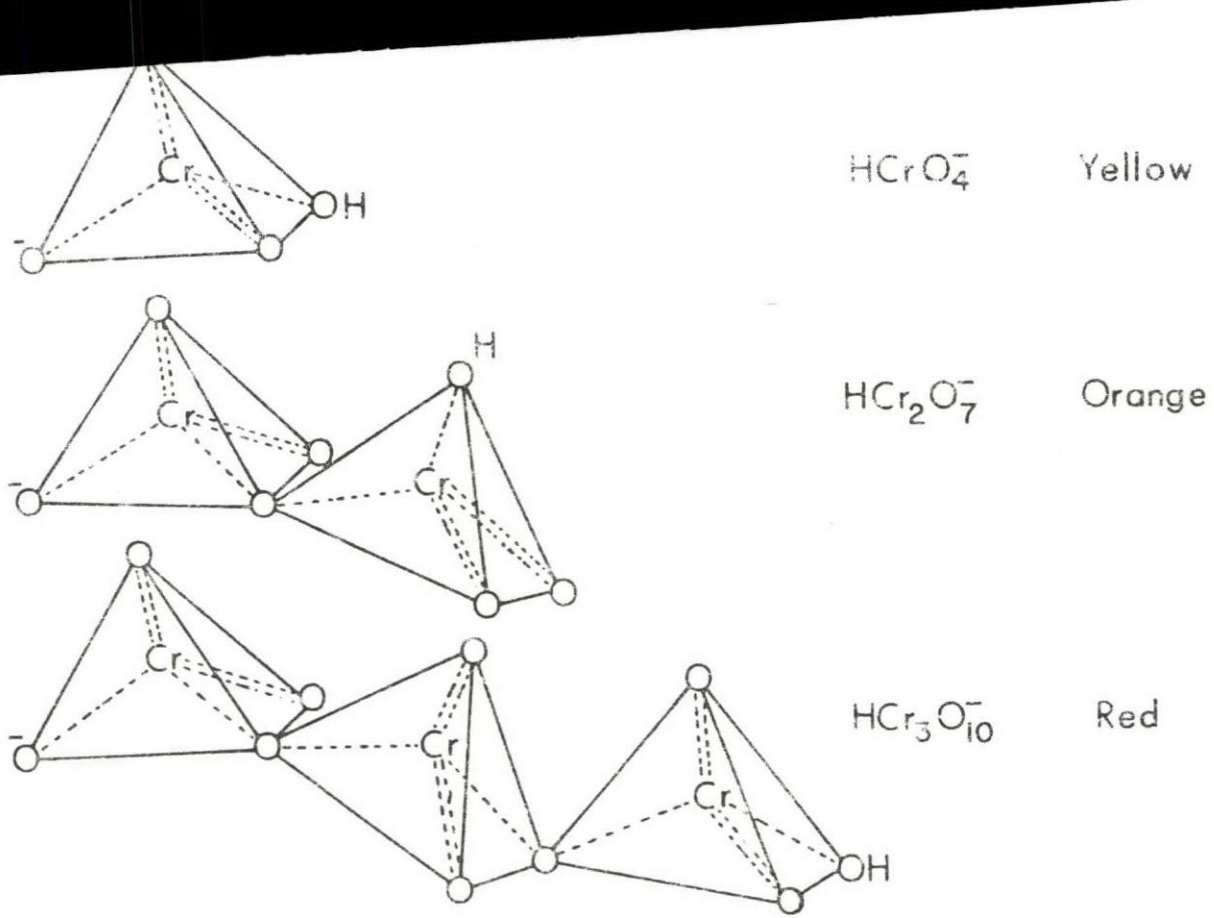
20. R. E. Wilson and M. A. Youtz, Ind. Eng. Chem., 15, 603 (1923).

21. S. Glasstone, Trans. Electrochem. Soc., 59, 277 (1931).

22. H. A. Laitinen and I. M. Koltoff, J. Phys. Chem., 45, 1061 (1941).



...de-solution interface.



$HCrO_4^-$ Yellow

$HCr_2O_7^-$ Orange

$HCr_3O_{10}^-$ Red

Fig. 2. Chromate structures.

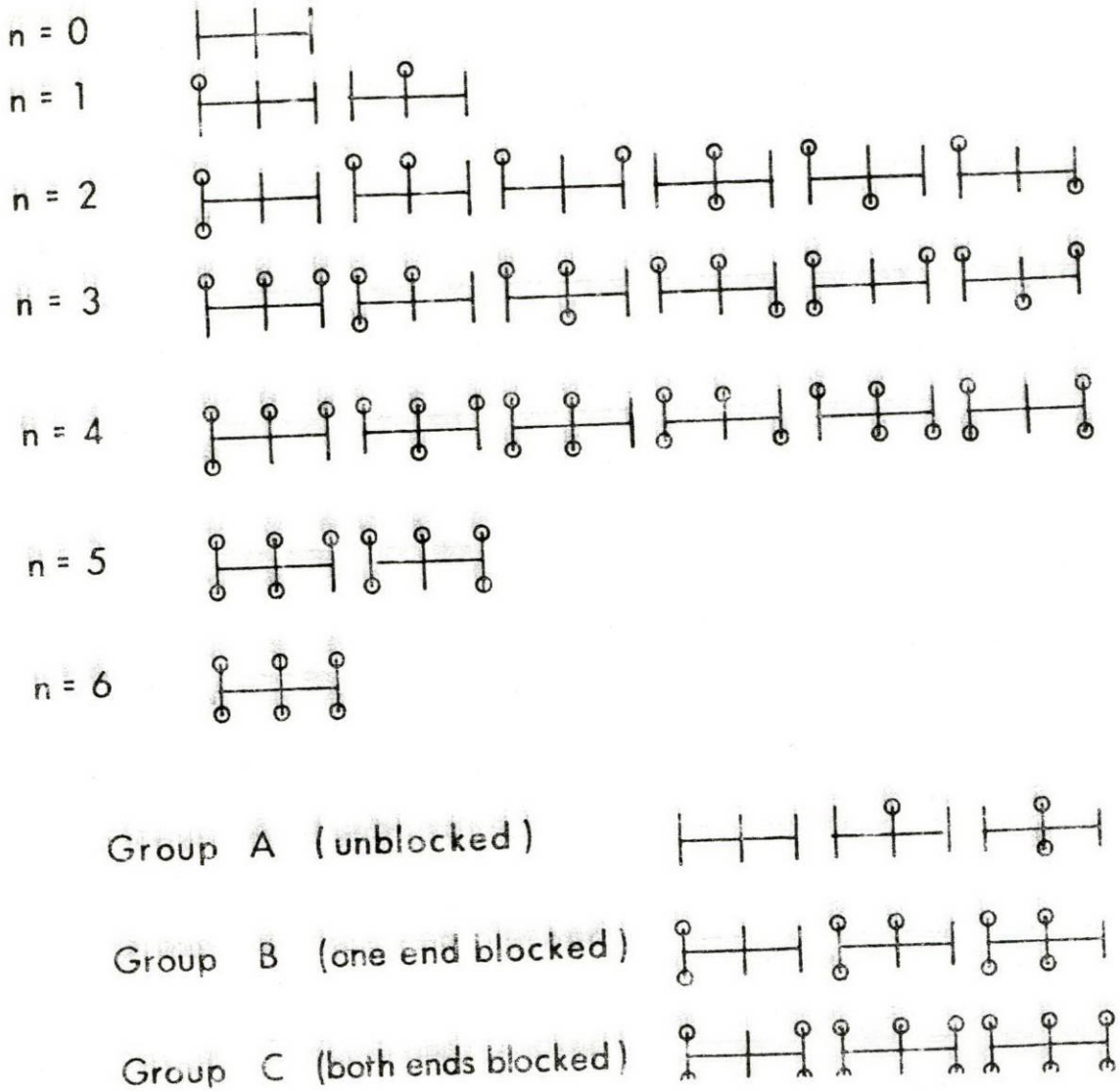


Fig. 3. Distinguishable trichromate-bisulfate complexes.

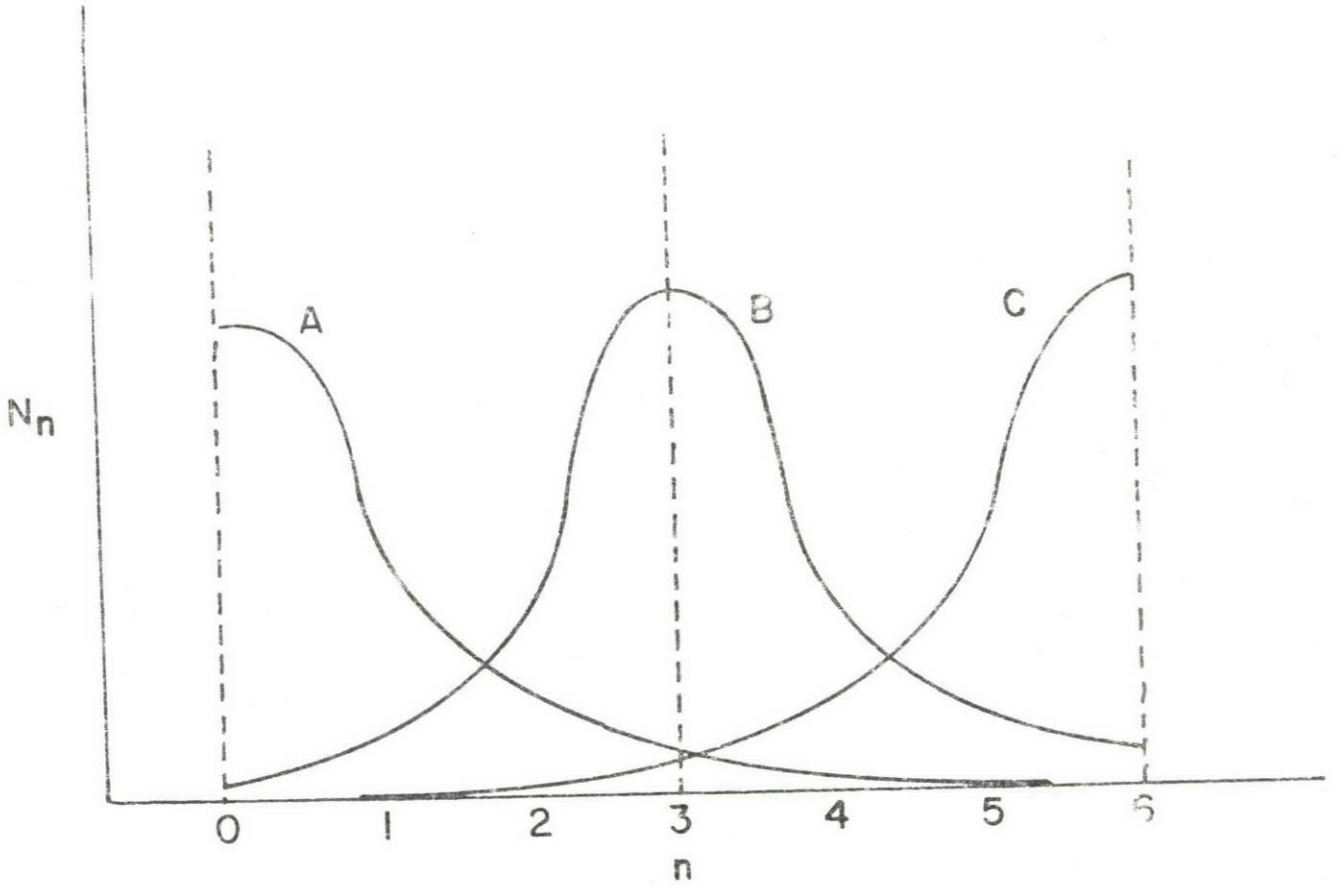


Fig. 4. Ideal distribution curves for the number, N_n, of trichromate-bisulfate complexes as a function of the number, n, of Cr=0 bonds hydrogen-bonded to HSO_4^- ions was for three values of CrO_3/H_2SO_4 ratios: (A) $10^6/1$, (B) 100/1, (C) 1/1.

#1 6V
155 20PSI
#2 6V
155 40PSI
#9 6V
155 30PSI
#6 6V
155 50 PSI

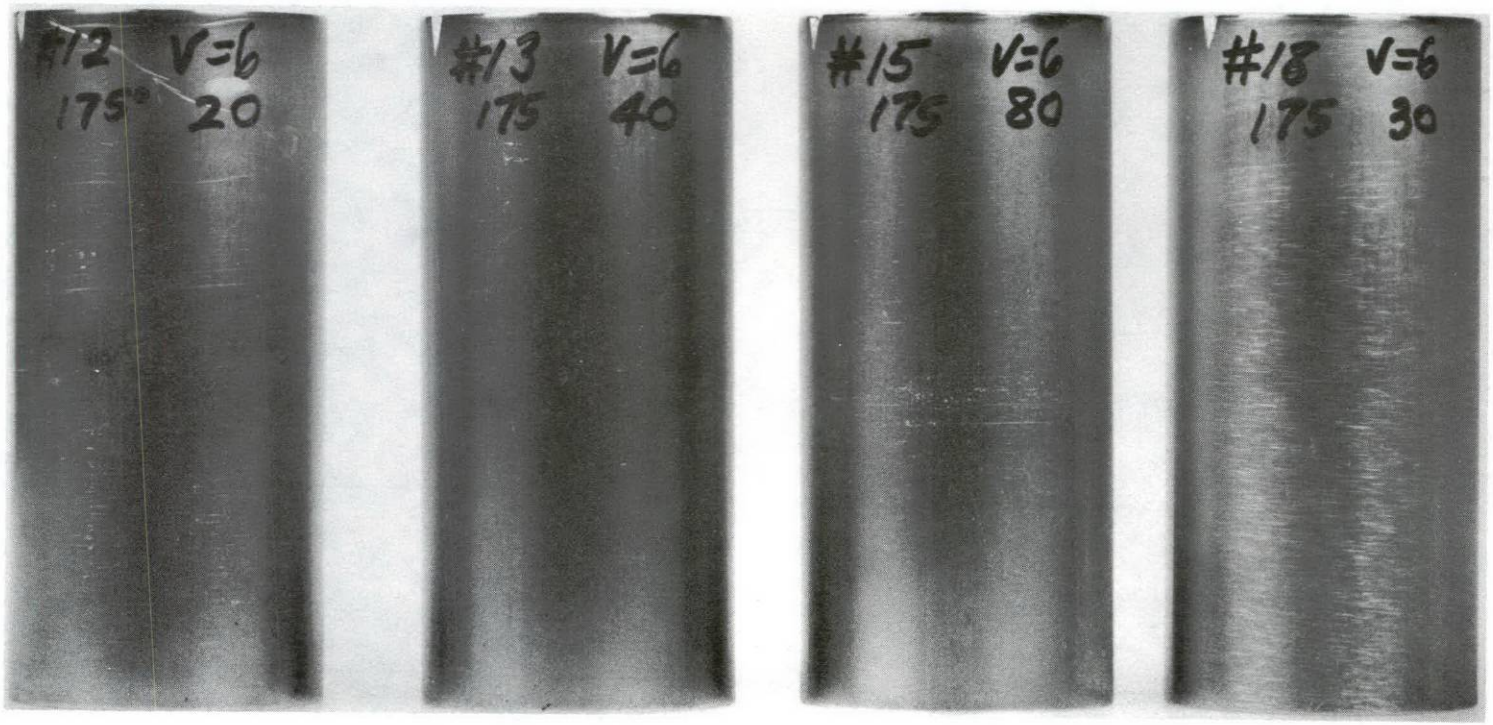
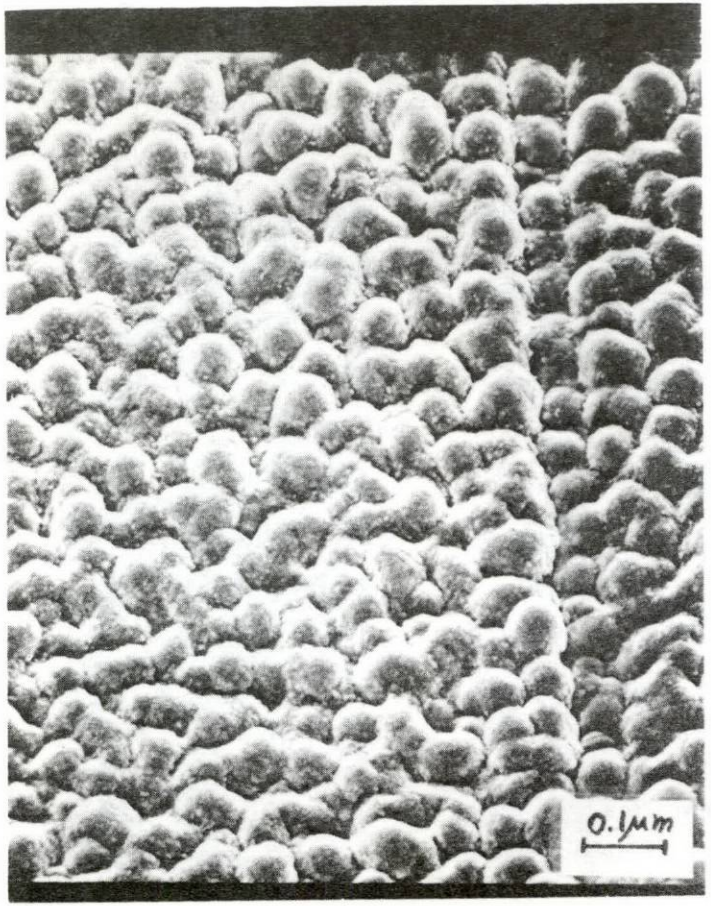
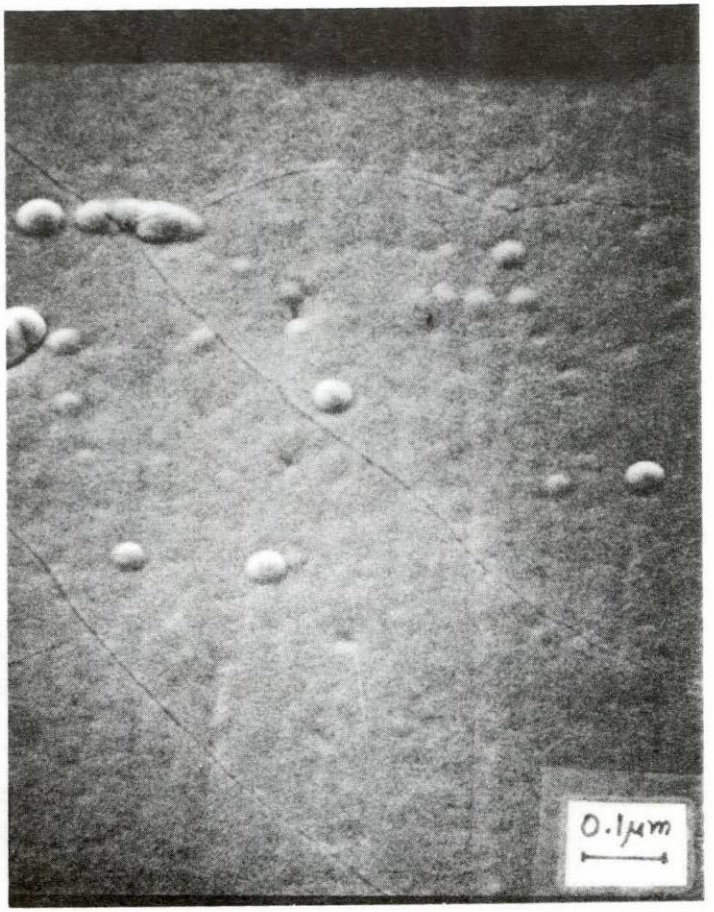


Fig. 6. Mild steel tubes plated at 6 V, 15.5 A/cm^2, 100 L/min, and 79°C for 1 min in chromic acid solution (300 g/L) with 100/1 ratio of CrO_3/H_2SO_4 by the high speed plating process.





B

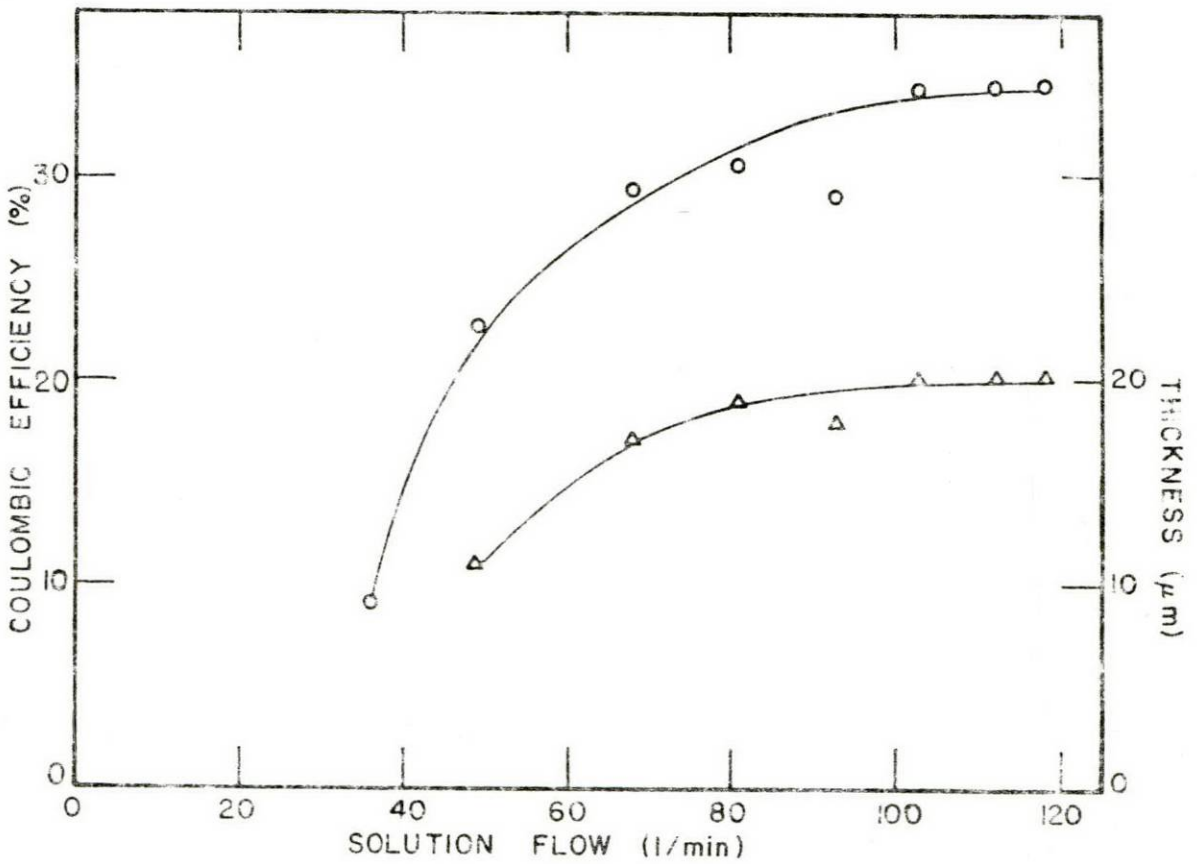
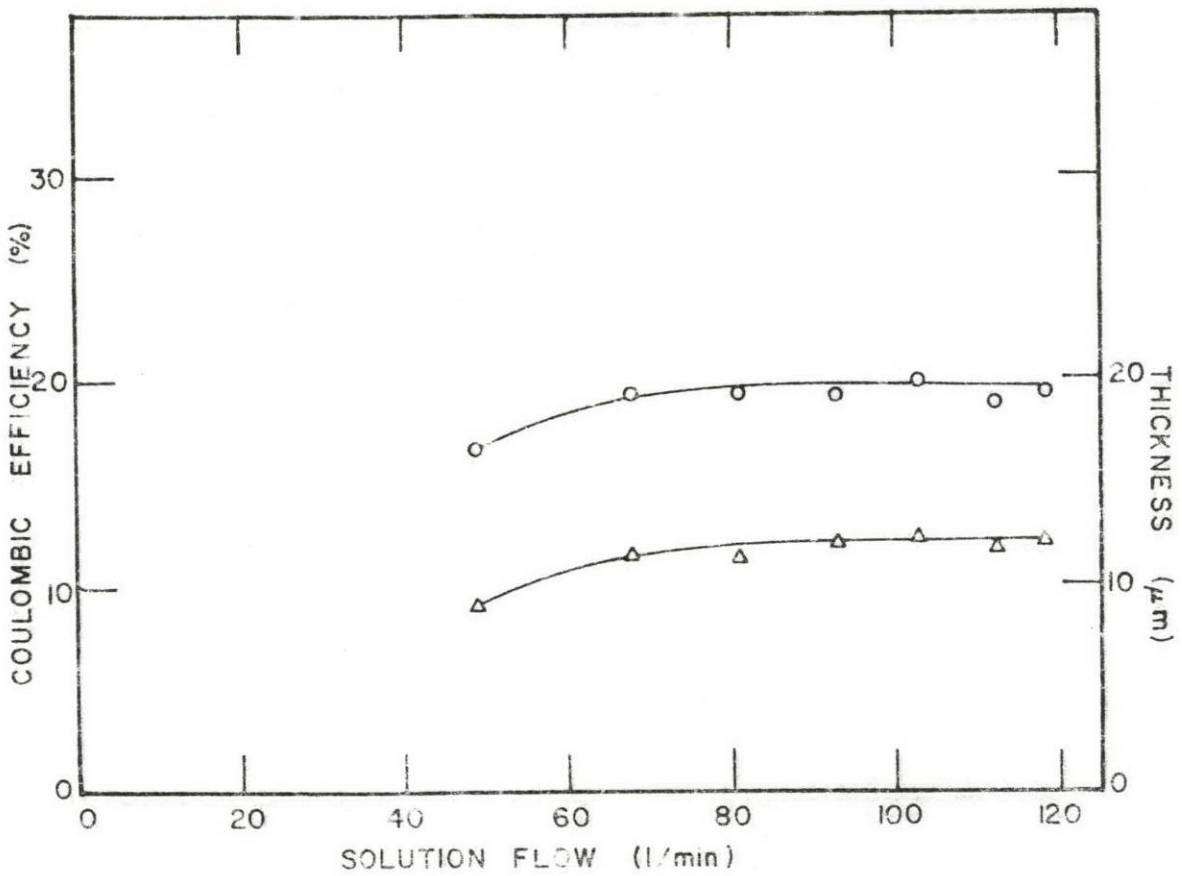


Fig. 8. Plot of coulombic efficiency (circles) and deposit thickness (triangles) for high speed deposition of Cr on mild steel at 68°C.



thickness (triangles)

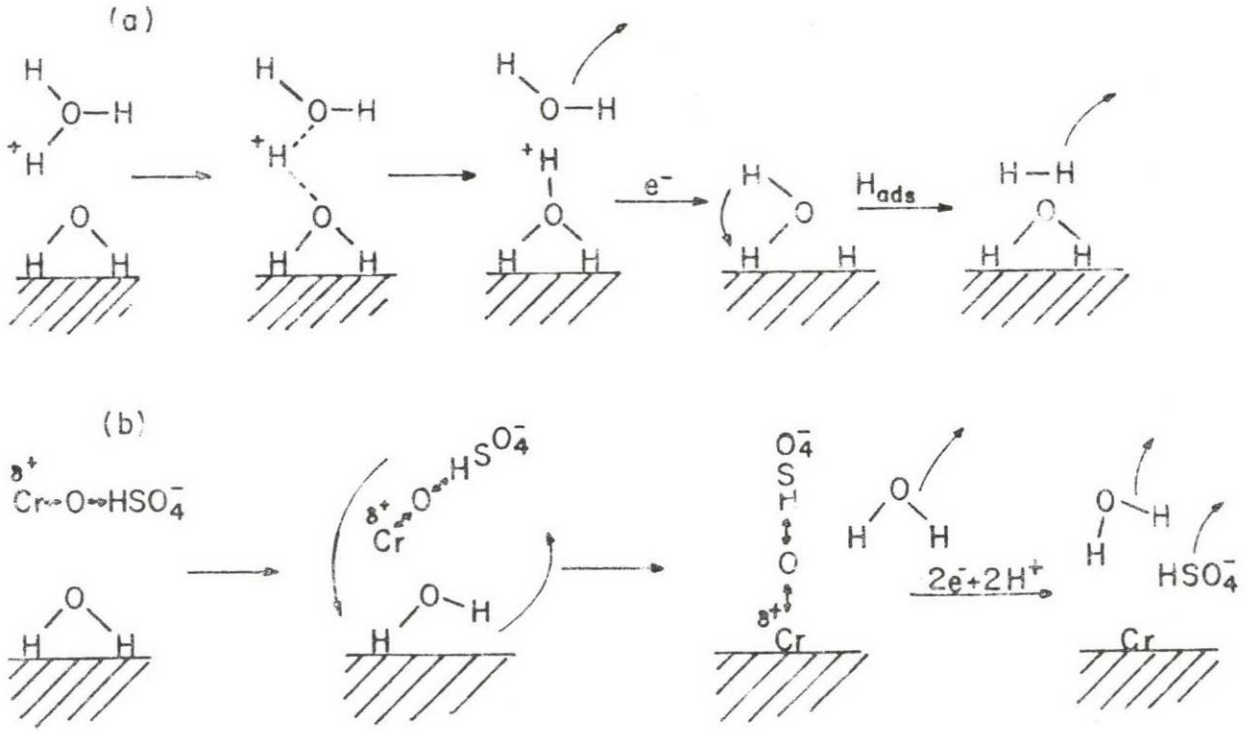


Fig. 10. Kinetic representations of electrode reactions for (a) the specific adsorption of hydrated H^+ ions and their reduction to gaseous H_2, and (b) the specific adsorption of the chromousoxybisulfate complexes and their reduction to metallic Cr.

J-5

Chromium I
Session J

Production Coating of Plastics by High Rate Sputter Deposition

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INTRODUCTION

The pressures exerted by energy saving legislation and antipollution gulations have challenged the technical community to come up with new d effective responses.

Car manufacturers, for example, must reduce weight to increase gas eage, and are using more and more plated plastic parts in automobiles. le electroplating is an established and very effective technique for ome plating plastic parts, alternative approaches are now available. e offer the promise of being nonpolluting, energy-efficient, and cost- ctive.

The equipment described in this paper employs the technique of high sputtering to deposit bright chrome or chrome alloys onto plastic. metallizing process is: nonpolluting, uses an inert argon atmosphere; efficient use of chromium; involves no dangerous chamicals; easily olled electronically; and capable of full automation.

ROCESS

Sputtering -

The advantages of depositing metal films by sputtering have been recognized for a very long period of time. The early observation (1852) that material from the negative electrode in a cold cathode glow discharge tube was sputtered away to redeposit as a film on the envelope was soon developed into a method for depositing metal films.[1]

The sputtering sources of today have passed through many stages of evolution from those early days and have advanced to the poi where their characteristics can be tailored to a specific appli

An excellent review of the state-of-the-art of sputtering up to the late 1960's will be found in reference (2). As of then, th major characteristics of sputtering were as follows: Advantage superior film adhesion compared to evaporation; alloys can be deposited without fractionation; refractory metals such as tun can be deposited; reactive depositions can be done by using a chemically reactive gas with the argon; insulating materials, s as SiO_2, can be deposited by using r.f. techniques. Disadvan a relative slow deposition process, limited by applied power substrate heating; up to 15% of source power appears as bomba at the substrate; complex r.f. techniques necessary to sputt certain materials such as aluminum.

During the past five years, significant advantages have beer in the design of sputter sources, particularly in relation depositing onto heat sensitive materials. High rate magnet sources now exist which have a thirty-fold increase in depo rate, a rate that competes very effectively with films dep by evaporation. (3,4) Electron bombardment of the substra has also been reduced to a level where catastrophic overhe of a plastic substrate is no longer a factor to be conten with in sputtering.

b. Sputter Sources -

The sputter source employed in the application discussed here is the Conical Cathode Magnetron* shown in Fig. 1. (5,6)

Referring to Fig. 1, the source features a specially profiled cathode (the source of sputtering material); a ground shield and a centrally located anode that confine the discharge to the region adjacent to the cathode surface and provide the fields that initiate the discharge; a magnet assembly that provides a magnetic field in the discharge region; and a cooling jacket that surrounds the cathode assembly. To initiate the sputtering action, the system after being evacuated to a suitable vacuum (approximately 10^{-5} Torr) is backfilled with argon to a pressure of 2×10^{-3} Torr. When a dc voltage (negative to ground) is applied to the cathode, a toriodally-shaped high intensity glow discharge is produced in the region between the central anode and the ground shield. Positive argon ions from the discharge bombard the surface of the negatively biased cathode and sputter material at a very high rate. The sputtering action is concentrated into a narrow annular strip, giving the gun a "distributed ring source" characteristic.

The magnetic field plays a key role. From Fig. 2, we see that between the discharge and the cathode there is a region where

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* S-gun ™ Source

crossed electric and magnetic fields exist ($\overline{E}x\overline{B}$). Secondary electrons from the cathode, due to the bombarding ions, are bent under the influence of the crossed fields as they are accelerated (through several hundred volts) toward the discharg on trajectories that take them toward the ground shields and away from the substrates. A major source of substrate bombard- ment which is present in conventional sputtering is essentiall eliminated in this device.

Lower velocity electrons in the discharge, that result from ionization caused by cathode secondary electrons and from secondary electrons produced by electron impact at the anode and ground shield, are "trapped" by the magnetic field. Thes plasma electrons perform cyclotron gyrations under the influe of the magnetic field, thus producing a very intense dischar the interaction region. The central anode (operated at posi bias) also acts as a collector for electrons and provides a symmetry that improves stability of the discharge.

The cathode (approximately 5 in. dia) is a drop-in fit to t cooling jacket (0.005 in. max clearance in dia) and is read removed for replacement. High contact pressures at the cat cooling jacket interface produced by thermally-induced str ensures excellent thermal contact without the need for int mediate bonding agents.

By design then, the conical magnetron source has characteristics that provide the following capabilities: high sputtering rates; low substrate bombardment; distributed ring source characteristics; arc-free operation; compact, easily removable cathodes; dc deposition of aluminum.

c. Source Characteristics -

The measured flux distribution for sputtered material leaving the source is shown plotted in Fig. 3. The distribution is circularly symmetric and is very close in its general characteristic to that associated with material originating with a cosine distribution from a annular ring source of about 4.8 inches diameter.

An array of these sources can be employed for deposition on to a moving plate to provide uniform coverage across its width. The positioning of the sources was initially determined theoretically using a computer to suit the requirements of the equipment specifications. The array used in our equipment consists of four sources spaced evenly on twelve-inch centers spanning the width of the system. The geometry for a half section of the machine and the location of the sources relative to that of the moving platen is shown in Fig. 4. When the parts to be coated move past the sources at a constant speed in the direction shown, a relatively uniform deposit is obtained across the desired 34-inch deposition zone for a source-to-substrate distance of 14 inches. The solid

curve shows the calculated distribution onto the deposition plane and is seen to be in substantial agreement with the measured distribution.

The uniformity varies with the source-to-substrate distance. With the given source arrangement deposition becomes unacceptab nonuniform at source-to-substrate spacings of less then seven inches.

d. Film Characteristics -

The desirable characteristics of the deposited films must be considered strictly in relation to the practical requirements for the part. The equipment discussed here is designed to pu down films that are compatible with the exterior vacuum meta lizing requirements of the automotive industry. Ultimately, is anticipated that the sputter deposition process will be a cable to a range of plastics; for the present, however, the definitive work has been done relative to ABS plastic.

For ABS, present technology requires a system of basecoat/m topcoat for the exterior applications. Lacquer systems tha compatible with the process have been developed and are ge described in the pertinent literature (7). While research tinues at a very active pace in this general area of proce substantial body of information has been built up in the that characterizes the general nature of the process (8).

For the equipment discussed here, the following observations can be made relative to process. Relative to film brightness, tests were run to evaluate the effects of vacuum conditions on reflectivity. The effect of taking the substrate from atmosphere to vacuum to deposition in less than two (2) minutes was evaluated.

Reflectivity data for ABS, taken with a scanning reflectometer, are shown for sputtered chrome in Fig. 5. Here the parts were taken from atmosphere to vacuum to start of deposition in a time of one and one-half minutes. As a control, an electroplated plaque was measured over the same range. Note a range of reflectances at a given wavelength is found. Factors influencing the reflectivity were as follows: More reflective films are obtained with shorter source/substrate distance; a ten-inch spacing, or closer, will yield films with reflectivity at the top of the range; at fifteen inches, it approaches the bottom of the range.

A strong sensitivity to the argon pressure during sputtering was also observed performing in a similar fashion to that discussed by Thornton for the coaxial magnetron sputtering source (9). The threshold pressure determined for our system was 2×10^{-3} Torr; that is, for maximum brightness, the operating pressure should be less than 2×10^{-3} Torr.

Another vacuum related condition that requires control is the background pressure of water vapor in the deposition chamber.

To maintain adequate brightness, the pressure should be less than 5×10^{-5} Torr, a condition which is met by adding sufficient cryopumping capacity.

3. SYSTEM DESCRIPTION

To meet the production requirements of this new process, a new line equipment was developed. This equipment incorporates the design paramet of process compatability; rapid cycling for high productivity; and rugge construction for a high degree of reliability. Modular construction is utilized throughout the system to simplify maintenance and permit tailo the system to specific customer requirements.

The basic system is shown in plan-view in Fig. 6. The major segm of the system are: process section with sputtering sources; entrance/ locks; substrate handling; and electrical control system.

a. Process Section -

The process section is maintained at the proper background ment of argon for operation of the coating sources located at the center of this section. Vacuum pumping is provided two ten-inch diffusion pump modules with appropriate baffl and backing pumps combined with two large cryo-panels for speed pumping of condensables. These panels, located at entrance and exit of the process section, perform a criti function in removal of the high background of water emana from the surfaces of the plastic substrates. The argon

environment is controlled by a constant mass flow control system.

The entrance and exit areas of the process section are used as a "buffer" space to permit rapid entrance and exit from the coating zone while maintaining constant flow of parts beneath the sources. Multiple transport sections are used operating at either high speed transport or slower coating speeds.

b. Sputter-Sources

The sources, which have been previously described, are located in the center of the process section arranged in six banks of four each. The location of the sources across the width of the system provides uniformity across the span of the workholder platen while the multiple banks provide production capacity.

Sources are located on removable dome sections of the chamber to permit simple cathode (target) replacement and access to the coating section of routine cleaning and servicing.

. Entrance/Exit Locks -

The entrance and exit locks are identical in function--to permit high speed access to and departure from the process section without adverse effect on the parts in process. Each load-lock contains a rectangular vacuum valve at each end. A combination Roots-blower/mechanical vacuum pump with associated valving is provided at each lock for high-speed evacuation of the lock to a

vacuum level compatible with the process within the coating time for each platen.

d. Substrate Handling -

Substrates are loaded on a special workholder platen with a usef coating area, 34 inches wide and 42 inches long, which is compat ible with the materials handling equipment and transport throug the system. All transport sections (except power-and-free) hav stepper motor drives for absolute control over platen location throughout the process. The return conveyor system consists o four corner sections, two straight sections, plus a load/ unload power-and-free section. The corner sections are desig for translation of the platen through a 90°C direction change without turning the platen.

e. Electrical/Control System -

Electrical equipment includes a conventional power distribut center for control of pumps and main controls; six power supply modules, each capable of operating one bank of four S-guns; one logic control module for control of the transpor and vacuum systems; and one master control module for overa system control and interface with the operator. The contro system incorporates programmable layer control

Operation of the system is fully automatic. Productivity of a system is 500 ft^2/hr of substrate holder load area. The system is s

Fig. 7 at final assembly. An additional system has been designed with a rger platen (coating area 34 inches wide by 86 inches long) which is cape of coating at production rates of 800 ft^2/hr.

Fig. 8 shows a typical load of automotive grilles passing through the tem's coating zone.

Fig. 9 shows the same load of grilles exiting the system in transit he load/unload area.

CONCLUSIONS

The system described is pushing the state-of-the-art for the production ng of plastic parts with a bright metal finish. A scale-up in throughrom 500 ft^2/hr to 800 ft^2/hr has now been attained in systems built quent to the system described here.

n highlighting areas requiring further refinement it is recognized ew sputter sources of advanced design optimized for this particular ation will be required. In terms of satisfying the total coating pro- t is apparent that while the manufacturer of the vacuum equipment can it to optimize the metal deposition, the success overall requires of the process from beginning to end. While, as of now, successful an be produced using plating grade ABS and the presently available s and topcoats, additional process steps and more complex procedures, stress relief and hot substrate depositions, are required which it ved could be eliminated by taking a look at the overall process

requirements. Excellent cooperation is being received from major plastic and lacquer manufacturers, and active R & D programs are underway to look at the total system.

EFERENCES

1. L. Holland, "Vacuum Deposition of Thin Films", London, Chapman and Hall, 1963, p. 401

2. L.I. Maissel and R. Glang, "Handbook of Thin Film Technology" New York, McGraw Hill, Inc., 1970

3. P.J. Clarke, U.S. patent 3,616,450 (1971)

4. J.F. Chapin, Research and Development, 25, 37 (1974)

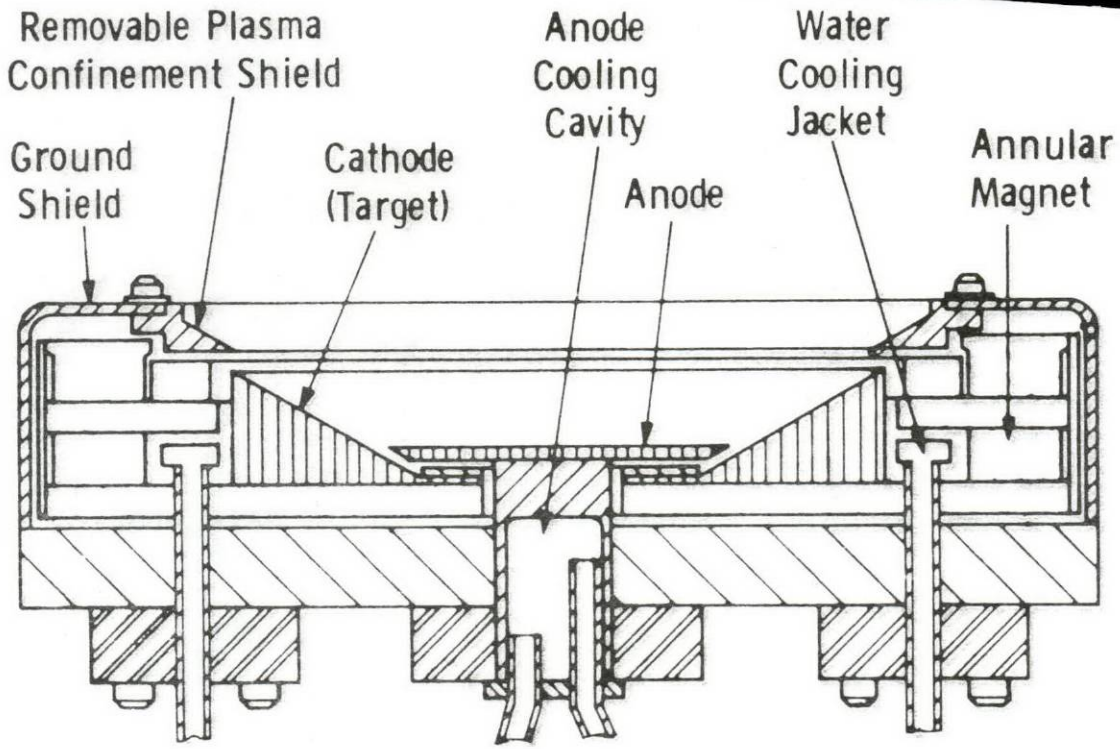
5. P.J. Clarke, Solid State Technology, 19, 12 p. 77 (1976)

6. F.T. Turner, Varian VR-100, (1975)

7. C.C. Storms, Proc. "Soc Vac Coaters", 1, (1976)

8. A.S. Penfold, J.A. Thornton, Proc. "Soc Vac Coaters", 8, (1976)

9. J.A. Thornton 32, Metal Finishing, (Aug. 1976)



S-Gun Source Cross Section

FIGURE 1

S-GUN™ CROSS SECTION

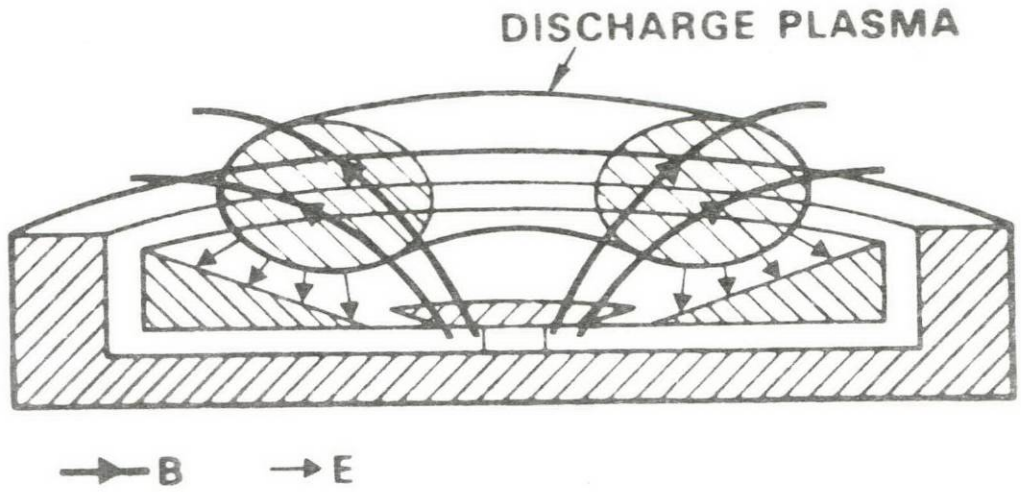
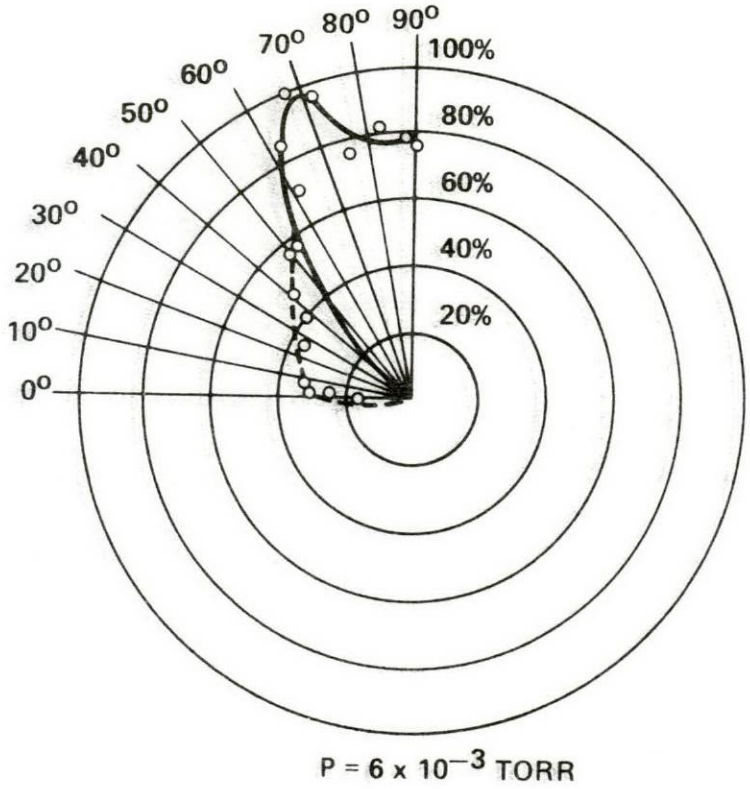


FIGURE 2

DISCHARGE GEOMETRY



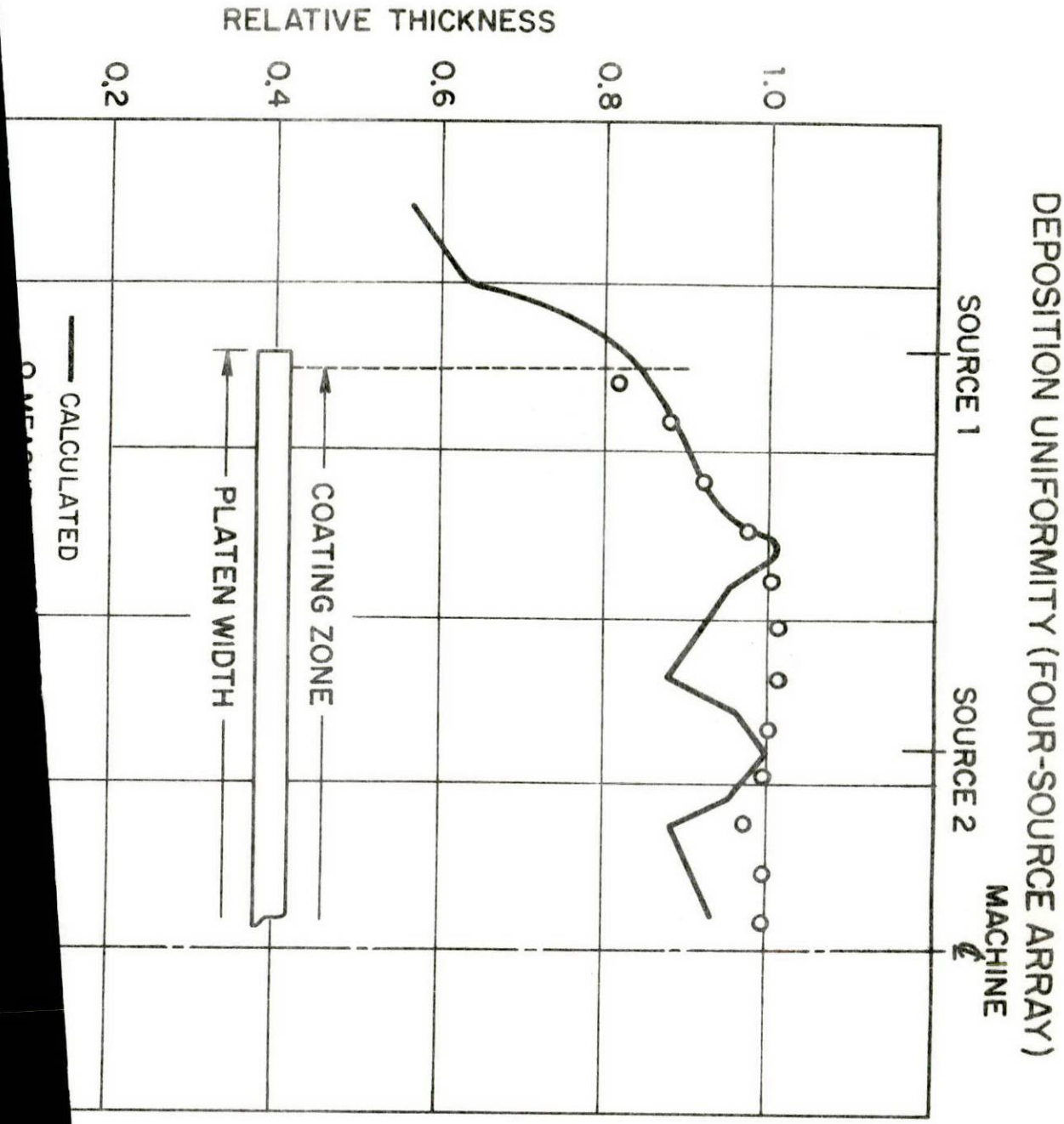
ANGULAR DISTRIBUTION OF SPUTTERED MATERIAL

FIGURE 3

ANGULAR DISTRIBUTION of SPUTTERED MATERIAL

FIGURE 4

DEPOSITION UNIFORMITY



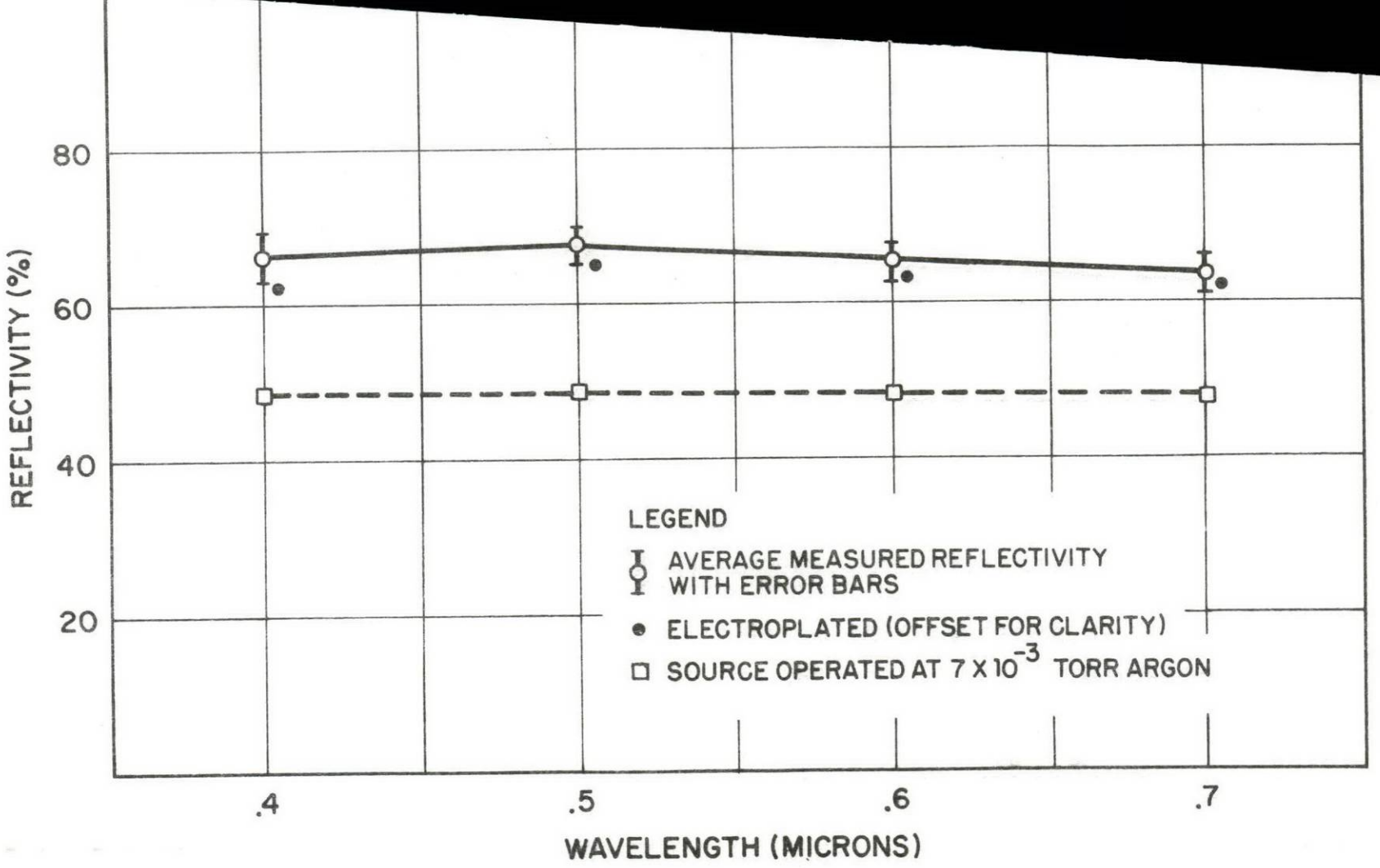


FIGURE 5

REFLECTIVITY (VISIBLE RANGE)

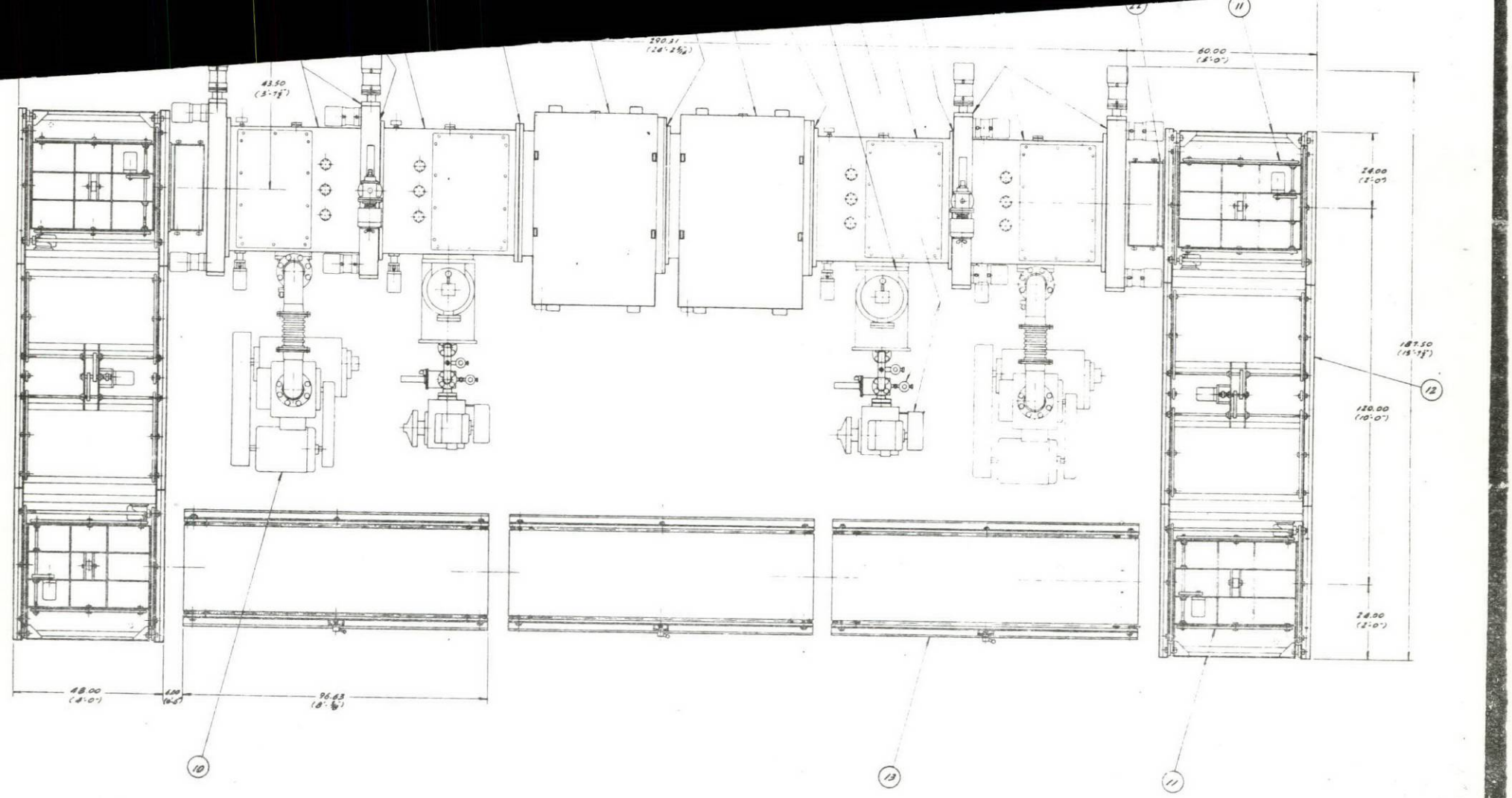


FIGURE 6

SYSTEM PLAN-VIEW

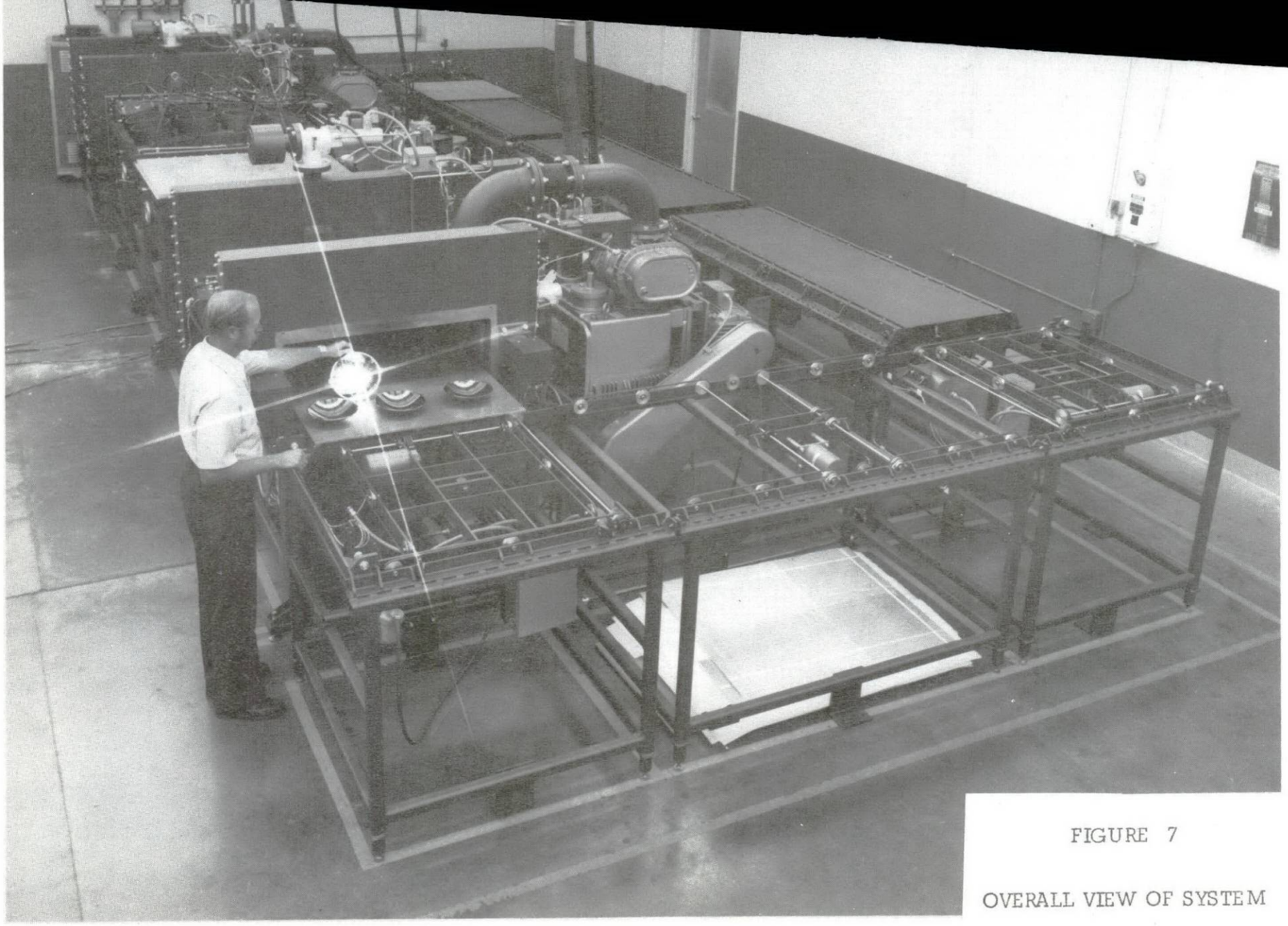


FIGURE 7

OVERALL VIEW OF SYSTEM

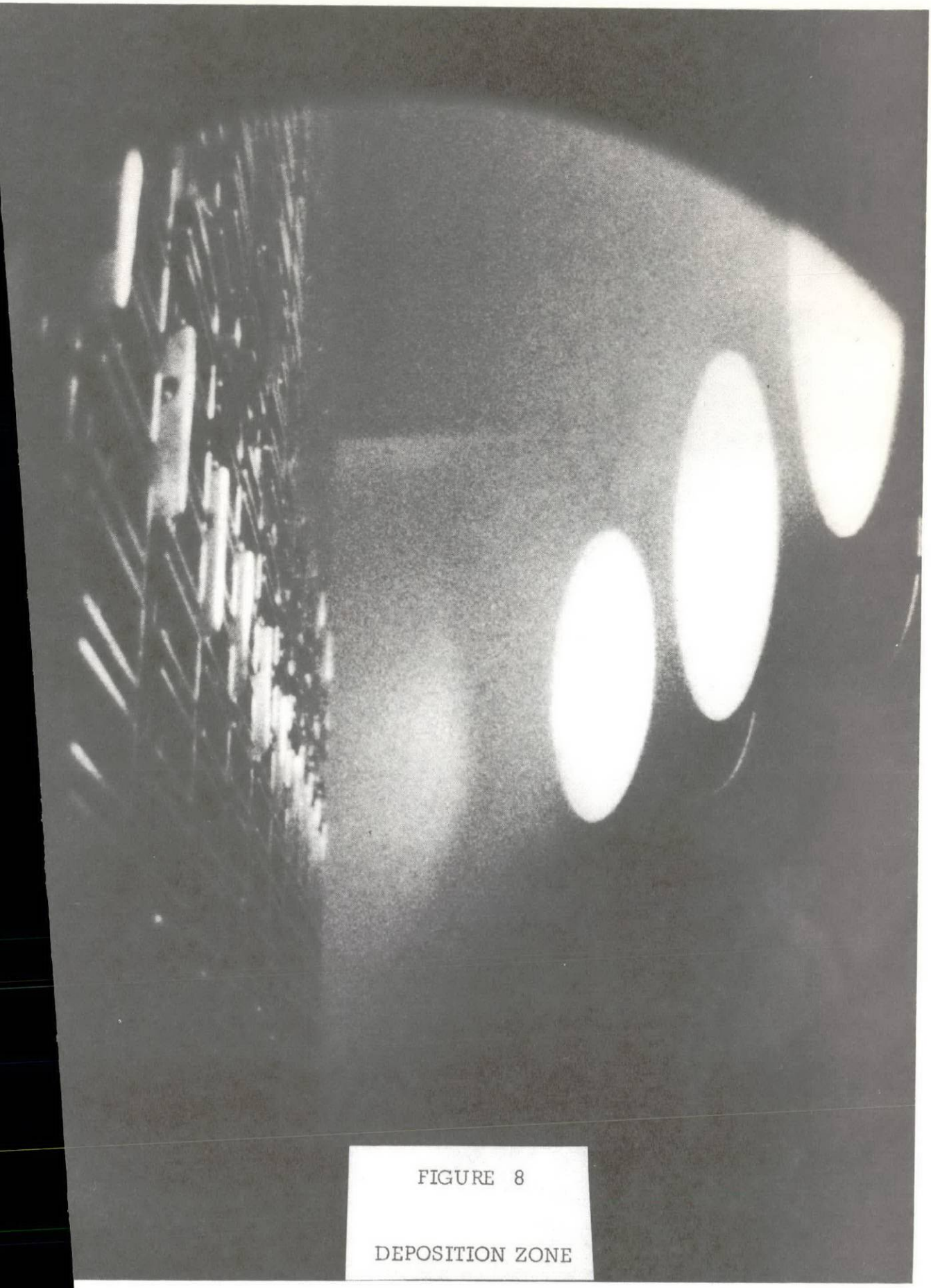


FIGURE 8

DEPOSITION ZONE

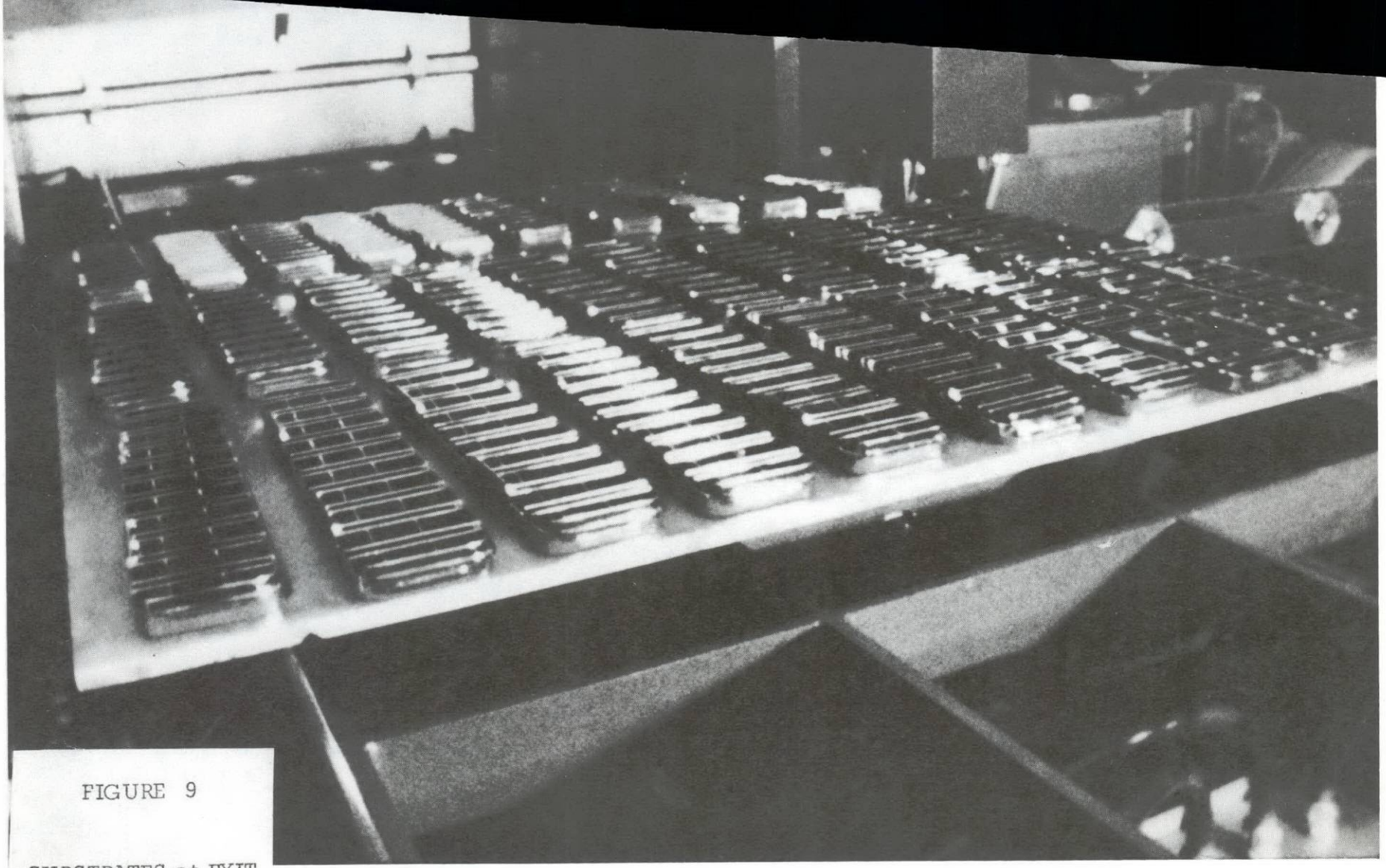


FIGURE 9

SUBSTRATES at EXIT

K-1

Energy Conservation I
Session K

Energy Conservation For the Plating and Surface Finishing Industry

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ENERGY CONSERVATION STUDY OF THE PLATING AND SURFACE FINISHING INDUSTRY

Plating and surface finishing operations are ancillary processes in many major industries, such as the automotive, electronics, aircraft and fastener industries. The industry is composed of approximately 12-13,000 plating and surface finishing facilities throughout the United States, which range from very large facilities that are segments of major manufacturers to small, independently owned contract shops.

Regardless of the size or degree of sophistication, each facility utilizes similiar types of processes in plating and surface finishing. First, the base material must be prepared. This is generally done through a series of cleaners, chemical treatments, and rinses. These processes can be either hot or cold, depending on the type of contaminant and perform the function of removing or diluting the contaminant to an acceptable level.

Once the base material is prepared for plating it is submerged in an electrolyte, where direct current is applied between the anode and the cathode to drive the plating reaction. After each plating step is complete, the product is rinsed to remove residual electrolyte. All of these processes require energy. Alternate processes for anodizing, conversion coating and surface coloring use similiar type operations and also require energy.

Additionally, the environmental conditioning of the facility for worker safety and comfort requires the use of large amounts of energy. Dust systems are often required to draw off toxic or noxious fumes from the process tanks, degreasers, spray booths, and dryer ovent. Heat from these processes must be removed or dissipated to allow workers reasonable comfort. Many of these environmental systems in themselves contribute to or increase the energy requirements for the operations of open rinse tanks, process tanks, degreasers, ovens and space conditioning among other items.

Over the last few years, environmental considerations have increased energy usage in plating and surface finishing facilities. Waste water from the plants must be treated to remove objectionable materials before effluent discharge. In addition, waste treatment system energy requirements increase with increasing volumetric flow and pollutant concentration. In order to reduce treatment costs, some chemical concentrations have been reduced, however, this requires greater voltages for plating or surface finishing, or longer dwell times for the base material. In either case, energy requirements are increased.

Energy Survey Needed

The plating and surface finishing industry is a billion dollar indust employing an estimated one-half million people. Energy consumption patte were of interest to the Department of Energy as well as to the AES. Georg Tech's and AES' proposal to the DOE to survey the energy patterns of the p ting and surface finishing industry was co-sponsored by AES. This projec was designated AES research project no. 46.

To accomplish the purposes of this survey, five broad tasks have bee defined:

Task I: to identify energy consuming processes in the plating and surface finishing industry.

Task II: to establish the amounts of energy used in each process, and to determine the mechanisms by which energy is consu

Task III: to develop energy saving modifications and modified oper tional procedures for energy intensive processes to redu consumed energy.

Task IV: to estimate the energy saving potential for each proces or procedural modification.

Task V: to disseminate the developed energy saving modification and operational procedures throughout the industry for implementation.

The initial task of identifying energy consuming processes in the plating and surface finishing industry started with a survey of twenty representative facilities, selected with the aid of the American Elect platers' Society. This survey consists of an energy audit of each of facilities visited, noting the contribution of each process to total e consumption. Each plant is referred to by an assigned letter to maint confidentiality. Of the twenty plants, eleven are job shops, nine are capitive shops.

The plating plants surveyed process a very wide range of plated ducts. Screws, nuts and bolts, staplers, scissors, aircraft and auto parts, electronic parts and circuitry, appliances large and small, fu ture hardware, and locks are some of the items handled by these plant Plating practices vary just as widely, as do priorities and thus atti toward energy and energy conservation.

Results: Quantities of Energy Consumed in Plating Operations

A detailed energy audit, estimating the amount of energy used i each operation, has been performed for each of the twenty survey pla The energy audits are based on one year of operation. Specifically, twelve months preceeding the plant audit were used. Electrical ene consumption ranged from 3.03×10^5 kwhs/yr to 1.31×10^7 kwhs/yr wi average of 2.65×10^6 kwhs/yr. Process heat energy consumption ran from 1.04×10^9 Btu/yr to 4.69×10^{11} Btu/yr with an average of 5.3 Btu/yr. These figures need be qualified in that they include some

not strictly related to plating. For instance, the painting operations at Plant M are included as is the injection molding department at Plant Q. This however, will not change our conclusions.

Tables 1 and 2 contain average results for all plants surveyed for electrical and process heat energy usage.

Electrically the largest consumers are exhaust fans, plating and anodizing, and lighting. These three categories consume 60.2% of the total electrical energy usage. Process heat energy consumption is greatest in the area of tank heating. Note that all tank heating amounts to 45.1% of the total. Boiler losses and space heat consume the next largest amounts.

The above treatment of the data does not reveal the two patterns of energy usage which have emerged. Sixteen plants in this pattern group anodize aluinum and/or plate zinc, copper, nickel and chromium, among other metals, in large quantities for decorative purposes and corrosion protection. Tables 3 and 4 contain average energy usages for these plants. Plating is the highest single consumer of electrical energy. Exhaust fans and lighting are second and third highest consumers of electrical energy. Thus, electrically, this pattern group is largely similar to the results for all plants. Process heat usage differs in one significant area, space heat. Plants in this first pattern group consume 8.5% of their process heat energy in space heating. It is the sixth largest consumer of process heat energy. For all plants this figure is 18.2%. Space heating is the third largest consumer for all plants. In other respects this group is similar to the usages for all plants.

A second pattern group is characterized by the plating of parts that small in size. Tables 5 and 6 contain average energy usages for these plants, which consume far less energy in actual plating than do plants in first pattern group. Exhaust fan motors, electric tank heating, air-conditioning and lighting consume 68.1% of the electrical energy used by these plants. Space heat is the largest single consumer of heat energy these plants with respect to energy conservation projects.

It is worth noting that three of the four plants in this second pattern group are engaged in electronics related work. Although three plants may not represent an industry, the results here indicate that energy conservation priorities for electronics industry plating plants should be different than those for the fasteners, hardware and automotive industry users.

Plants in the first pattern group (large shops) should look to the following areas first for energy conservation opportunities:

1. Electrically
   a. Plating/anodizing
   b. Exhaust fans

c. Lighting

2. Process heat
   a. Tank heating (all)
   b. Boiler operations
   c. Ovens and dryers
   d. Space heat

Plants in the second pattern group (small shops) should look to the following areas first for energy conservation opportunities:

1. Electrically
   a. Exhaust fans
   b. Tank heating
   c. Air-conditioning
   d. Lighting

2. Process heat
   a. Space heat
   b. Tank heating
   c. Boiler operations

Discussion

The American plating and surface finishing industry currently uses an estimated 52 million barrels-of-oil equivalent energy annually. Of this 52 million barrels-of-oil equivalent, our data indicates that 86 p cent was consumed as natural gas in processes such as steam boilers an dryers. Fossil fuel usage in the plants surveyed is almost exclusivel natural gas. Propane and fuel oil are maintained as standby fuels in few of the plants surveyed but their usage is minimal. Approximately 14 percent was used as electricity for materials handling, environment conditioning, and in plating and surface finishing processes themselve Georgia Tech's experience with other industries, such as poultry proc indicates that at least a 20 percent reduction in total energy consum can be realized from a well researched and broadly implemented progra energy conservation.

Of the twenty plants surveyed, eleven had done nothing or very l to investigate or implement energy conservation measures at the time the plant visit. Four had done something in the way of energy conse items, and one plant had implemented numerous energy conservation it with very satisfactory results. In most cases energy is not the pla highest operational expense. It is second or third behind labor and materials and thus, does not receive a great deal of attention. Cap money for energy saving measures has had to compete most often with production equipment and pollution control equipment among other ite

Energy conservation efforts in the plating and surface finishing industry will continue to grow as fuel costs rise. Energy saving capital projects will show a higher return on investment and thus will be more attractive. Implementation of these projects will serve to keep the individual plating facility competitive in a time of rising fuel costs.

TABLE 1

Average Electrical Energy Consumption for All Plants

Total Annual Kilowatthours	5.30×10^7
Average Annual Kilowatthours Per Plant	2.65×10^6

		Percent of total
1.	Exhaust fans	24.6
2.	Electroplating and/or anodizing	23.9
3.	Lighting	11.7
4.	Hoists and drives	5.0
5.	Oven heat	4.5
6.	Filter pumps	3.0
7.	Electric tank heating	2.9
8.	Waste treatment equipment	2.7
9.	Air agitation	2.7
10.	Chillers	2.6
11.	All other pumps	2.6
12.	Grinding, polishing, buffing	2.4
13.	Electrocleaning	2.4
14.	Air-conditioning	2.3
15.	Other uses	6.7
		100.0%

TABLE 2

Average Process Heat Energy Consumption

All Plants

Total Annual Btu's 1.08×10^{12}

Average Annual Btu's Per Plant 5.38×10^{10}

		Percent of tota
1.	Process tank heating	23.1
2.	Boiler losses	18.2
3.	Space heat	18.2
4.	Cleaner tank heating	12.0
5.	Rinse tank heating	10.0
6.	Ovens and dryers	7.0
7.	Vapor degreaser heaters and stills	4.0
8.	Waste recovery evaporators	3.8
9.	Other uses	3.7
		100.0%

TABLE 3

Average Electrical Energy Consumption;
First Pattern Group* - sixteen plants

Total Annual Kilowatthours 4.61×10^7

Average Annual Kilowatthours Per Plant 2.88×10^6

		Percent of total
1.	Electroplating and/or anodizing	29.5
2.	Exhaust fans	22.4
3.	Lighting	12.2
4.	Hoists and drives	5.9
5.	Filter pumps	3.4
6.	Grinding, polishing, buffing	3.0
7.	Electrocleaning	2.9
8.	Air agitation	2.7
9.	All other pumps	2.5
10.	Waste treatment equipment	2.2
11.	Other uses	13.3
		100.0%

*11 plants except A, K, R and T

TABLE 4

Average Process Heat Energy Consumption

First Pattern Group*

Total Annual Btu's 1.05×10^{12}

Average Annual Btu's Per Plant 6.57×10^{10}

		Percent of tota
1.	Process tank heat	23.3
2.	Boiler losses	19.7
3.	Cleaner tank heat	13.2
4.	Rinse tank heat	11.2
5.	Ovens and dryers	8.7
6.	Space heat	8.5
7.	Waste recovery evaporators	4.7
8.	Vapor degreaser heaters and stills	4.1
9.	Other uses	6.1
		100.0%

*All plants except A, K, R and T

TABLE 5

Average Electrical Energy Consumption

Second Pattern Group*

Total Annual Kilowatthours 6.92×10^6

Average Annual Killowatthours Per Plant 1.73×10^6

		Percent of total
1.	Exhaust fans	33.2
2.	Electric tank heating	14.5
3.	Air-conditioning	10.6
4.	Lighting	9.8
5.	Waste treatment	4.7
6.	Agitation air	2.3
7.	Filter pumps	2.3
8.	Hoists and drives	1.4
9.	Electroplating	1.3
10.	Other uses	19.9
		100.0%

* Includes plants A, K, R and T

TABLE 6

Average Process Heat Energy Consumption
Second Pattern Group*

Total Annual Btu's 2.43×10^{10}

Average Annual Btu's 6.08×10^{9}
Per Plant

		Percent of tota
1.	Space heat	56.7
2.	Process tank heating	15.7
3.	Boiler losses	12.2
4.	Rinse tank heating	5.8
5.	Cleaner tank heating	5.2
6.	Vapor degreaser heaters and stills	3.7
7.	Ovens and dryers	.3
8.	Other uses	.4
		100.0%

*Includes plants A, K, R and T

K-2

Energy Conservation I
Session K

Application of Low Energy Consuming Processes and Techniques To the Metal Finishing Industry

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Warren, Michigan

Application of Low Energy Consuming Processes and Techniques To The Metal Finishing Industry

By R. S. (Steve) Lewis

ENERGY MANAGEMENT - WHY? — PROFIT DOLLARS, SAVED OR LOST

approach to energy management
es from the on off switch, to a
plex industrial commitment of its
neering and technological capability
ed by a substantial capital commit-
.

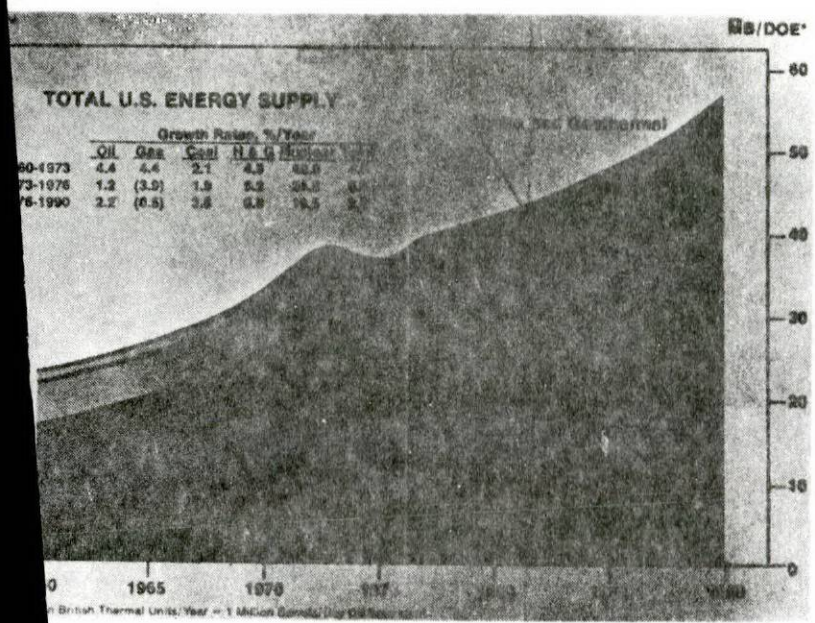
RGY RESOURCES

ime has come for action, according
ilson Clark in, "Energy for Sur-
' known reserves of energy sources
ural gas are 22 years, oil 20 years,
m 20 years, and coal 111 years.
oncerns the Federal Energy Ad-
ration (FEA). Their goal for 1980 is for top energy consuming industries to use less energy than a decade ago.

ENERGY USAGE

Why should the FEA focus on industry? Consider the fact that industry uses 33% of our total energy output, the FEA has no choice. Furthermore, residential and commercial use another 34% and transportation 24%. The U.S. gets their energy supply from petroleum 49%, natural gas 22%, coal 20%, and hydroelectric, nuclear power, and others contribute to 9%. (See Figure 1)

TOTAL U.S. ENERGY SUPPLY



SHARE OF TOTAL U.S. ENERGY SUPPLY (%)

	1960	1976	1980	1990
	---	3	5	16
eo	4	4	4	3
	22	18	20	20
	30	28	22	17
	44	47	49	44
TAL	100	100	100	100

(Figure 1)

NATIONAL ENERGY PLAN

Congress has developed a National Energy Plan which outlines four goals. They are:

(1) Reduce the annual growth rate for energy demand of 3.5% to below 2%.

(2) Reduce gasoline consumption by 10% below 1976 levels.

(3) Reduce imported oil by 40% by 1985.

(4) Increase coal production by 66%.

The days of inexpensive energy have long gone. Energy costs will continue to rise simply because of a basic principle. ENERGY IS A BASIC WORLD NEED FOR WHICH DEMAND CONTINUES TO GROW.

If industry fails to achieve the goals of our National Energy Plan on a voluntary basis, the FEA has few options; price controls, oil import quota's (resulting in energy shortages), and oil company divestiture.

One approach in helping to achieve the FEA goals is for industry to produce more production from present BTU levels. It seems obvious that what is needed in industry, or for that matter in all our lives, is a realistic energy conservation program. An effective energy conservation program begins at the top and is generated down through the ranks of management.

ENERGY CONSERVATION PROGRAM

Our objective in reviewing this subject is not to tell you to turn off light switches or how to operate your equipment more efficiently. Rather, to direct your attention toward energy conserving processes and to illustrate the actual savings realized through the use of these processes. It is our opinion that this is an approach that can be taken with immediate impact on your own energy conservation program.

Production proven processes are available which enable the plater to operate effectively at temperatures that were once considered impossible.

Whoever heard of soak cleaners operating at 110° F, or bright nickel baths operating at 100° F. Five years ago this would have been considered unthinkable. Today it is a reality.

ENERGY COSTS

WHY CONSIDER A LOW TEMPERATURE PROCESS? Consider electricity at a cost of 5¢ a kilowatt hour, natural gas at $2.40 1000 cubic feet, and fuel oil at 35¢ a gallon. Those expensive BTU's add up quickly. (See Figure 2)

INSULATE TANKS

First in the plating cycle and first to be reviewed are cleaners. There are two steps that can and should be taken to save BTU's when dealing with cleaners. First, insulate all tanks that are heated, the sides and the bottom. As much as 90% in heat loss can be saved through insulating the tank. (See Figure 3) This can be accomplished by insulating with 1 1/2 inch (minimum thickness) styrofoam sheets. When possible, use a foam blanket to insulate the surface to reduce evaporation and radiation losses.

Whether you are working with one gallon or 10,000 gallons, BTU savings can be impressive. If the cleaning tanks are in a workroom that is maintained at 60° F and the cleaners call for an operating temperature of 180° F, 2,000 BTU's are lost through radiation to the room. This is calculated at BTU's per hour, per square foot of surface area of the tank at zero air velocity. As illustrated, 1,740 BTU's are lost through evaporation and 260 BTU's are lost through radiated heat.

THINK BTU's

Begin thinking in terms of heating cost as BTU usage. For example, to increase a thousand gallons of solution 50°, each rise in temperature will cost your energy budget 416,500 BTU's. To increase the same thousand gallons of solution by 100°, the energy cost will be 833,000 BTU's, almost a million BTU's. Consequently, low temperature processes that can save you even 10° F in operating temperature can greatly contribute to your BTU conservation program. (See Figure 4)

WORKING ENERGY/COMPARISON COSTS

	Unit Cost	BTU/Unit	Cost/1000 BTU's
Electricity	5¢/KWH	3413	0.0147¢
Natural Gas	.0024¢/Cu. Ft.	700	0.0034¢
Fuel Oil	35¢/gal	101,500	0.0035¢

(Figure 2)

ENERGY (BTU's/Hr/SqFt) LOST FROM TANK

Solution Temp °F	BTU's Radiated To Room	BTU's Lost Through Evaporation	Total* BTU's Lost
90	50	80	130
100	70	160	230
110	90	240	330
120	110	360	470
130	135	480	615
140	160	660	820
150	180	860	1,040
160	210	1,100	1,310
170	235	1,380	1,615
180	260	1,740	2,000
190	290	2,160	2,450
200	320	2,680	3,000

*Zero Air Velocity

(Figure 3)

ENERGY (BTU's TO RAISE 1000 SOLUTION TEMPERATURE

1000 GALLON S

Rise in Temperature
50° F
60
70
80
90
100
110
120

(Figure

Figures 3 and 4 can b
an approximate ene
specific operation.

LOW TEMPERATURE CLEANERS

Whether we review l
or electrocleaners, y
are much more sopl
then their high
predecessors. They
of a complex comb
and detergents for
remove a variety o
metal. Many pro
available that opera
temperatures. Succ
often depend on th
are expected to op
the soil, basis meta
in a given geograp
is advised that se
given to each clea
cleaning cycle.
difficult, as low te
been available t
years.

A typical ener
operates betwee
within a tempe
150° F at a cycle
The reason, of c
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However, low t
BTU's (See F
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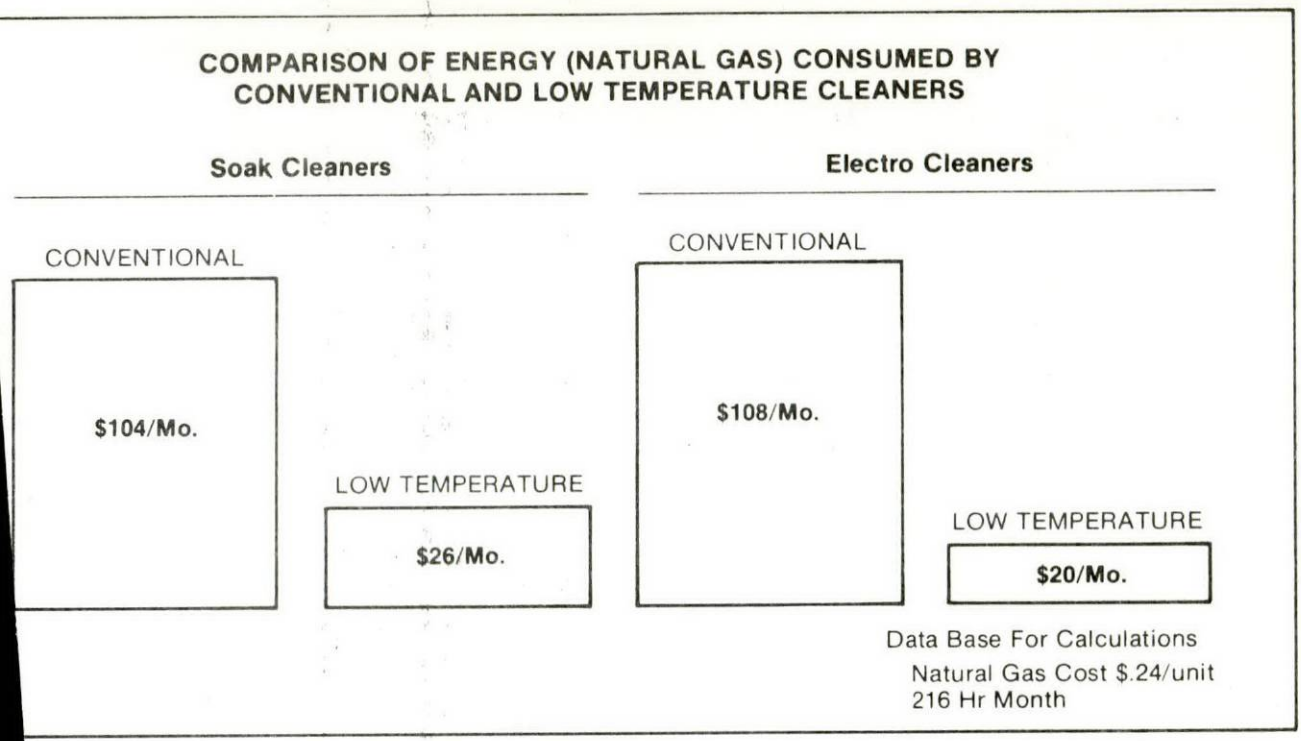
resulting in lon



(Figure 5)

save up to 80% in energy costs ting tanks and using low re cleaners at the lowest possi- ature range.

MPERATURE NICKEL

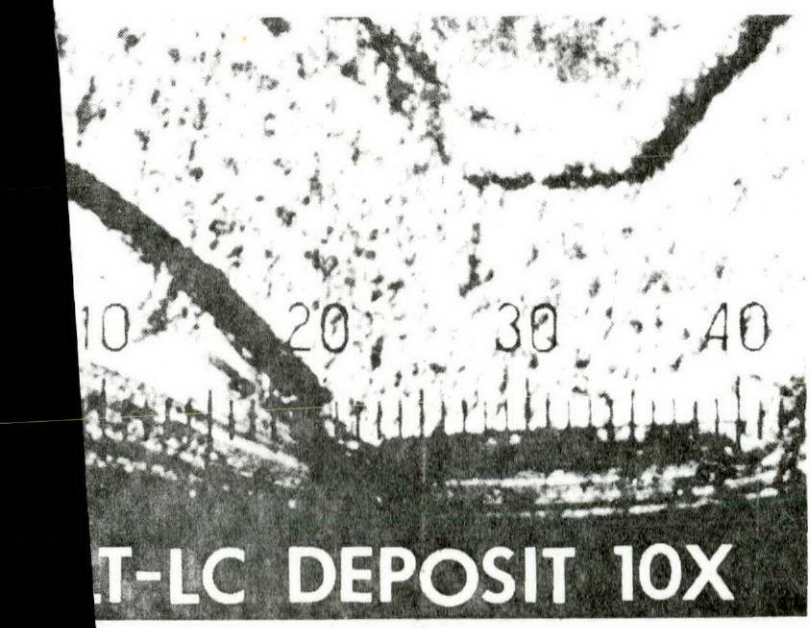
ea for immediate action is the ng bath. First, they should be the same manner as outlined . Then you should begin an program for selecting the best rature, low concentration ilable. There are many processes available all of which work well, some better than others.

Low temperature, low concentration bright nickel systems have been in use for years and many hundreds of thousands of gallons are presently being used throughout the metal finishing industry. Today, LT-LC bright nickel systems are used by the automobile, appliance, hardware, furniture, and bicycle industries. LT-LC nickel processes are proven and perfected. LT-LC nickel offers substantial BTU savings as well as chemical, waste treatment, and filtration costs without sacrificing product quality.

Today's low temperature baths offer high leveling, (See Photo A) brightness, excellent covering power, adhesion, and chromium receptivity.

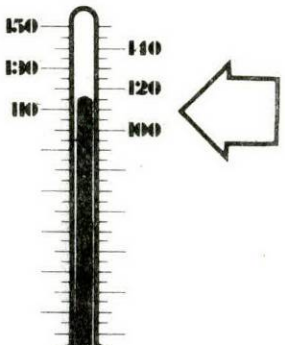
OPERATING TEMPERATURE

Operating temperatures of the bath are usually from 100° to 155° F. Most LT-LC baths operate between 115 - 120° F due to the plating amperage of the tank which maintains the solution temperature.



(Photo A)

Photomicrograph cross section of LT-LC nickel plated threads at 10X magnification. Note leveling properties of LT-LC into thread recess. (Point A)



plating amperage holds the bath within the 110-115° F. operating range.

(Figure 6)

Normal plating amperage of 0.7 to 1.0 per gallon of solution will maintain solution temperature at approximately 115° F, plus or minus 5° F. (See Figure 6) Should these baths exceed the amp per gallon plating amperage and subsequently exceed the 115° F operating temperature, cooling would not be required since most LT-LC baths work very well up to 155° F.

CONVERSION

Conversion to a low temperature nickel system from a WATTS formulation can be accomplished through one of two ways. The first and the easiest method, would be to dilute the existing WATTS bath to the chemical concentrations as outlined in Figure 7.

LOW CONCENTRATION
LOW TEMPERATURE

BRIGHT NICKEL PROCESS

OPERATING CHARACTERISTICS

	Range	Typical
Nickel (as metal)	4.6 - 8.6 oz/gal 34.5 - 64.5 g/1	6.0 oz/gal 45.0 g/1
Nickel Sulfate	8.0 - 20.0 oz/gal 60.0 - 150.0 g/1	10.0 oz/gal 75.0 g/1
Nickel Chloride	12.0 - 16.0 oz/gal 90.0 - 120 g/1	15.0 oz/gal 112.5 g/1
Boric Acid	7.0 - 9.0 oz/gal 52.5 - 67.5 g/1	7.0 oz/gal 52.5 g/1
Carrier	2.0 - 4.0% by vol	3.0% by vol
Brightener	0.1 - 0.2% by vol	0.15% by vol
Additive (normally required for make-up and conversions only)	See Section Regarding Additive	
Wetter (If required)	0.1 - 0.3% by vol	0.1% by vol
Temperature	100 - 150° F 38 - 65° C	115° F 46° C
Current Density	10 - 100 ASF	
Agitation	Low Pressure Air or Cathode Rod	
pH	3.8 - 4.3	4.2
Filtration	Continuous - Through Activated Carbon (3 to 5 lbs/1000 gal)	

(Figure 7)

Or you can slide convert
dragout to lower the bath
This, of course, requires clos
attention and it could be se
before the actual conver
complished.

CHEMICAL COMPOSI

Figure 7 also outlines t
perimeter of a typical LT-
Nickel sulfate is maintain
range of 8 to 20 oz gal and ni
at 15 oz gal. The nickel sulf
chloride act as the source f
in the plating solution.
chloride content increases
allows for higher cathode
sities, improves the low c
areas, and is instrumental
anode corrosion. Nickel s
the additional nickel ions
achieving the total meta
quired. The bath operat
nickel metal content of 6
range of 4.6 to 8.6 oz gal.
as the buffer, preventing
peel, and exfoliation.

ADDITION AGENT

Most LT-LC systems c
addition agents, (See
primary (carrier) or gra
tion agent.

The primary is essent
ductility and levelin
conjunction with
brightener. Normally,
wide operating range
critical. The second
secondary or strong b
and its concentration
maintained within s
perimeters as outline
manual. Careful cont
brightener is essen
results. The secondar
brightness, and depth
if used in excess, duc
coverage are usuall
In most cases, the
unnecessary as the c
additives possess s
ties. This is especial
solutions. However
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to overcome thes
Wetters are easily
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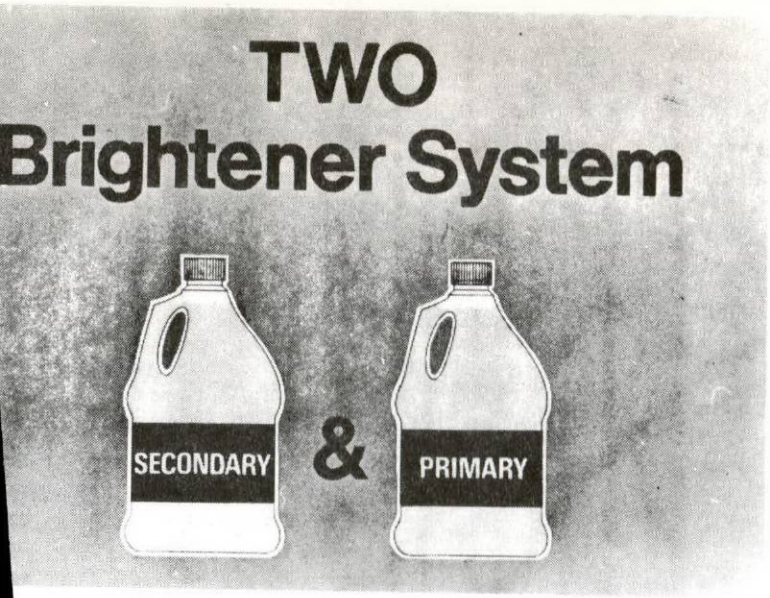
stalogmometer.



(Photo B)

TH MAKE UP

t that a new nickel plating bath pared, there is no question that bright nickel approach should e dollars saved in making up e substantial. Figure 8 offers ring the chemical composi- ATTS type bright nickel bath C bright nickel.

emical savings of up to 40% ed. Also note that the make ditives for both systems is his should hold true in ampere hour consumption as well.

pH

pH and pH control of a LT-LC bright nickel has a wide operating range of 3.5 to 4.4. Lower values result in a dulling effect on brightness. Higher values of pH promote better brightness and leveling. However, in values above 4.5, chromium coverage can be affected and may cause percipitation of iron resulting in chromium misplate and/or stardusting in the deposit. Therefore, the recommended pH range is between the value of 3.8 - 4.2.

FILTRATION

All air agitated bright nickel baths should be continuously filtered through activated carbon. This procedure enables the bright nickel bath to operate free of long chained organic compounds, which are usually additive by-products of electrolytic decomposition and/or other organic contaminants. The filter should be precoated and then charged with three to five pounds of activated carbon per 1,000 gallons of plating solution each week and sized to turn the solution over a minimum of 1 1/2 times per hour. The filter flow rate of the LT-LC baths is greatly extended due to the lower chemical concentration of the bath, resulting in less filter maintenance and extended pump life.

AGITATION

As with all modern high speed bright nickel processes, air agitation is a must. The air must be free of oils, greases, or other contaminating materials. The air itself should impinge directly on the work. This, therefore, requires properly designed air coils. The combination of agitation and solution freeboard should be such as to prevent overflowing of the solution over the top of the anode baskets, otherwise severe roughness can occur from the anode sludge released into the nickel solution. The LT-LC bath seldom experiences air coil plugging due to its lower chemical composition and higher solubility factor.

MAKE UP COSTS
FOR 1000 GALLON TANK

WATTS			LT-LC		
$NiSO_4 \cdot 6H_2O$ @ 40 oz/gal	= $	1,875	$NiSO_4 \cdot 6H_2O$ @ 10 oz/gal	= $	469
$NiCl_2 \cdot 6H_2O$ @ 6 oz/gal	= $	383	$NiCl_2 \cdot 6H_2O$ @ 15 oz/gal	= $	956
H_3BO_3 @ 6 oz/gal	= $	79	H_3BO_3 @ 7 oz/gal	= $	92
ves -			Additives -		
per recommendation	= $	11	per recommendation	= $	11
TOTAL	$	2,348	TOTAL	$	1,528

SAVINGS
$820/1000 GALLONS

ANODE/ANODE BAGS

S-rounds or 1 x 1 electrolytic squares in titanium baskets are the most popular due to price, ease of anode replacement, and anode efficiency. Titanium baskets using S-nickel rounds operate best with a 10 ounce unbleached cotton duck having a thread count of 40 x 56, or 42 x 54 with an inner canton flannel liner to untrap the finer anode sludge and fines.

ENERGY SAVINGS

At this point, the similarity of the two systems stop. The LT-LC bright nickel system immediately saves energy (BTU's) through lower operating temperature (Figure 8) and through the usage of l chemicals and the resultant need for l chemical dragout to waste treat. illustrate the LT-LC savings, a 1,0 gallon bright nickel plating operati with two turnovers (dragout) per year w be used as our example.

SAVINGS IN HEAT BY USING LT-LC SYSTEM

A. *Using a 1,000 gallon tank with the following dimensions:*

1. 4 ft. wide x 5 ft. deep x 6.5 ft. long
2. 4 x 6.5 = 26 sq. ft. of top surface area
3. 40 + 65 + 26 = 121 sq. ft. of tank wall and bottom surface.

B. *Heat loss at 150° F:*

1. 1,040 BTU x 26 sq. ft. = 27,040 BTU loss/hr. from surface.
2. 180 BTU x 121 sq. ft. = 21,780 BTU loss/hr. from tank walls.

TOTAL..... 48,820 BTU

C. *Heat loss at 115°F:*

1. 400 BTU x 26 sq. ft. = 10,400 BTU loss/hr. from surface
2. 100 BTU x 121 sq. ft. = 12,100 BTU loss/hr. from tank walls

TOTAL..... 22,500 BTU

D. *Difference in heat loss is:*

48,810 - 22,500 = 26,320 BTU/hr

26,320 BTU/hr. x 24 x 365 = 230,563,200 BTU loss difference/year

E. *Cost for electricity:*

$$\frac{230,563,200}{3,413 \text{ BTU/KWH}} = 67,554 \text{ KWH saved/year}$$

at 5¢KWH = 67,554 x .05 = $3,378 saving/year

F. *Fuel oil:*

$$\frac{230,563,200}{101,500 \text{ BTU/gal.}} = 2,271 \text{ gallons fuel oil saved/year}$$

at 35¢/gal. = 2,271 x .35 = $794 savings/year

G. *Natural gas:*

$$\frac{230,563,200}{700 \text{ BTU/cu. ft.}} = 329,376 \text{ cu. ft. of gas saved/year}$$

at .0024¢/cu. ft. = 329,376 x .0024 = $790 savings/year

All based on 1,000 gallon tank with above dimension, 60° F ambient temperature.

NOTE: No corrections made for air currents which increase evaporation and tank wall heat loss. Cost of energy will vary with each location. Calculations based on table in Electroplating Engineer's Handbook.

No corrections made for heat input to bath from amperage and voltage used for plating. Calculations based on continuous heating period of 365 days. No corrections made for heat loss due to cold racks entering the nickel solution and resultant carry out of heat, or heat loss due to air agitation.

For periods less than 365 days, use following:

$$\text{Formula: } \frac{\text{No. of days heated x savings}}{365}$$

SAVINGS IN NICKEL SALTS BY USING LT-LC SYSTEM

Savings are approximately $2.00/gallon/year, depending upon loc conditions. The following calculations substantiate this.

Calculations assume no nickel salt additions for LT-LC baths except boric acid.

In reality, some nickel salts will be needed; however, the percenta based on production installations, has been little if any.

CONDITIONS

1,000 gallon bath
2 turnovers/year

40 oz/gal $NiSO_4$	$0.75/lb 22% nickel metal
8 oz/gal $NiCl_2 \cdot 6H_2O$	1.02/lb 24% nickel metal
Nickel metal	2.08/lb

NICKEL SALT USAGE PER YEAR:

2 x 2,500 lbs = 5,000 lbs $NiSO_4$/year
2 x 500 lbs = 1,000 lbs. $NiCl_2 \cdot 6H_2O$/year

ABOVE SALTS CONVERT TO:

5,000 lb $NiSO_4$ x 22% = 1,100 lbs nickel metal
1,000 lb $NiCl_2 \cdot 6H_2O$ x 24% = 240 lbs nickel metal

Total Nickel Metal in Above 1,3

1,340 lbs of nickel metal in above salt form costs:

$$NiSO_4 = \frac{.75}{.22} = \$3.41/\text{lb} \times 110 \text{ lbs} = \$3,751$$

$$NiCl_2 = \frac{1.02}{.24} = \$4.25/\text{lb} \times 240 \text{ lbs} = \$1,020$$

TOTAL $4,771

Therefore, 1,340 lbs nickel metal in above salt form would co as nickel metal.

It would have cost in anode form:

1,340 lbs x $2.08 = $2,787.00

The saving would be $4,771 - $2,787 = $1,984 per 1,000 gal year, by using an LT-LC bath, or

$$\frac{1,984}{1,000} = \$1.98/\text{gal/year savings}$$

ERGY LOSS

other contributor to energy (BTU) sumption is the energy required to up the work and racks as they enter exit from the work solution and equently drop the operating erature resulting in a call for energy aintain bath temperature.

s a difficult area to define due to the bles that influence this problem. ver, in order to impress upon the tor the effect of this situation on consumption, we will attempt to te the effect by combining work ack expressed as total pounds g the operating tank.

9 illustrates 20, 40, 60, and 80 of combined work and rack at tering a tank at 115° and 150°F. ual savings to maintain operating tures is calculated as the difference in temperature between the LT-LC and WATTS system (35°F) and calculated in energy source, electricity, natural gas, and fuel oil.

The data in Figure 9 is provided with the intention of availing the reader with a work guideline to define energy uses and resultant needs which affect his BTU budget due to the cooling effect of work entering a heated operating solution. Again, the low temperature approach saves energy, and a side benefit from operating a low temperature process is the need for less bath maintenance water. Additionally, lower temperatures provide for safer working conditions and a more comfortable atmosphere for the tank operators during summer months.

In summary, let us add up the facts through another example. If your company is operating on a 5% net profit margin and you have saved $12,000 a year in related energy savings through insulating tanks using foam blankets where possible, operating with low temperature soak and electrocleaners, using the low temperature, low concentration nickel bath, and following a realistic energy conservation program, your company would have to increase sales by $240,000

$12,000 Energy Savings
5% Net Profit

in order to realize the $12,000 net profit which you have saved through a relatively simple energy conservation program utilizing low energy conserving processes and techniques.

In conclusion, we leave you with this thought. You can begin conserving energy now with proven and perfected processes and techniques, and your effort will have direct and positive influence on the economic health of your company.

COMPARISON OF ENERGY SOURCES AND RELATED SAVINGS WHEN USING A LT-LC vs A WATTS BRIGHT NICKEL SYSTEM

Various weight of racks and work	Savings realized through difference in temperature, 150 vs. 115°F of Nickel bath		
	Electricity @ 5¢/KWH	Natural Gas @ .24¢/unit	Fuel Oil @ 35¢/gal
20 Pounds	$ 443	$105	$109
40 Pounds	886	210	218
60 Pounds	1,329	315	327
80 Pounds	1,772	420	436

DATA BASE - LT-LC operating at 115°F
Watts operating at 150°F
120 racks/hr
4000 Hour year
Natural Gas Unit = 100 Cu. Ft.

(Figure 9)

K-3

Energy Conservation I
Session K

Economics of Sputtered Metallic Decorative Surfaces

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ECONOMICS OF SPUTTERED METALLIC DECORATIVE SURFACES

To better acquaint those of you who do not understand just what puttered films are, we will offer the following explanation: Sputtering nvolves the use of high vacuum chambers similar to those used in decor- tive vaporization of aluminum, a process used mostly for first and second urface plastics for many varied cosmetic effects. Automotively speaking, econd surface was used for exterior and interior applications, with first urface applications remaining inside the automobile for armrest bases, nstrument panels, and other interior parts where a "simulated" bright inish would suffice.

Because of the low resistance to galvanic creepage corrosion of aporized aluminum films for exterior use, either first or second surface, e automative industry took on the task of developing a better way to hieve the desired bright finish.

One of the first things necessary was a specification, covering the flectivity needed-and the performance of the product. Naturally,because would be competing in a sense with electroplating substrates, the spec- cation took on many of the same items as its forerunner.

In 1966, Red Spot Paint & Varnish Company began its first big research ject orientated at supplying coatings which could be used for vacuum allizing exterior first surface grilles, fender extensions, etc. Early he program, we determined along with others who were testing vacuum llizing for the application that aluminum just didn't hold up as well t could or should for the application. Later, certain of the auto- ve industry determined that they could vacuum metallize via the electron process,and of course, selected antimony as the material be be evapo- d. Our early research pointed out that antimony via the electron beam water missible and did not hold up in Florida Exposure and UV resistance ell as it should. Basically, the antimony began dissipation and its ctive film continued to do so until complete loss of brillant surface ffected. The time allowed between failure depended upon the film ness of the evaporated film. At that time, we decided to call off urther research concerning antimony films and moved on with other s to be evaporated.

Because of the problems associated with electron beam, and especially concerning a continuous chemical metal film throughout a surface which en metallized, and the problems associated with these surfaces with g adhesion, etc., we discontinued electron beam research.

ater, our Research Department evaluated sputtering, which is not a ocess but was more associated with the functional coating industry ic lens. We felt that it would have some merit for the type of tion that we sought. Various work was done by two California es, and finally sputtering became the choice method of evaporating ver electron beam and resist firing methods.

One of these companies, namely Airco Temescal of Berkley,Califor developed a reflective material alloy which yielded a much brighter s face and came closer to producing the brillance of a electroplated su face. It comes close to doing the job insofar as reflectivity, but w a coating is applied over the evaporated film, it has a tendency to d color somewhat and darken the film cutting down on its reflectivity a the same time.

Sputtering was never intended to become a competitive method for the electroplating industry. I think it would be better to say that sputtering enhances and offers a choice to all users of reflective f

Naturally, sputtering is not the same process as electroplating this presentation today is intended to be very informative to you ab sputtering only.

Sputtering is accomplished very similar to the old method of va metallizing. Basically, what is involved is the application of a co to the substrate, whereas this particular coating must be cured in or oven device followed by evaporation of the sputtered film in the chamber, followed by a clear topcoat to be applied to protect the v ized film. Often, a decorative overlay may be applied to certain a of the part to produce the desired cosmetic effect.

There are various methods available to obtain a sputtered fil however, sputtering itself is a process, and the vacuum deposition the chrome film is identifiable as sputtered fired, resist fired, possibly even electron beam fired; however, the sputtered method f a target itself is the most commonly accepted practice of evaporat the material, with resist firing a close second method.

Next, we would like to talk about substrates involved. First all, as you are well aware of, sputtering lends itself to deposit bright metallic surfaces to flexible substrates which at this tim known electroplated process is available. The idea here being th the part is flexed either in use on an automobile or by hand arou 3/8 inch mandrel for flexing and then returned to its original sh The specification and the designers for such parts ask that the p return to its original form with very little bending or flexing a there is no visable or no noticable effects that take place afte particular flexing. This is especially a desirable application fender extensions, hood extensions, and ornamentation. Presentl type of application is being used on flexible substrates by the automotive market. So, the application of sputtered films to fl substrates has no competition. It is, at present, the only prac method as well as a production proven method of applying a brig film to a flexible substrate.

We should momentarily talk about what is expected of the sputtered film and why sputtering is being done. First of all, going back to the early days of electroplating, the substrate itself was usually steel or zinc or a very heavy substance. With the advent of weight and cost reduction programs and the demands placed on the industry, specifically the automotive industry, sputtering is the only method in which really any particular savings is allowed. Those savings are as follows: First, it has become necessary to sputter films rather than electroplate them in many instances because of the Environmental Protection Agency's restrictions placed upon the electroplating industry for polluting streams, rivers and/or the nation's supply of water. Sputtering, on the other hand, doesn't pollute the water but if certain solvent systems are used in their application, they too fall under the rules and regulations of the EPA and could create problems in the atmosphere. However, the amount of air pollution is at a far less degree than that of the electroplating industry with old methods. The only way to overcome this problem is by installing new equipment with tremendous capital outlays for removing the contaminants from rinse waters, waste waters, etc.

The cost of vacuum metallizing equipment for sputtering applications is extremely high and in many cases probably if a company were comtemplating getting into sputtering rather than say, electroplating, the expeniture insofar as the capital outlay, would probably be close to the same. It becomes a situation at this point as to whether or not you would prefer to spend your money for "cleaning up or devising methods to clean your waste water or purchase equipment that doesn't contaminate the streams or the waste water because there is very little involved.

The main purpose of the sputtered film that is often overlooked is the fact that the automotive designers and engineers are looking for ways to lighten the weight of the automobile. Naturally, plastics is one of those methods. 1979 finds us utilizing more plastics than ever on automobiles with predictions that by 1984 twice the present use will be needed. You can see there is to be a considerable amount of emphasis placed upon the availability of other methods of achieve bright metallic surfaces.

Keep in mind when you are speaking of sputtering that you are also talking about the use of coatings similar to those that are placed on exterior of the automobile. However, we are speaking of clear versions of resins and coatings rather than pigmented versions. Because of the nature of an electroplated substrate and their ability to withstand abrasion, mar, scratches, wear, salt spray, UV light, and their hardness, makes it difficult for an organic coating to compete with such tremendous physical properties as electroplated substrates and finishes hold. Therefore, it is necessary to educate the automotive, marine, cosmetics, hardware industry, all of the users of those surfaces which have been electroplated in the past, and all of the companies using electroplated finishes, must be re-educated to accept something less hard, less abrasive resistant, less wear resistant, slightly less in reflectivity,

maybe less salt spray resistant. Although specifications have been written that these coatings do meet and in many surpass many times over the specification, it is a known fact that the end product does not yie the same physical properties. Yet there are advantages such as polluti and application to more substrates than electroplating has.

So, when speaking of sputtering we should keep in mind that we are working with an organic coating, rather than an electroplated coatings. Another area that we should stop to think about when comparing sputteri with electroplated films is the cost of the chemicals involved and the time involved with each process. I need not get into a discussion with the time and the different rinses, surface preparations, plating and r after plating, that is involved with the electroplated industry. First all, I wouldn't be near as qualified probably as the most neophyte amo you today. However, I know just enough about it you might say to be d gerous, maybe to myself or to the industry. But because of the organi coatings involved and the fact that we, or I, represent a manufacturer coatings for all substrates, I do not look upon what is being done in sputtering industry as exactly competitive to someone like you because are involved with manufacturing coatings also for the electroplating dustry. When I speak of coatings, I talk about decorative overlays, keep this in mind as we continue.

Basically, what we are involved here in is the fact that sputter can be done on flexible, rigid, and possibly even semi-rigid substrat There has been no evaluation of sputtering on metal substrates other for one appliance concern because first of all we would be defeating real purpose from which sputtering became known for in the beginning was not developed specifically for flexible but rigid substrates suc ABS; Polycarbonates are also the big name in sputtered finishes at t time. The main idea behind a sputtered finish is to effect a cost r tion in the cosmetic results or values expected in a metallic film. instance, a plastic grille electroplated weighs much less than a zi cast grille electroplated so the savings is generally in many areas plastic verses the zinc die cast, but weight reduction being the ma Then, of course, there are many labor saving shortcuts with the plas strate other than the zinc insofar as deburring, cleaning, etc. Ba when we are working with an electroplated plastic part with the sam of electroplating waste and chemicals going into the streams and wa a zinc die cast, the pollution is about the same. There may be so difference but not enough to really make a big showing. However, vacuum metallizing and particularly the method utilizing flowcoati the method of the application of the basecoat and topcoat you are about considerable amount of savings in chemicals for that partic grille; so, what we come up is the fact that we are able to lower with organic coatings and the sputtering process as compared to th plated process. Also, where organic coatings are used we are able pigmented overlays to the coating which adhere much better and pas more stringent specifications in the automotive industry than pai

electroplating substrates.

It is an opinion shared by many in the automotive industry that a need also exists that allows designers more freedom in selecting bright metallic finishes which lend themselves to more substrates. Sputtering is one of the materials which will be available for them when matched to the proper substrate and specification.

Additionally, many have expressed the opinion that for years, electroplating has been utilized where lesser performing bright finishes could have been used which would have effected cost savings. Others have been of the opinion that over engineering of bright finishes has been occuring. Some automotive engineers periodically visit junk yards and inspect all types of finishes to determine their conditions and try to attempt a conclusion as to whether or not over engineering has occured.

With sputtered finishes on all substrates, consideration of over engineering hasn't been the question, but rather one of being under-engineered.

Although no embarrassing side effects have come to pass at present, everyone is trying to quality control the finishes and the process as closely as experience will allow. Improvements have been made and will continue as more applications are put into process.

A list of manufactures of equipment used in the process-or related after plating processes will follow at the end for your use should you desire more information. Although no costs figures are available, equipment is available and quotations would also be furnished by these companies dpenedent upon your specific needs.

SPECIALIZED FINISHING EQUIPMENT

Vacuum Metallizers

A. Conventional Filament Fired

Stokes Division
Pennwalt Corporation
5500 Tabor Road
Philadelphia, Pennsylvania 19120
215-289-0100

B. Sputtering

Airco Temescal
2950 Seventh Street
Berkeley, California 94710
415-841-5720

Varian Associates
611 Hansen Way
Palo Alto, California
415-493-4000

Telic Corporation
1631 Colorado Avenue
Santa Monica, California 90404
213-829-4551

K-4

Energy Conservation I
Session K

Energy and Organic Industrial Coatings

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ENERGY AND ORGANIC INDUSTRIAL COATINGS

ABSTRACT

Energy requirements of conventional solvent-borne, water-borne, high solids, powder coating, and electrocoating industrial finishing systems are compared. Factors affecting energy are discussed for a model system involving spray application or electrocoating.

BY

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Glidden Coatings and Resins

Division of SCM Corporation

FOR

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INTRODUCTION

Since conservation of energy is such an important issue for all industrial processes, it is of interest to compare the energy requirements of the modern organic finishing technologies. There have been a number of similar comparisons made in the past[1,2,3,4] which have been of value in showing relative energy requirements. What these previous studies did not show explicitly were the methods of caluculations used to arrive at their energy values. Knowledge of such methods would be valuable for the individual paint user because by nature, all generalized comparisons are theoretical, whereas, in practice, each finishing line is different. Thus, the purpose of this article is to re-examine and expand energy comparisons and to show how the calculations are done. Hopefully, this can serve as a basis for energy calculations on specific systems and as a starting point for further refinements in energy calculations.

First, a word of caution is in order. These comparisons are theoretical and based on assumptions. In this and all specific analyses the assumptions must be carefully analyzed before energy data is presented for management decision.

MODEL FINISHING LINE

As an example of what a typical paint finishing operation for metals involves, Figure 1 shows an electrocoating line. First there is the cleaning and phosphating of the metal. This requires electrical energy for pumps and heat for the detergent and phosphating baths. Then the phosphated product typically goes through a dry-off oven. However, it has now been demonstrated that this stage is not needed for electrocoating. In some instances it is not necessary for water-borne spray systems also. Next, the dried ware enters the paint application area. Requirements for this differ depending on the type of finishing system used. Then the coating must be baked. Again, major differences in energy requirements are observed due to the different types of finishing systems.

The choice of a model line is important because, as Hutchinson[1] strongly stresses, energy calculations are only as good as the assumptions made about the weight of metal coated per hour, the size of spray booths, the panel insulating factor (U) for the oven walls, etc. Hutchinson[1] has depicted a well-defined model system that considers most areas of electrical and heat energy as well as the energy of pretreatment. For reference purposes we will base our calculations on Hutchinson's model finishing line with the exceptions of the cleaning-phosphating stages and spray booth exhausts.

Table I contains an outline of the model system.

COATINGS

Table II lists the coatings that will be compared. For each

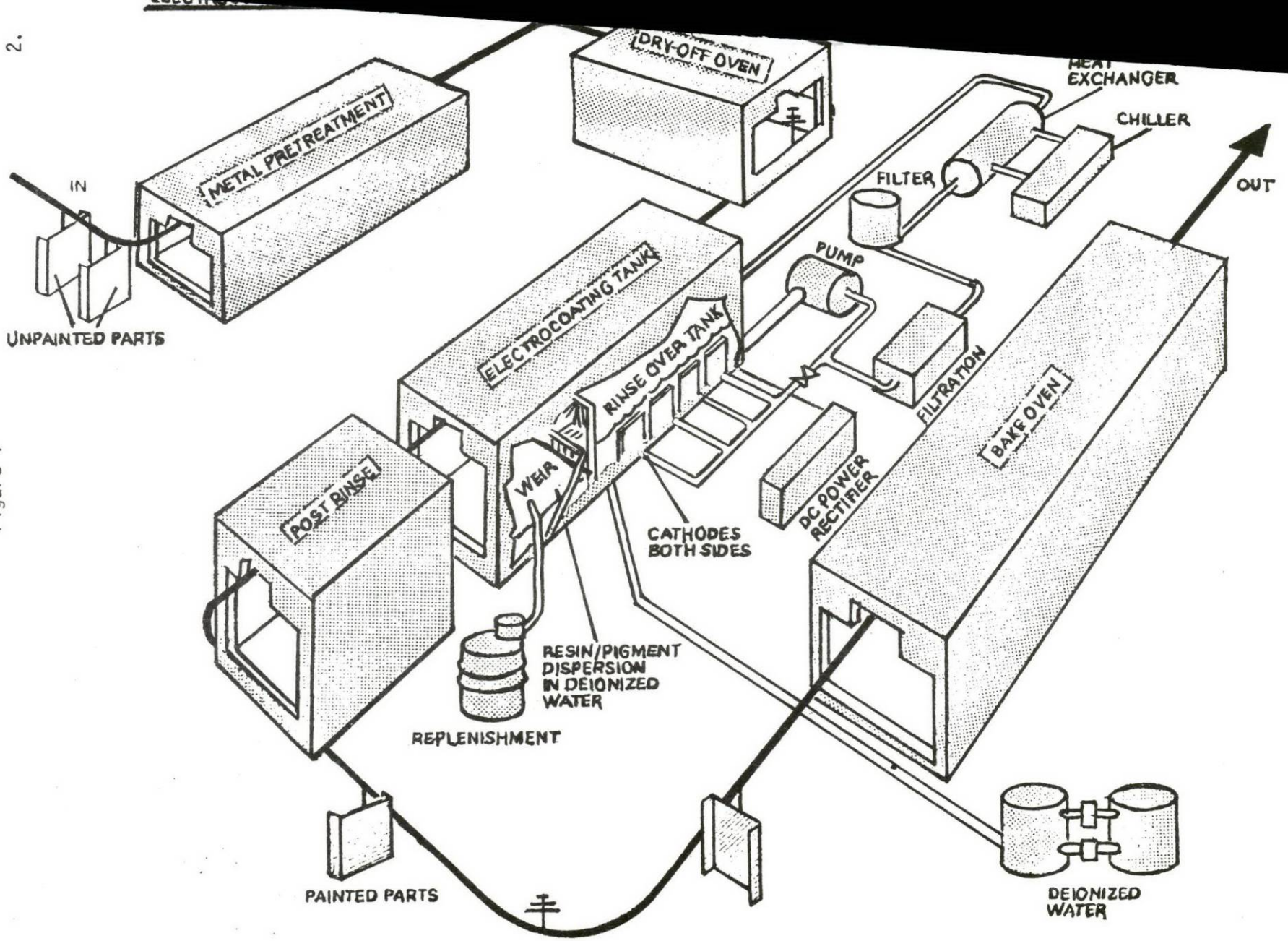
METAL PRETREATMENT
DRY-OFF OVEN
HEAT EXCHANGER
CHILLER
FILTER
OUT
IN
UNPAINTED PARTS
PUMP
ELECTROCOATING TANK
RINSE OVER TANK
FILTRATION
BAKE OVEN
POST RINSE
WEIR
DC POWER RECTIFIER
CATHODES BOTH SIDES
RESIN/PIGMENT DISPERSION IN DEIONIZED WATER
REPLENISHMENT
PAINTED PARTS
DEIONIZED WATER

Figure 1

TABLE I

MODEL FINISHING LINE

WARE:	24 gauge cold rolled steel 80" L X 36" W X 3" thick
COATING RATE:	18,000 square feet/hour
WEIGHT - METAL:	Ware - 9,000 lb./hour Conveyor - 6 lbs./lin. ft. Hanger, trolley, clevis - 10 lbs.
CLEAN AND PRETREAT:	7 stage iron phosphate
DRY-OFF OVEN:	300°F air temperature
SPRAY APPLICATION:	1 manual booth 25' L, 240 square feet 2 Ransburg loops
BAKE OVENS:	Spray applied - 32,000 cubic feet, 30 fpm Electrocoat - 12,500 cubic feet, 10 fpm 20 minutes baking time
FILM THICKNESS:	1 mil dry

TABLE II

COATING SYSTEMS

COATING SYSTEM	VOLUME SOLIDS %	GAL./HR. LIQUID EXHAUSTED SOLVENT	WATER
Solvent-borne	28	28.8	
Water-borne	28	5.8	23.0
High Solids	60	7.5	
Powder	96	0.5	
Electrocoat	95	0.2	0.4

is given realistic values of percentage solids by volume. 18,000 square feet/hour of metal will be painted to a thickness of 1 mil which means that 11.2 solid gallons per hour will be applied. Most of the volatile portion of the coating will have to be exhausted in the bake oven. Values for gal/hour exhausted are also given in Table II.

All of the coatings will be compared at three twenty minute bakes of 375°F, 300°F, and 180°F. These temperatures are representative of what is available on the market or in the advanced stages of development (180°F).

It should be noted that a two-package urethane has been omitted from the table. For energy comparison purposes this requires almost the same amount of energy as the high solids paint baked at 180°F. Note also that electrocoat paints are applied from a bath containing 6-20% solids but that the paint that goes on the ware and into the oven is approximately 95% non-volatile.

ENERGY CALCULATIONS

The basic energy calculations required for this study are those for heat loss on spraying, horsepower conversions for pumps and fans, heating metal and intake air in ovens, exhaust for products of combustion of natural gas and water evaporation. Table III contains the relevant equations and Table IV contains explanations of the numbers and abbreviations used in Table III and other necessary conversion factors.

ENERGY ANALYSIS

In the model system we assume that the cleaning and pretreating operation will be the same for all paint systems. Table V contains the energy requirements.

For all paints with the exception of electrocoat, the parts will have to go through a dry-off oven. This oven is 150' L, 10'H, 6' W, with an air temperature of 300°F and a metal temperature of 200°F. It is designed to evaporate 5.5 gal./hr. of water and make-up air required will be 5000 scf/gal. The parts will travel on a conveyor hung 48" apart at a line speed of 30 fpm. Table VI shows the energy requirements.

For spray application a modern energy-saving system will be used for solvent-borne, water borne, and high solids. This will consist of two Ransburg disc loops and one manual spray booth 25 feet long, with 240 square feet of exhaust area. Depending on the coating, different air velocities will be used in the spray booth with 100 fpm being the lowest allowable. The energy requirements are consist of heat needed for the make-up air and electrical energy for fan motors. For powder coatings the make-up air comes from the plant, is filtered and returned to the plant. Thus, virtually no energy is needed to heat the make-up air. The electrocoat tank requires 1000 SCFM ventillation. Table VII has energy values for these exhaust requirements.

TABLE III

ENERGY EQUATIONS

PRETREATMENT

BTU/HR. = (gpm) (60) (8.34) (°F Drop)

INTAKE AIR FOR SPRAY BOOTHS AND OVENS

BTU/HR. = (SCFM) (60) (.075) (.24) (TE-TI)

OTHER OVEN HEAT INPUT

Metal: BTU/HR. = (lb./hr.) (.12) (TE-TI)

Loss Through Walls: BTU/HR. = (A) (U) (TE-TI)

INTAKE AIR FOR PRODUCTS OF COMBUSTION

$$SCFM = \frac{\text{Burner rating (BTU/HR.)}}{(60)\ (95)}$$

TABLE IV

ABBREVIATIONS AND CONVERSION FACTORS

gpm	= gallons per minute
60	= 60 minutes/hour
8.34	= 8.34 lbs./gal. water
°F-Drop	= temperature drop due to spraying liquid
SCFM	= cubic feet of air per minute at 70°F
.075	= .075 lbs. of air per scf
.24	= .24 BTU per lbs. air per °F
TE	= exit or exhaust temperature
TI	= input or intake temperature
.12	= .12 BTU per lbs. steel per °F
A	= area
U	= .3 BTU/hr. - square feet - °F = panel loss factor
95	= BTU per cubic foot natural gas-air mixture
urner rating	= BTU/hr. capacity of oven
hp (horsepower)	= .746 KW (kilowatt)
KW	= 3,415 BTU
ter	= heat of vaporization 970 BTU/lb.
ter	= heat capacity 1 BTU/lb.

TABLE V

SPRAY CLEAN AND PHOSPHATE ENERGY

STAGE	TEMP. (°F)	TEMP. DROP °F	gpm	hp	BTU/hr.
Cleaner	180	8	775	20	3,102,480
Rinse	160	6	550	15	1,651,320
Cleaner	160	6	775	20	2,326,860
Rinse	160	6	550	15	1,651,320
Phosphate	160	6	625	20	1,876,500
Rinse	---	-	375	10	----------
Post Treatment	---	-	200	5	----------
D I Rinse	---	-	125	3	----------
					10,608,480

TABLE VI

DRY-OFF OVEN ENERGY

Ware (9,000 lbs.)	140,400
Conveyor (10,800 lbs.)	168,480
Hangers (4,500 lbs.)	70,200
Make-up air	123,750
Through walls	331,200
Evaporation	55,045
	889,075

TABLE VII

SPRAY APPLICATION REQUIREMENTS

COATING SYSTEM	SPRAY FPM	BOOTH SCFM	LOOP SCFM	BTU/hr.
Solvent	150	36,000	10,000	993,600
Water	125	30,000	10,000	864,000
High Solids	100	24,000	10,000	734,400
Powder	---	------	------	-------
Electrocoat	---	1,000	------	21,600

BAKE OVENS

For most finishing processes the energy used in baking is second in magnitude only to the cleaning and phosphating stage. In essence, the coated metal part, the trolley and clevis, the hanger and conveyor chain must be heated from room temperature to temperature as high as 375°F. This presents a problem when electrocoating is compared to spray applied systems since parts can be hung closer together (16 inch center) with the former because flash-off time is not required between spray applications. Thus the electrocoat oven can be smaller and requires less heat for the metal conveyor and less heat will be lost through the oven walls. Advocates of powder coating and high solids claim that it is unfair to use a smaller oven for electrocoat in a theoretical treatment. This model system will use two ovens. For comparisons using only one oven, the energy used for the powder coating bake oven can be substituted for the values given for electrocoat.

For the spray applied coatings the oven is 80' L, 40' W, 10' H with 600 feet of conveyor chain inside to accommodate a line moving at 30 fpm for twenty minutes. This oven would have an estimated burner rating of 3,500,000 BTU/hrs. and 8800 square feet of surface are

The electrocoat oven is 50' L, 25' W, 10' H with 200 feet of conveyor inside to accommodate a line moving at 10 fpm for twenty minutes. The estimated burner rating is 2,000,000 BTU/hr.

In one hour each oven will process 9000 lbs. of ware, 4,500 lbs. of hangers. The electrocoat oven will heat 17,100 lbs. of conveyor; the spray oven 24,300 lbs.

Intake make-up air requirements are 10,000 scf/gal. for solvent[5] an estimated 5,000 scf/gal. for water. Since there is such a small amount of liquid evaporated from electrocoat and powder coating, the bulk of the make-up air requirements must be caluculated from product of combustion equation using the oven burner rating.[5] Values of liquid exhausted for each coating system are listed in Table II.

For purposes of estimating blower capacity it must be realized that at elevated temperatures the make-up air expands by a factor equal to the ratio of the absolute temperatures of the exhaust gasse over the temperature of make-up air (50°F). Table VIII gives the exhaust capacities at different temperatures. Note that heat energy caluculations are only dependent on SCFM

Tables IX, X, and XI show heat energy requirements for the five different systems at 375°F, 300°F, and 180°F respectively.

ELECTRICAL ENERGY

With the exception of the phosphating stage the values for electrical energy are taken from Hutchinson.[1] These are shown in Table XII. Aspects of electrical energy could be more detailed as this model is fitted to actual installations. Note that the conve system for the spray applied systems is 2,200 feet long and requir two 50 hp motors. For the electrocoat line the total length of conveyor is 600 feet requiring one 50 hp drive.

TABLE VIII

EXHAUST VOLUME VS. TEMPERATURE

TEMPERATURE °F	70°	375°	300°	180°
EXPANSION FACTOR	----	1.64	1.49	1.25
SYSTEM	SCFM	CFM	CFM	CFM
Solvent	4,800	7,872	7,152	6,000
Water	2,883	4,730	4,296	3,604
High Solids	1,250	2,050	1,863	1,563
Powder	697	1,144	1,039	872
Electrocoat	418	685	622	522

TABLE IX

BAKE OVEN - 375°F

BTU/hr.

COATING SYSTEM	METAL AND WALLS	EXHAUST AND WATER EVAP.	TOTAL
Solvent	1,694,580	1,684,800	3,379,380
Water	1,694,580	1,256,621	2,951,201
High Solids	1,694,580	438,750	2,133,330
Powder	1,694,580	244,764	1,939,344
Electrocoat	991,860	150,853	1,142,713

TABLE X

BAKE OVEN - 300°F

BTU/hr.

COATING SYSTEM	METAL AND WALLS	EXHAUST AND WATER EVAP.	TOTAL
Solvent	1,277,880	1,296,000	2,573,880
Water	1,277,880	1,008,684	2,286,564
High Solids	1,277,880	337,500	1,615,380
Powder	1,277,880	188,280	1,466,160
Electrocoat	747,960	116,769	864,729

TABLE XI

BAKE OVEN - 180°F

BTU/hr.

COATING SYSTEM	METAL AND WALLS	EXHAUST AND WATER EVAP.	TOTAL
Solvent	611,160	673,920	1,285,080
Water	611,160	425,920	1,037,080
High Solids	611,160	175,500	786,660
Powder	611,160	97,906	709,066
Electrocoat	357,720	59,007	416,727

TABLE XII

ELECTRICAL ENERGY

KW

	LIQUID SPRAY	ELECTROCOATING	POWDER
Pumps (pretreatment)	80.6	80.6	80.6
Blowers - dry-off	9.0	----	9.0
Spray booth	17.4	----	2.0
Blowers - bake	44.8	22.4	44.8
Conveyor drive	74.5	37.3	74.5
Electrocoating[6]	----	252.9	----
TOTAL KW	226.3	393.2	210.9
TOTAL BTU/hr.	772,815	1,342,778	720,224

TABLE XIII

ENERGY SUMMARY

SYSTEM	SOLVENT	WATER	HIGH SOLIDS	POWDER	ELECTROCOAT
Pretreat	10,608,480	10,608,480	10,608,480	10,608,480	10,608,480
Dry-off	889,075	889,075	889,075	889,075	----------
Application	993,600	864,000	734,400	-------	21,600
lectrical	772,815	772,815	772,815	720,224	1,342,778
75°F bake	3,379,380	2,951,201	2,133,330	1,939,344	1,142,713
00°F bake	2,573,880	2,286,564	1,615,380	1,466,160	864,729
0°F bake	1,285,080	1,037,080	786,660	709,066	416,727

TABLE XIV

TOTAL ENERGY COMPARISON

EM	SOLVENT	WATER	HIGH SOLIDS	POWDER	ELECTROCOAT
F	16,643,350	16,085,571	15,138,100	14,157,123	13,255,971
F	15,837,850	15,420,934	14,620,150	13,683,939	12,977,987
	14,549,050	14,171,450	13,791,430	12,926,845	12,529,985

DISCUSSION

Table XIII contains the energy summaries and Table XIV total energy comparisons.

Are the energy comparisons of Table XIV realistic in terms of bake temperatures? What bakes are currently being used and what bakes are possible? The answers to these questions depend, of course, on the performance requirements of the paints and no answer can be given without qualification. Generally, the consensus is that paint qualities vary considerably with bake temperatures in solvent-borne and water-borne technology. There are, however, paints available that are baked in the 180°F to 375°F range as well as air dried.

High solids coatings generally are baked in the 300°F to 375°F range with the lower bake of 180°F limited to two-part systems at present.

A bake of 180°F is not possible with powder coatings. Current products are being baked in the 300°F to 375°F range with 275°F being feasible in the future.

Electrocoatings are generally baked in the 300°-400°F range with high performance coatings in the higher ranges. Coming on the market now are electrocoat paints with good performance that bake at 180°F and, for some applications, there is air dry electrocoat.

What is obvious from the table is that for a given bake temperatu going to lower hydrocarbon solvent content in a coating will save energy.

What is also obvious is that the bulk of energy in the organic finishing process is used for cleaning and phosphating. Thus, it seems logical to direct efforts to reducing the amount of energy in this step. Two approaches can be taken. One, by coatings manufactur is to develop coatings that will perform over poorer substrates or those pretreated at lower temperatures. The other approach is for th manufacturers of cleaning and phosphating products to develop lower temperature systems. There is presently in use a cleaning and iron phosphating process in which the maximum line temperature is 110°F. Using such a process in our model system would only require 16% of the pretreatment energy. Hopefully, this new low temperature pre-treatment will have more widespread use in the future.

It must be pointed out that elimination of the dry-off oven gives electrocoating an energy savings advantage. This is also being done with more water-borne coatings. For powder coatings there is a big energy savings in eliminating the heating of the make-up air in spray booths. This may be offset by the need for mo precise control of humidity and temperature.

CONCLUSION

In summary, this study has shown energy requirements for some the modern coatings technologies. The calculations are generalize

and theoretical. The variations in metal ware, coating lines, equipment type and placement, plant size and location and many other factors, are infinite. More accurate energy comparisons can only be make when all the specifics are identified and the options quantified. In addition, there are many ways to conserve and re-use energy from even the most energy intensive processes. The comparisons made here show the trends and hopefully can serve as a starting point for more specific analyses of energy for organic industrial coatings.

REFERENCES

1. Hutchinson, C. O., Products Finishing Directory, pp. 66-81 (1976).

2. Gribble, P. R., and Martin, R. A., Glidden Coatings and Resins Industrial Review (1976).

3. McElroy, M. I., and Ramig, A., Coatings in Canada, pp. 50-52, (Sept./Oct., 1978).

4. Brushwell, W., American Paint and Coatings Journal, pp. 49-52 (January 8, 1979).

5. NFPA, Article 86A, Chapter 4, pp. 61-80.

6. Horton, M., Electrocoat '72 (1972).

K-5

Energy Conservation I
Session K

Energy Conservation Ventilation Practices In the Metal Finishing Industry

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ENERGY CONSERVATION IN VENTILATION

NTRODUCTION

here are two prime areas where energy can be conserved in the design and modification of any entilation system. These two prime areas are the total volume of air being exhausted as well as he static pressure drop that the exhaust system is working against. There are many different venues which can be investigated in order to reduce the total volume of air and these areas will e the subject of this presentation.

XTERNAL FACTORS

here are several possibilities that should be considered when examining any existing ventilation stem for energy conservation practices. The least costly modifications to an existing system equently have to do with external factors which are not necessarily a part of the overall system. ese areas include but are not limited to the following:

A) cross drafts
B) makeup air systems
C) velocity of work entry
D) velocity of work withdrawal
E) air patterns within the area
F) containment of fumes

following is a brief discussion of each of these areas including methods of analysis for current tions, alternatives which should be considered, and potential corrective steps that could be n.

A, Cross drafts – This particular area is probably the largest single factor in the inability for exhaust systems to operate at minimum volumes. Cross drafts caused by open windows, , movement of traffic and improper location of makeup air systems can usually be controlled he best cost/benefit ratio (lowest cost with the highest benefits) of any of the factors to be sed. The presence of cross drafts and their effects can many times be ascertained through observation of the fumes and vapor as they evolve from the process. Observations during rature extremes are critical to proper analysis. Observations should be made during the mmer months when perhaps doors and windows are kept open for ventilation purposes as are usually the most critical periods of the presence of cross drafts. However, during ex- cold weather, further observations should be made to determine if traffic movement, p air systems, or other factors are decreasing the efficiency of the ventilation system. bombs or similar devices can be employed during the observation periods to enhance the y and determine the presence of cross drafts. It is in the author's experience that pipe makes an ideal assistant in this regard. This is especially true since pipe smokers generally heavier thicker blanket of smoke which does not dissipate as readily as cigarette smoke efore is more useful in this regard. This type of assistance is of special benefit when the involved creates little or no visible fumes or vapors. If the observation reveals the of cross drafts, the sources of these cross drafts should be determined and eliminated. be accomplished by the positive sealing off of all openings, installation of curtains penings which cannot be sealed, or installation of curtains or other "walls" around ss which essentially isolates the process from the presence of these cross drafts. Once drafts have been eliminated or at the very minimum, reduced to an insignificant amount, duction in ventilation rates can be attempted. Caution should be used however, before n rates are reduced by any significant amounts. A significant reduction in ventilation create a violation of OSHA or other regulatory agency requirements.

ITEM B, Makeup air – The two most serious problems with this aspect of most ventilation systen is the lack of adequate makeup air facilities and the improper direction or location of the makeu air coming back into the room. Of these two, the inadequate supply of makeup air is by far th most prevalent problem and probably the least understood. One only has to close off all th openings in the room and turn on the makeup air system and then attempt to open a single wal in door to determine whether or not the makeup air system is adequate for the ventilatio system. If the door opens inward and tends to be pulled from the individual's hand who is ope ing the door, then there is an obvious lack of makeup air. If the door opens outward and it extremely difficult to open this door, then again the same conclusion can be drawn.

Most people believe that an inadequate makeup air supply is a economical way of reducing the total fuel bill. This is a fallacy. An inadequate supply of makeup air will generally cause t operators of the ventilation system to increase the ventilation rates in order to achieve sa working conditions around the process or as a visual improvement.

It is important to remember that for every cubic foot of air exhausted through a ventilati system, one cubic foot of air must be brought into the building. The cascading, multiplying effects that can be a direct result of inadequate makeup air are too numerous to mention he Suffice it to say that the first order of priority should be to achieve the best ventilation at lowest possible exhaust rate. Once this has been done then the makeup air system should sized to adequately handle the worst possible conditions during winter time operations.

Improper location of makeup air units or outlets can be observed in much the same fashion cross drafts are detected. Obviously, if it is merely the location of the discharge points from air makeup system, the movement or relocation of these discharge points to some other loca will be relatively inexpensive. However, if it is a complete makeup air system that is integ mounted in the roof, then the only solution may be the addition of a duct system. The disch points should be arranged so as to adequately control and direct the makeup air movement erly into the process area so that the exhaust system works at its maximum efficiency. Discu of the reasons behind this relocation and the analysis of the best location can be found u Section F "Containment of Fumes."

ITEM C, Velocity of work entry – This is a particular subject which can create some overa duction problems. The possibilities of reduction in ventilation requirements do make it v while mentioning. Frequently the velocity with which the work enters the bath determin rate of fume or gaseous evolution. The question of exact control over this velocity will d to a great extent on the nature of the operation i.e. hand, semi-automatic or automatic. hand operations, it would be up to the individual operator and his training and superv determine the ideal velocity at which the work should enter the bath to minimize fuming semi-automated lines and automated lines, the equipment program can sometimes be alt achieve the optimum results. Trial and error in this particular case is the only way of deter whether or not this is a viable method of minimizing the evolution of the gases and/or fu is suggested that the normal speed be used during observation periods immediately follo the minimum possible speed that can be achieved consistent with the equipment type and of operation. In this fashion, a rough determination can be made whether or not the s work entering will have any significant impact on the total amount of fumes and/or gase are evolved by the process during this stage of the operation. If there seems to be a sig reduction, then the speed of entry will have to be measured against the overall throug the line. The potential profit loss due to a slight reduction in the output level of the eq must be determined to ascertain if this is an acceptable route towards reduction in ve

ITEM D, Velocity of work withdrawal – The speed with which the work is withdrawn process normally has a direct bearing on the efficiency of the exhaust system particula

lateral exhaust hoods are employed. As the work passes the point in which the fumes are normally collected, the work itself interferes with the normal path of air entering the hoods. Frequently the rate at which the work is removed far surpasses the ability of the lateral exhaust hood to effectively remove the fumes evolving from the work at that moment. At the time of work withdrawal from the process bath, the amount of fumes and/or gases being evolved is frequently at the maximum, particularly when operations such as bright dipping and pickling are involved.

This particular area of study can prove to be extremely beneficial when attempting to minimize the total amount of exhaust air required in a system. Particular attention should be given during the periods of observation to the manner in which the fumes may evolve from the work as it passes any lateral exhaust pickup points. Detailed analysis of this crucial time should be coordinated with the comments made in the following section entitled "Containment of fumes" (Section F). Once again, it is suggested that observations include normal operations followed immediately by observations made with the work being withdrawn at the slowest possible speed from the bath. This will give the individual who is analyzing the situation an appropriate benchmark in order to effectively determine the magnitude of exhaust reduction that could be achieved if the speed of withdrawal is slowed appreciably.

TEM E, Air patterns within the area – In general combination with all of the above studies, me determination should be made to check the overall flow patterns of air within the general ea of the process. Ideally, all the airflow should be directed past the worker's stations toward e exhaust system. This study will be crucial to the effectiveness of any reduction in exhaust umes. It is suggested that the air patterns be examined in detail prior to any exhaust reduction and following any exhaust reduction. In this manner, the net effect on the overall air movent within the immediate area of the process can be verified to be in accordance with the best tilation practice – flow of air past the workers station towards the exhaust system. Obusly, the overall movement of air within the immediate area is closely related to the presence ross drafts and the position of makeup air supply discussed above.

M F, Containment of fumes – It is axiomatic in the design of a ventilation system that the es must be contained within the general area of the exhaust system for a period of time long gh for them to be captured completely by the exhaust system. Containment of the fumes take the form of completely enclosing the entire process (at its maximum) to the addition of ins, flanges, etc. which help to hold the fumes in the immediate area of the exhaust pickup s. Additions of walls and/or curtains in the center of a automatic plating machine or the of an in-line hand operation, frequently are beneficial to this overall containment. A l study should be made to determine if some type of roof structure immediately over the ss can be coupled with these curtains behind the exhaust system. This will serve to contain mes within the process area for a sufficient period of time so that the exhaust system can e them before they escape into the general room air. In several instances, a complete el" enclosing the entire operation has proven to be particularly effective in minimizing the mount of exhaust air required from a particular system. In reality, this "tunnel" means e system is completely enclosed in its own separate room and this room is treated as a te enclosed hood. If this can be accomplished without exposing the workers to excessive levels of the contaminants, then this particular method will achieve the greatest reduction ust volume. However, operator presence and accessibility to the process frequently negate e of approach as a viable alternative. Consequently, the enclosure of a system through of a "back wall" and "roof" may be the only approach to the containment of the fumes he exhaust area until they are removed by the exhaust system.

ficult within the scope of this paper to present all the possible alternatives and methods ing the total exhaust volume of a given system to effect an energy savings. The myriad of ns, types of equipment, and installation variables make this a practical impossibility. It

is hoped that the preceding comments will be sufficient to lead the operator to investigate the c vious areas to determine if a reduction in exhaust volume is possible in an existing operation in a new installation.

There may be some question as to the total value of energy savings that can be accomplish through this means. Presented below are a series of charts which indicate the savings which c be achieved for each 1700M^3/HR (1000 CFM) of exhaust air that is reduced in the overall e haust system provided means such as those outlined in this paper are followed. Note that fo large ventilation system, a reduction of several thousand M^3/HR is frequently possible. In ad tion to reducing the total flow of exhaust air, the static pressure of the system in an existi installation can also be reduced. This will also have an effect on the overall horsepower requi ments and electrical energy requirements for the system. For the purposes of this presentatio savings for each 1700M^3/HR (1000 CFM) on the electrical power requirements for the motor are presented without any regard to any reduction in the static pressure. We are prese ing this data with a range of electrical power costs as well as several cost levels for natural or fuel oil. The costs for natural gas or fuel oil were based on a relatively large user of th products in a major metropolitan center in the northeast. In general, most industries pay proximately $.01 per kw/hr for their electrical power. There are many small electroplaters report their cost to be as high as $0.046 per kw/hr. Obviously, savings in natural gas or fue should be tempered with the knowledge curtailment and/or shortage of supply will prob have a greater economic impact.

CHART NO. I

ELECTRICAL COST PER H.P/YR.

HRS. OF OPERATION FOR EXHAUST SYSTEM*	ELECTRICAL ENERGY COST, ¢/KW Hr 0.5	1.0	1.5	2.0	4.6
a 2,000 hrs	$ 7.46	14.92	22.38	29.84	68.63
b 4,800	17.90	35.81	53.71	71.62	164.73
c 6,240	23.28	46.55	69.83	93.10	214.13
d 8,736	$ 32.59	65.17	97.76	130.34	299.78

ASSUMPTION: Exhaust system is in operation only during periods when work is in process.

Based on 1 shift per day, 5 days per week, 50 weeks per year.
Based on 2 shifts per day, 6 days per week, 50 weeks per year.
Based on 3 shifts per day, 5 days per week, 52 weeks per year.
Based on 3 shifts per day, 7 days per week, 52 weeks per year.

CHART NO. II

OST SAVINGS FOR EACH 1700M^3/HR (1000 CFM) REDUCTION IN VENTILATION (BASED ON REDUCTION IN H.P. FOR FAN ONLY)**

OF OPERATION FOR XHAUST SYSTEM*	ELECTRICAL ENERGY COST, ¢/KW Hr 0.5	1.0	1.5	2.0	4.6
a 2,000 hrs	$ 6.71	13.43	20.14	26.86	61.78
b 4,800	16.11	32.23	48.34	64.48	148.30
c 6,240	20.95	41.90	62.85	83.79	192.72
d 8,736	29.33	58.65	87.98	117.31	269.81

gs range from 0.75 H.P/1700M^3/HR (1000 CFM) to 1.0 H.P/1700M^3/HR (1000 CFM) nding on mechanical efficiency of fan. Average will be approximately 0.90 H.P/1700M^3/HR) CFM).

MPTION: Exhaust system is in operation only during periods when work is in process.

on 1 shift per day, 5 days per week, 50 weeks per year.
on 2 shifts per day, 6 days per week, 50 weeks per year.
on 3 shifts per day, 5 days per week, 52 weeks per year.
on 3 shifts per day, 7 days per week, 52 weeks per year.

CHART NO. III

TOTAL COST SAVINGS INCLUDING NATURAL GAS FOR MAKEUP AIR UNIT

(FOR EACH 1700 M^3/HR (1000 CFM) REDUCTION IN VENTILATION SYSTEM REQUIREMENT)**

HOURS OF OPERATION FOR EXHAUST SYSTEM		ELECTRICAL ENERGY COST, ¢/KW HR 0.5	1.0	1.5	2.0	4.6
a 2,000	x	$ 36.75	50.19	63.61	77.05	146.89
	y	37.42	50.86	64.28	77.72	147.56
	z	41.42	54.86	68.28	81.72	151.56
b 4,800	x	78.89	111.13	143.35	175.63	343.27
	y	80.23	112.47	144.69	176.97	344.61
	z	88.22	130.46	152.68	184.96	352.60
c 6,240	x	114.70	156.60	198.60	240.38	458.24
	y	116.79	158.69	200.59	242.47	460.3
	z	129.96	171.16	213.06	254.94	472.8
d 8,736	x	160.58	219.22	277.88	336.54	641.5
	y	163.51	222.15	280.81	339.47	644.4
	z	180.96	239.60	298.26	356.92	661.9

** Kilojoules (K-calorie) (BTU/HR) = (0.67) (0.16) (0.635)M^3/HR D_{TD} (^oF)

= 1.14 (0.27) (1.08)CFM D_{TD} (^oF)

Where D_{TD} = Temperature differential for heating air assuming 11.1° C (20° F) average temperature rise required for 1/3 year to raise makeup air to 18.3° C (65° F) for factory air.

Assuming exhaust system is in operation only during periods when work is in process, therefo

a) Based on 1 shift per day, 5 days per week, 50 weeks per year.
b) Based on 2 shifts per day, 6 days per week, 50 weeks per year.
c) Based on 3 shifts per day, 5 days per week, 52 weeks per year.
d) Based on 3 shifts per day, 7 days per week, 52 weeks per year.

BASIS:

A) Based on the formula (**) listed above, it can be shown that approximately 22,800 kil (5440 K-calories) (21,600 BTU/HR) will be required to heat each 1700M^3/HR (1000 from 7.22° C (45°F) to 18.33° C (65° F) at 100% efficiency. The above costs are bas

1) 75% efficiency for natural gas
2) Natural gas costs of: x = $1.20
   y = $1.25
   z = $1.46
   per 28.3M^3 (1000 ft^3)
3) Natural gas having a heat value of 1055 kilojoules (252 Kg-calories) (1000 BTU) p 0.03M^3 (ft^3)

B) Fuel cost savings per hour for each 1700M^3/HR (1000 CFM) of exhaust rate reducti is therefore:
   $0.035 for x fuel cost ($1.20)
   $0.036 for y fuel cost ($1.25)
   $0.042 for z fuel cost ($1.46)

C) Above total cost reduction includes cost savings in ventilation system HP plus identi savings for HP in air makeup units plus fuel cost as outlined immediately above.

CHART NO. IV

TOTAL COST SAVINGS INCLUDING FUEL OIL FOR MAKEUP AIR UNIT

(FOR EACH 1700M^3/HR (1000 CFM) REDUCTION IN VENTILATION SYSTEM REQUIREMENT)**

HOURS OF OPERATION FOR EXHAUST SYSTEM		ELECTRICAL ENERGY COST, ¢/KW HR 0.5	1.0	1.5	2.0	4.6
a	x	$ 64.75	78.19	91.61	105.05	174.89
2,000	y	68.09	81.53	94.95	108.39	178.23
	z	72.09	85.53	98.95	112.39	182.23
b	x	155.42	187.66	219.88	252.16	419.80
4,800	y	163.42	195.66	227.88	260.16	427.80
	z	173.02	205.26	237.48	269.76	437.40
c	x	202.06	243.96	285.86	327.74	545.60
6,240	y	212.46	254.36	296.26	338.14	556.00
	z	224.94	266.84	308.74	350.62	568.48
d	x	282.88	341.52	400.18	458.84	763.84
8,736	y	297.44	356.08	414.74	473.40	778.40
	z	314.92	373.56	432.22	490.88	795.88

Kilojoules (K-calorie) (BTU/HR) = (0.67) (0.16) (0.635)M^3/HR D_{TD} (^{o}F)

or = 1.14 (0.27) (1.08) CFM D_{TD} (^{o}F)

re D_{TD} = Temperature differential for heating air assuming 11.1^o C (20° F) average temper- rise required for 1/3 year to raise makeup air to 18.3^o C (65° F) for factory air.

ming exhaust system is in operation only during periods when work is in process, therefore:

sed on 1 shift per day, 5 days per week, 50 weeks per year.
sed on 2 shifts per day, 6 days per week, 50 weeks per year.
sed on 3 shifts per day, 5 days per week, 52 weeks per year.
sed on 3 shifts per day, 7 days per week, 52 weeks per year.

:

ased on the formula (**) listed above, it can be shown that approximately 22,800 kilojoules 440 K-calories) (21,600 BTU/HR) will be required to heat each 1700M^3/HR (1,000 CFM) om 7.22^{o}C (45° F) to 18.33^{o}C (65°F) at 100% efficiency. The above costs are based on:

70% efficiency for fuel oil
Fuel oil costs of: x = $0.35
y = $0.37
z = $0.40

per 3.79 liters (U.S. gallon)

Fuel oil having a heat value of 147.671 kilojoules (35,277 K-calories) (140,000 BTU) per 3.79 liters (U.S. gallon)

cost savings per hour for each 1700M^3/HR (1000 CFM) of exhaust rate reduction is efore:
$0.077 for x fuel cost ($0.35)
$0.082 for y fuel cost ($0.37)
$0.088 for z fuel cost ($0.40)

e total cost reduction includes cost savings in ventilation system HP plus identical cost gs for HP in air makeup units plus fuel cost as outlined immediately above.

L-1

Research I
Session L

Some Property-Structure Relationships In Electrodeposits
AES Research Project #38

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ES Project 38

Some Property-Structure Relationships in Electrodeposits

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The unique properties of electrodeposits, brightness and a easing appearance, corrosion resistance, hardness and wear sistance, are to a large extent attained by incorporating into e plating solution small quantities of certain modifying chem- ls, the addition agents. The selection of the addition agents progressed from the classical "off the shelf" additives such tobacco juice and yellow dextrin, to the complex organic tures presently used. The random experimentation of the old- plater has been replaced by an organized selection procedure d on related structures, redox potentials and the presence in molecules of known effective radicals. Remarkable improve- and a great degree of control have been attained, but the tion of additives still remains basically empirical.

Foreign substances in the plating solution can also have ul effects. These substrates can be introduced accidentally, from the breakdown of the additives or other chemical ons. It becomes important then to understand the mechan- which the various foreign materials in the plating solu- xert such a powerful influence on the structure and proper- the deposit, particularly as in many cases these effects duced without any of the acting material being incorpor- to the deposit.

number of hypotheses have been proposed to explain the of the additives on the basis of chemical or electro-

chemical theory. But the properties affected are those of the metals themselves and should be explainable on the basis of metallurgical theory, i.e., the relationship between structure and properties. It is this aspect of the problem that the AES-sponsored research at Stevens has been investigating. The ultimate objective is to be able to control and optimize the desirable properties of electrodeposits on a scientific rather than a empirical basis.

The details of our findings have been, or are in the proce of being published in Plating and Surface Finishing. Briefly, the breakthrough which led to the understanding of how the prop ties of the initial deposits are determined was the discovery that deposition occurs by the formation and subsequent joining of tiny crystallites. These crystallites, which in nickel dep are of the order of 5-10 nm (about half a millionth of an inch are thus much smaller than the grain size of the so-called fi grained deposits. The crystallites can only be resolved by transmission electron microscopy.

From the results of examinations of the way these crysta lites grow and join to form a continuous film, we can explai for example, the origin of internal stress in electrodeposit It has been shown that at the beginning of nickel plating wh the internal stresses have their highest tensile values, the are two determining factors. The first of these is the mism in the spacing of the atoms in the plate and the basis meta As long as the deposit copies the structure of the substrat which seems to be important in obtaining good adhesion, thi stress will exist. There is nothing we can do to lower the

ther than to alter the plate, or the substrate, or to intersperse layer of another metal with less mismatch. Fortunately, this tress falls off rapidly with thickness. The second factor which etermines the stress is the way in which the crystallites join. hen they are pulled together by surface tension before the spaces etween them are completely filled, a tensile stress develops. is stress can be controlled to some degree by the plating con- tions and additives. Crystallite joining becomes the main urce of stress as the thickness increases. Using a theoretical proach, it has been possible to calculate expected stress values, ch were in good agreement with the experimentally determined s. The mimimum thickness at which this second factor becomes inant is about 50 nm (a few millionths of an inch). At greater cknesses, additives and plating conditions can be used to con- stress by impeding the coalescence of the crystallites so the spaces between them have more time to be filled. Saccha- works this way in the initial stages of nickel plating. Studies his type with other additives could very well elucidate the ionship of structure to performance and permit the selection ress-relieving addition agents on a more scientific basis. The mechanical properties of thin deposits and probably also r ones are also greatly affected by crystllite formation alescence. When the crystallites cannot align themselves n perfectly, defects known as dislocations develop. These ations play a dominant role in the plastic deformation of In general, the more dislocations there are present, rer the ductility and the higher the yield strength and

hardness of the plated metal. Proper application of the informa tion gained on the effect of additives on crystallite formation and coalescence should present better control of the mechanical properties of the deposits. Since the mechanical properties als affect cracking and adhesion, control by proper use of additives should improve corrosion resistance as well. The presence and distribution of porosity also affect the corrosion resistance. Studies to date indicate that the spacing of pores is essential the same as the size of the crystallites. Therefore, the porosi is also related to improper crystallite joining.

In related work, not sponosred by AES, it has been found that the coalescence of crystallites determines the path of fracture and its rate of propagation. This find can be extend to explain why plated deposits will sometimes exhibit low duct ity, high hardness, but not necessarily high strength.

Currently, the AES-sponsored studies have progressed to deposits of commercial thicknesses. Results to date indicate crystallite formation and coalescence takes place not only at the onset of plating, but throughout the deposit. The conce discussed here are apparently generally applicable to commer deposits. Related studies, not sponsored by AES, indicate t the principles can be extended to metals other than nickel a

Although it has not been extensively investigated yet, is ample evidence that the negative ions used in the platin tion, e.g., the sulfate or sulfamate ions for nickel and th cyanide ions for gold also affect crystallite formation and coalescence. Information found on these affects should he optimize the properties of plating solutions.

It is becoming increasingly clear that crystallite formation
d coalescence have a profound effect on the nature of the plated
posit, and can be controlled by certain additives and possibly
rmfully affected by other foreign materials in the plating solu-
on. Investigation of the influence and activity of additives
crystallite formation as a function of the structure of the
ditive should be of tremendous importance in improving the
trol of the plating process.

L-2

Research I
Session L

Immersion Plating on Aluminum
AES Research Project #41

Dr. D. S. Lashmore
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ABSTRACT

Immersion Coatings on Aluminum: Part I, Morphology

The morphologies of both zinc and tin immersion deposits on aluminum and its alloys are presented. As was previously found on pure aluminum, zinc was found to form epitaxial deposits on alloys. Similarities between the zincate and stannate processes are shown to exist; in particular, studies of deposits on single crystal spheres show that the same crystallographic orientations are active in both systems. Comparisons between zinc deposits produced from solutions containing ferric chloride and Rochelle salt and deposits from the same solution without these additions indicate that a fundamental role is played by ferric chloride, both in the morphologies of the deposit and in the number of nuclei observed.

Immersion Coatings on Aluminum: Part I, Morphology

NTRODUCTION

In order to electroplate onto aluminum, it is standard practice to irst apply an immersion deposit of either zinc or tin. Of these, zinc eems to be the more common (1), even though the stannate process is aining acceptance (2). The function of these immersion coatings is the eplacement of the natural oxide, always present on aluminum, irre- ective of the cleaning process, with an oxide-free metal onto which bsequent metallic coatings could be adherent. Of the two processes tioned above, the zincate process better lends itself to investi- ion, not only because it is widely used but also because its simple position and non-proprietary nature, facilitate the understanding and note the reproduction of results of different investigators. As be shown below, close parallels exist between these two processes, hat a study of one process aids the understanding of the other. The te process has been reviewed by a number of investigators (3-9) and scribed by an ASTM standard (10), so a review of the previous work not be presented here.

In this study, two types of zincate solutions are considered. on I consists of 525 g/l sodium hydroxide, solution II has in on 1.0 g/l ferric chloride and 10 g/l Rochelle salts. The overall on which takes place in solution I can be represented by

$$_2ZnO_2 + \underline{2Al} + 2H_2O \rightarrow 2NaAlO_2 + \underline{3Zn} + 4NaOH$$

The actual form of the zincate ion in solution is probably Zn(OH (11), so that the specific reactions can be written as:

(2) Anodic: $Al + 3OH^- \rightarrow Al(OH)_3 + 3e^-$

$Al(OH)_3 \rightarrow AlO_2^- + H_2O + H^+$

Cathodic: $Zn(OH)_4^{2-} \rightarrow Zn^{2+} + 4OH^-$

$Zn^{2+} + 2e^- \rightarrow Zn$

$H^+ + e^- \rightarrow H \rightarrow 1/2\ H_2(g)$

Even though equation (1) has been experimentally verified only solutions of type I (12), the implication of the literature is that must also hold for solutions of type II. This is not the case as sh by weight gain - loss measurements in figure 1. These measurements made by weighing a specimen before and after zincating, stripping t zinc in a solution of 50% nitirc acid, then reweighing. The specim were prepared from metallographically polished 99.99% aluminum zinc for 1 minute according to the appropriate ASTM standard (10). Fro slope of the solution II curve (3.7), it can be inferred that, for one zinc atom deposited on the surface, nine aluminum atoms must h been dissolved. Therefore, it can be concluded that the overall r for solutions containing ferric chloride and Rochelle salt is mor complex than that indicated by equation (1).

It is not only the reactions involved which are not understo also the morphology of the zinc itself. Since the adhesion of su sequently deposited layers depends critically upon the nature of interface, as a first step in this investigation, the structure zinc and its relationship to the substrate orientation was deter To supplement these results, futher studies were undertaken on aluminum single crystal sphere.

ROCEDURE

The morphology of the zinc deposits was investigated by electron icroscopy of zincated thin aluminum foils. The 3mm diameter specimens ere prepared by polishing 99.999% aluminum to electron transparency sing a twin jet electropolishing device. The electrolyte used was a lution of 20% perchloric acid and methanol cooled to 240°K and erated at about 22 volts. Alloy specimens were prepared from spark t foils about 0.3 mm thick, which were then thinned to electron trans- ency using the same procedure as with pure aluminum. The specimens e examined in a transmission electron microscope equipped with an icontamination stage and a double tilt specimen holder.

The zincate solution was applied to only one side of the specimen. deposition times were for one minute unless otherwise stated.

A single crystal sphere was prepared by appropriately machining a single crystal of 99.99% aluminum. It then was chemically polished solution of 94% phosphoric acid, 6% nitric acid at 373°K until the sive cold work induced by the maching process was removed. The ction of the crystal was determined by first etching in 15% NaOH amining the perfection of the etch patterns and finally by taking ack reflection x-ray patterns of the various orientation and then ing the perfection of the resultant spot patterns.

number of differences in deposits formed from two kinds of ns were repeatedly observed. These differences are illustrated rect comparison between TEM micrographs taken under identical

conditions, of zinc coated substrates both of the (100) orientation. seen in figures 2a and 2b, a number of differences are immediately apparent. In 1a, deposits grown from solution I exhibit a number of quite long rectangular crystallites, the presence of large numbers of extremely small crystallites and an absence of the larger rectangular crystallites. As shown in figure 1b, deposits formed from solution I contain none of the extremely small crystallites of 2 fold symmetry. Perhaps equally important, few of the crystallites of 6 fold symmetry are electron transparent, whereas very many of those formed from solu I are, implying a more rapid growth along the c-axis in deposits for from solution II. In deposits from both solutions, one crystal grow on another can be observed. Some of these results are summarized in distribution of morphologies, estimated from the micrographs of figu as shown in table 1. The very large number of small crystallites o

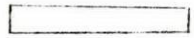
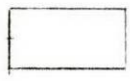
Morphology	Solution I density No/M^2	Solution II density No/M^2
	$4x10^{11}$	$9x10^{9}$
	$9x10^{11}$	$7x10^{9}$
	$2x10^{10}$	$3x10^{10}$
	$8x10^{10}$	$3x10^{11}$
	$5x10^{10}$	$9x10^{9}$
	$4x10^{10}$	$6x10^{10}$
	$1x10^{14}$	~ 0
	$2x10^{11}$	$2x10^{11}$

Table 1: The numb of crystallites of given morpholog square meter. No very large number small crystallite duced from soluti

in deposits from solution I ($1x10^{14}$) implies a rapid heterogened nucleation of the zinc on the aluminum. In solution II, these stallites are essentially absent, implying a more uniform nucle growth process.

A previous study (13) of the orientation relationships of the zinc crystallites with the substrate revealed that the zinc is epitaxial on all of the aluminum principal planes and, moreover, that under these zinc crystallites a thin semicontinuous zinc film exists upon which the larger crystallites grow. The zinc epitaxial relationships were summarized (13) as Al: (100)[100]//Zn(0001)<1120> Al:(110)[111]//Zn(001) 2110> and Al: (111)[110]//Zn(0001)<1120>.

The study reported above was only on pure aluminum; however, the orientation relationships between the substrate and the coating occur as ll in alloys. An example of a typical zincated alloy 6061-T6 is shown the bright field-dark field TEM micrographs in figure 3 abc, with the responding selected area diffraction pattern shown in 3c. Note that y aluminum reflections are present in the selected area diffraction tern and that the zinc crystallites show up in bright contrast in dark field micrographs. The similiarity of this diffraction ern with the pure aluminum pattern of the same orientation (13) ies that the same epitaxial relationships exist. The morphology of leposits is much different, as a comparison between figure 2 and 3 show. The number of separate crystallites is far less on the , even though their habit (6 fold symmetry, 3 fold symmetry, etc.) ns the same. Similiar studies on other alloys seem to confirm that ientation relationship found on pure aluminum also holds for the . Electrochemical effects in the vicinity of inclusions and concentrations, say, at grain boundaries have an important influence sit morphology. For example, a specimen of 97% aluminum whose le impurities are magnesium and iron was metallurgically polished

then zincated in solution II and, as can be seen in figure 4a, the zi crystallites form predominantly at the grain boundaries. On pure aluminum (99.999%) this behavior is not observed. The same alloy following a stannate treatment is shown in figure 4b. The morphology the tin deposit zones on either side of the grain boundary which are electrochemically different from the material in the grain interior.

It would seem from the appearance of the above micrographs that stannate process operates somewhat differently than does the zincate process. The procedure recommended by the supplier (14) is also different. Namely, following a similiar cleaning step, the article be coated is first immersed in the proprietary alkaline tin solution where the aluminum oxide is thought to be stripped off; however, unl the zincate process, the article is then transferred, without rinsi to a bronze electroplating electrolyte, with electrical contact mad prior to entering the solution. A TEM specimen subjected to this treatment with a 5 second (3.2 Amps/dm^2) bronze strike is shown in figure 5a & b. The bronze crystallites, if left in the bronze ele lyte, will coalesce to form a continuous film. The preferred orie tion of the bronze is clearly apparent in the selected area diffra pattern of 5b. However, if the specimen is rinsed following the t immersion, a tin coating is repeatedly observed, as shown in the micrographs of figure 6. In fact, adhesion measurements, to be r in part II of this paper, indicate that on pure aluminum no delet effects are introduced by rinsing following the tin immersion; ho on alloys, the adhesion is significantly reduced. These results

hat, at least on pure aluminum, a thin coating of tin exists underneath
he bronze. Tin is clearly present on an etched specimen of pure aluminum
9.99%), as shown in the SEM micrograph of figure 7. Thus, it can be
ncluded that tin is deposited by immersion onto pure aluminum in much
e same way as zinc.

Both the stannate and zincate processes require the dissolution of
uminum. This dissolution is not a random process, but rather, occurs
some crystallographic plans at a faster rate than on others. In
er to further investigate the effects of crystallography on the
ersion deposition process, a single crystal sphere was fabricated in
manner described above. The advantages of investigating a coated
re become apparent when it is realized that all planes are tangent
he surface at one point or another.

The etch patterns caused by aluminum removal in either the zincate
e stannate solutions are exactly the same, and, as might be expected,
spond to the etching in a caustic solution, as has been confirmed
nerous experiments. Optical micrographs of a 25mm sphere, which
ncated for one minute, rinsed, then dipped in a 50% nitric acid
on (to improve the contrast of the etch pattern for the photo-
, are shown in figures 8a of a (100) plane, 8b of a (110) plane,
of a (111) plane. Note that the etching seems to be most severe
e high index planes surrounding the (100) and extends along [110]
The nitric acid dip does not change the etch pattern. The zinc
on the sphere was apparently too thin to allow Laue back re-
patterns to be made, so that the TEM had to be relied upon to
he orientation relationships. (13)

The process known as the double zincate is quite commonly used, it is reported to result in improved adhesion (8). This progress is simply a zincate immersion, a rinse, a nitric acid dip to strip off t surface zinc, a rinse, followed by a final zinc immersion. Specimens subjected to various steps of the double zincate treatment were exami using a nuclear microanalysis technique. In this technique, 1.8 MeV neutrons were used to induce nuclear reactions on the above specimen The reaction products are scattered at specific energies and angles characteristic of the material on the surface. The sensitivity of t technique can be as high as 10^{12} atoms/cm^2, the results being indep of the chemical or physical binding of the nuclei in the matrix. T results of these experiments are summarized in table II. The zinca solution used in these specimens contained ferric chloride and Roch salts, so that it is not too surprising that iron (from the ferric chloride) was deposited along with the zinc. In specimens subject a single zincate treatment, there was so much iron on the surface the iron and zinc peaks overlapped and so a quantitative determina could not be made. After the zinc was stripped in a solution of nitric acid for 30 seconds and then throughly rinsed, both zinc a still were detected on the surface in about equal quantities of a two monolayers. Tin was found on the surface on specimens subje a proprietory stannate immersion treatment (14) in a quantity of 15 monolayers. From these results it can be concluded that iron an important role in the deposition process and, moreover, that surface alloy on the aluminum is found that is comparatively in

n nitric acid. These conclusions are supported by transmission
lectron microscopy of specimens subjected to a double zincate treatment
n solution II. As is seen in figure 9, a number of rectangular regions
xist which, in some cases, protrude into the hole in the specimen,
ndicating a lack of solubility in the acid solution.

ISCUSSION AND CONCLUSIONS

It has been shown above that the substrate orientation plays an
portant role in the zincate process. Not only is the dissolution of
aluminum in the caustic zincate solution a sensitive function of the
stallographic orientation of the substrate, but, further, the zinc
elf forms epitaxial deposits, at least on the principal planes. In
ually every description of a process for the plating on aluminum, a
tic cleaning step has been found necessary. This work has demon-
ted the necessity for this step. it indicates that the adhesion of
inc to the substrate will be maximized when a single epitaxial film
s the surface. The highly deformed surface usually present on most
ials subjected to mechanical polishing, mechining, etc., known as
lby layer (15), interfers with any epitaxial phenanoma. In addition
s, the Bilby layer would be expected to dissolve very rapidly,
d to crystallographic material, permitting a rapid thick zinc
to form, so that its removal is advantageous on both grounds.
, if the etching is allowed to proceed too long, the adhesion
equently deposited layers is reduced (as discussed in part II
paper). The reason for this drop off in adhesion can be
d with the aid of figure 7 abc. The etching of crystallographic
luminum substrates is a selective phenoma, that is, the most

active material is removed first, so when an over-etched specimen is immersed in the zincate solution, the reaction will be, of necessity much slower than on specimens which are not etched. If allowance is made for this in the deposition time, then, most likely, the coverage will be incomplete. In light of these observations, it would seem th rather than using a caustic etch cleaner, it would be more desireable devise an electro or chemical polish that would remove material more uniformily.

An in-depth study of immersion deposits on alloys has not yet b undertaken. However, preliminary studies indicate that the structur relations found on pure aluminum (13) will also hold for alloys, wit the thickness and morphology determined by the electrochemical inho genities in the alloy material.

ACKNOWLEDGEMENTS

I would like to thank both the Aluminum Association and the Am Electroplaters' Society for their financial support of this progra am also grateful to Mr. Fielding Ogburn and to Dr. Jerome Kruger f Critical review of the manuscript. Special thanks are due to Prof B. Agius of the Groupe de Physique des Solides de l'Ecole Normale Superieure, for the nuclear reaction analysis.

able II: Helium Backscatter Data from 99.99% Aluminum Substrates Processed in Various Ways.

	Substrate Description	Surface Coating and Comments
.	Single zincate immersion in solution II (60 seconds)	1. Both iron and zinc are present in very "large" quantity. The iron and zinc peaks overlap so that quantitative measurements were not easily made.
	Single zincated substrate (60 seconds) dipped into nitric acid for 20 seconds.	2a. The zinc concentration on the surface was found to be about 1.97×10^{15} atoms/cm^2 or about two monolayers. b. The iron concentration was about 1.5×10^{15} atoms/cm^2. Note: That iron is present in deposites on both substrates 1 & 2. And that there must be a comparibly insoluble (in 50% nitric acid) alloy formed in the interface between the zinc, iron and the aluminum.
	Substrate dipped for 60 seconds in the stannate immersion solution (14).	3. Tin was found on the surface in a concentration of 0.26×10^{17} atoms/cm^2 or about 15 monolayers.

References

(1) S Wernick and R. Pinner, "The Surface Treatment and Finishing of Aluminum and Its Alloys", Vol. 2, pg. 898, Robert Draper LTD, Teddington, 1971.

(2) H. E. Chandler and Donald F. Baxter, Jr., "Metals Progress", January 1979, pg. 53.

(3) F. Keller and W. G. Zelly, "Journal of the Electrochemical Society", 97, 143, (April 1950).

(4) G. L. Bailey, "Journal Electrodepositors Technical Society", 27, 233, (1951).

(5) R. V. Vanden Berg, Aluminum, Ed. by K. R. Van Horn, Vol. III, 685, ASTM publication, Metals Park, OH (1967).

(6) S. Wernick and R. Pinner, The Surface Treatment and Finishing of Aluminum and Its Alloys, Robert Draper Ltd., Great Britain, Vol. 2, pg. 898, 1972.

(7) W. Bullough and G. E. Gardam, J. Electrodepositors Technical Society, 22, 169 (1947).

(8) F. Keller and W. G. Zelley, J. Electrochemical Society, 97, 143 (1950).

(9) D. S. Lashmore, Plating and Surface Finishing, 44, April 1978.

(10) ASTM 8753-73 The Preparation of and Electroplating on Aluminum Alloys by the Zincate Process, ASTM, Pa., 1978, pg. 73.

(11) T. P. Dirkse, Journal Electrochemical Society, 1954, 101, No. 328-31.

(12) H. Benston, Trans. Electrochemical Society, 1945, 88, 307-24.

(13) D. S. Lashmore, Submitted to Journal Electrochemical Society.

Figure Captions

1) Weight Gain Measurements of Various Alloys in Zincate Solution.

2) Bright Field TEM micrographs comparing the morphologies of zinc deposited by Immersion (a) in Solution I (b) in Solution II (100kev).

3) TEM Micrographs of zincated 6060-T6 (a) Bright Field (b) Dark Field (c) Selected area diffraction patter from (b) (100kev).

4) (a) SEM Micrograph of Zinc deposits at Grain Boundaries in 97% Aluminum Containing Both Iron and Magnesium (20kev) (b) SEM Micrograph of Tin deposits at Grain Boundaries on the same alloy.

5) (a) A TEM micrograph of 99.999% Aluminum subjected to An Immersion Tin Treatment Followed by a 5 second Bronze Strike (100kev) (b) Selected Area Diffraction Patter from the above area.

Dark Field Micrographs of Tin deposits on Etched 99.99% Aluminum (100kev).

SEM Micrographs of Tin deposits on Etched 99.99% Aluminum (lookev).

Optical Micrographs of a Single Crystal Sphere subjected to a one minute Zincate Immersion followed by a dip in 50% nitric acid to strip off the zinc (a) the (100) plane (b) the (110) plane and (c) the (111) plane.

A TEM Micrograph of a specimen subjected to a nitric acid immersion.

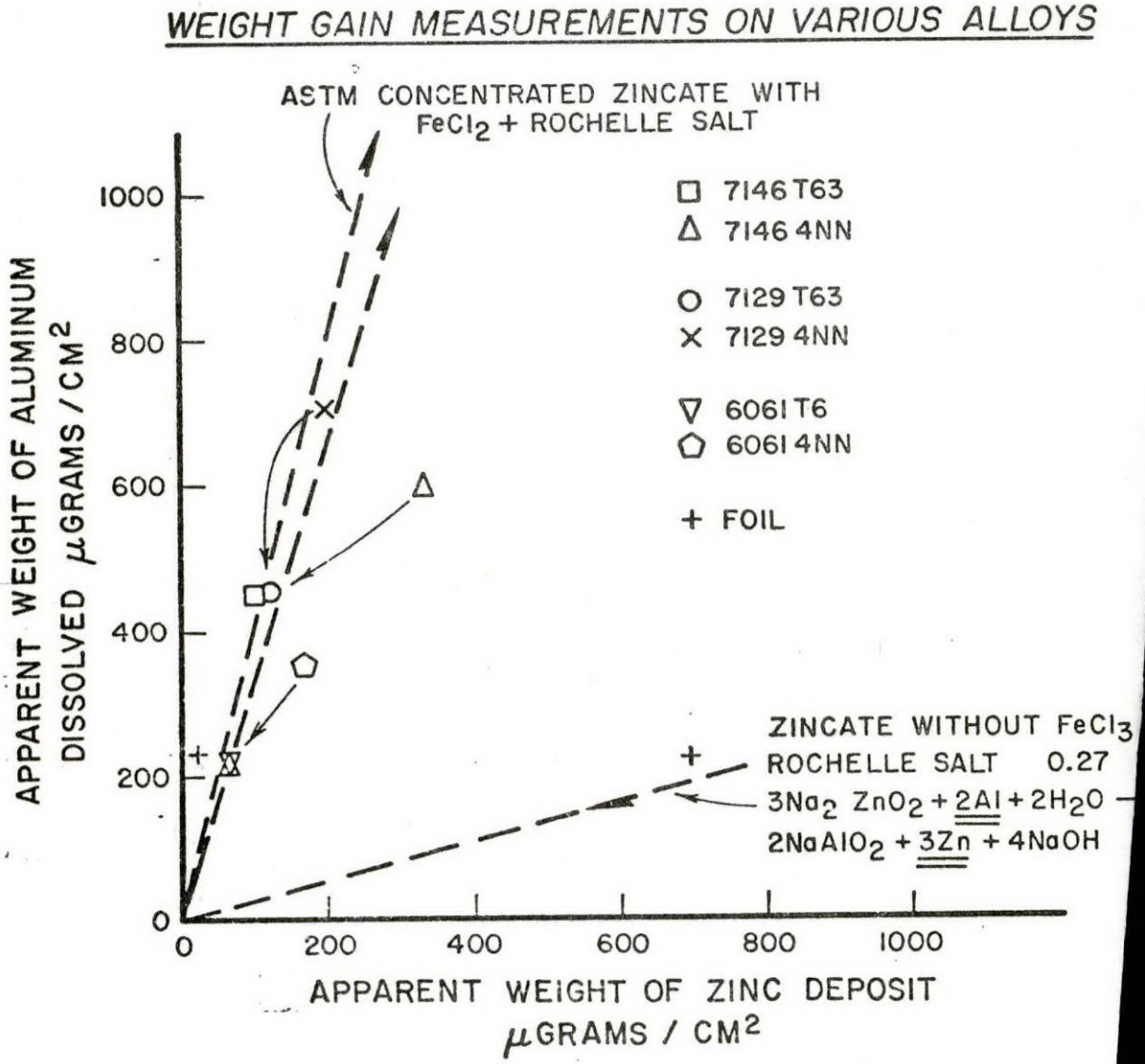

WEIGHT GAIN MEASUREMENTS ON VARIOUS ALLOYS
ASTM CONCENTRATED ZINCATE WITH
FeCl2 + ROCHELLE SALT
7146 T63
7146 4NN
7129 T63
7129 4NN
6061 T6
6061 4NN
+ FOIL
ZINCATE WITHOUT FeCl3
ROCHELLE SALT 0.27
3Na2 ZnO2 + 2Al + 2H2O
2NaAlO2 + 3Zn + 4NaOH
APPARENT WEIGHT OF ALUMINUM
DISSOLVED μGRAMS / CM2
APPARENT WEIGHT OF ZINC DEPOSIT
μGRAMS / CM2
0
200
400
600
800
1000

Figure 1

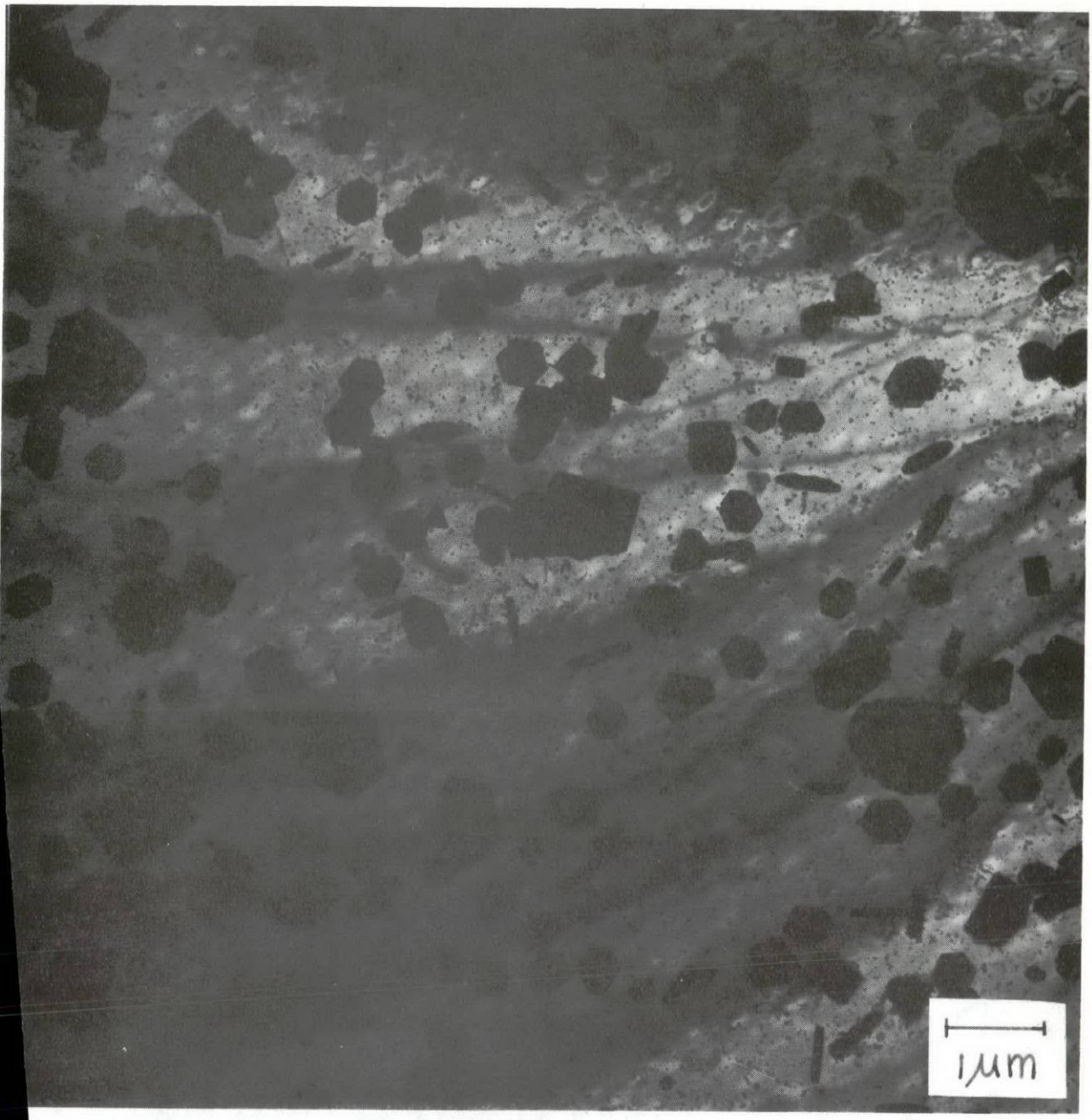


Figure 2a

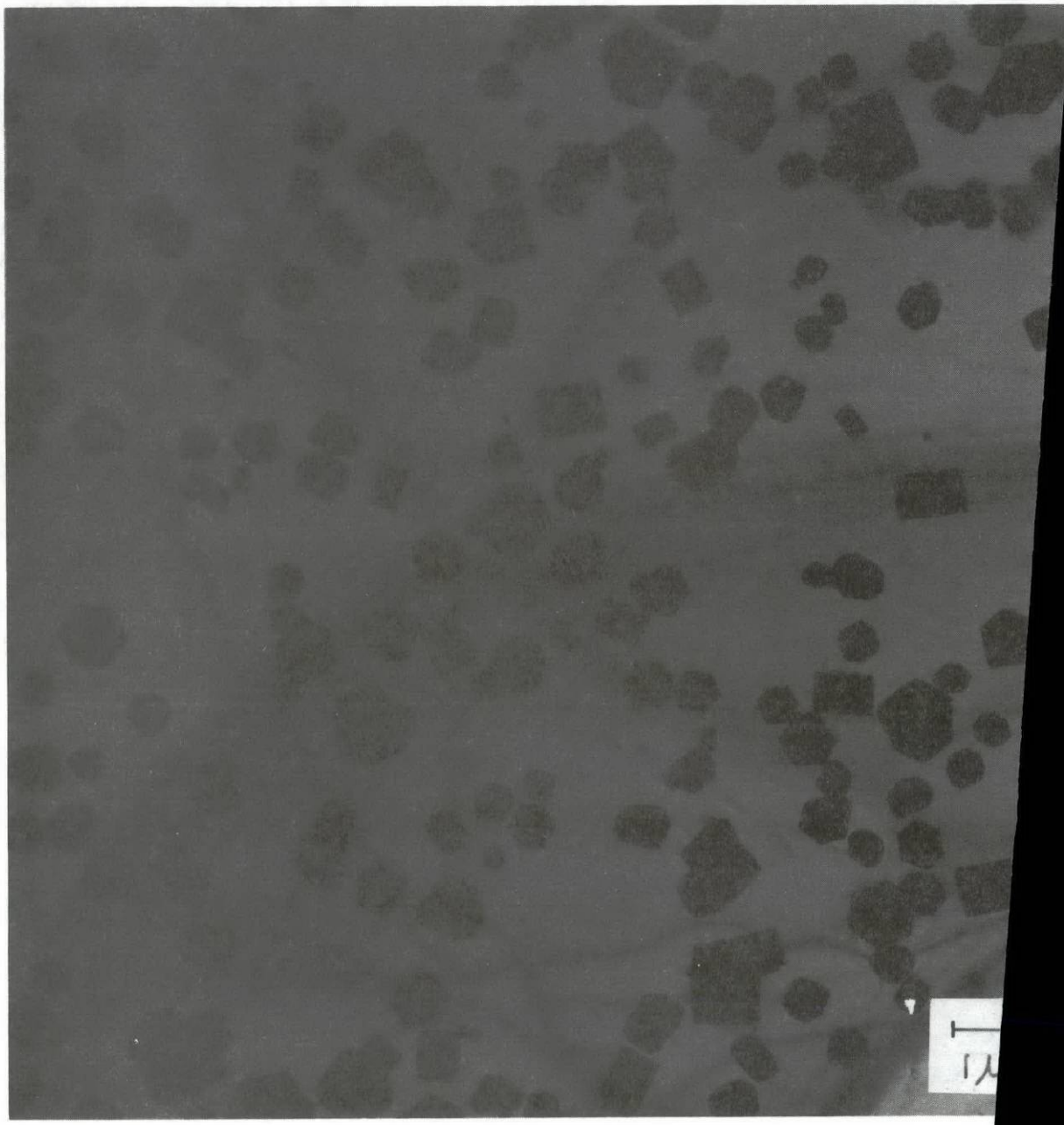


Figure 2b

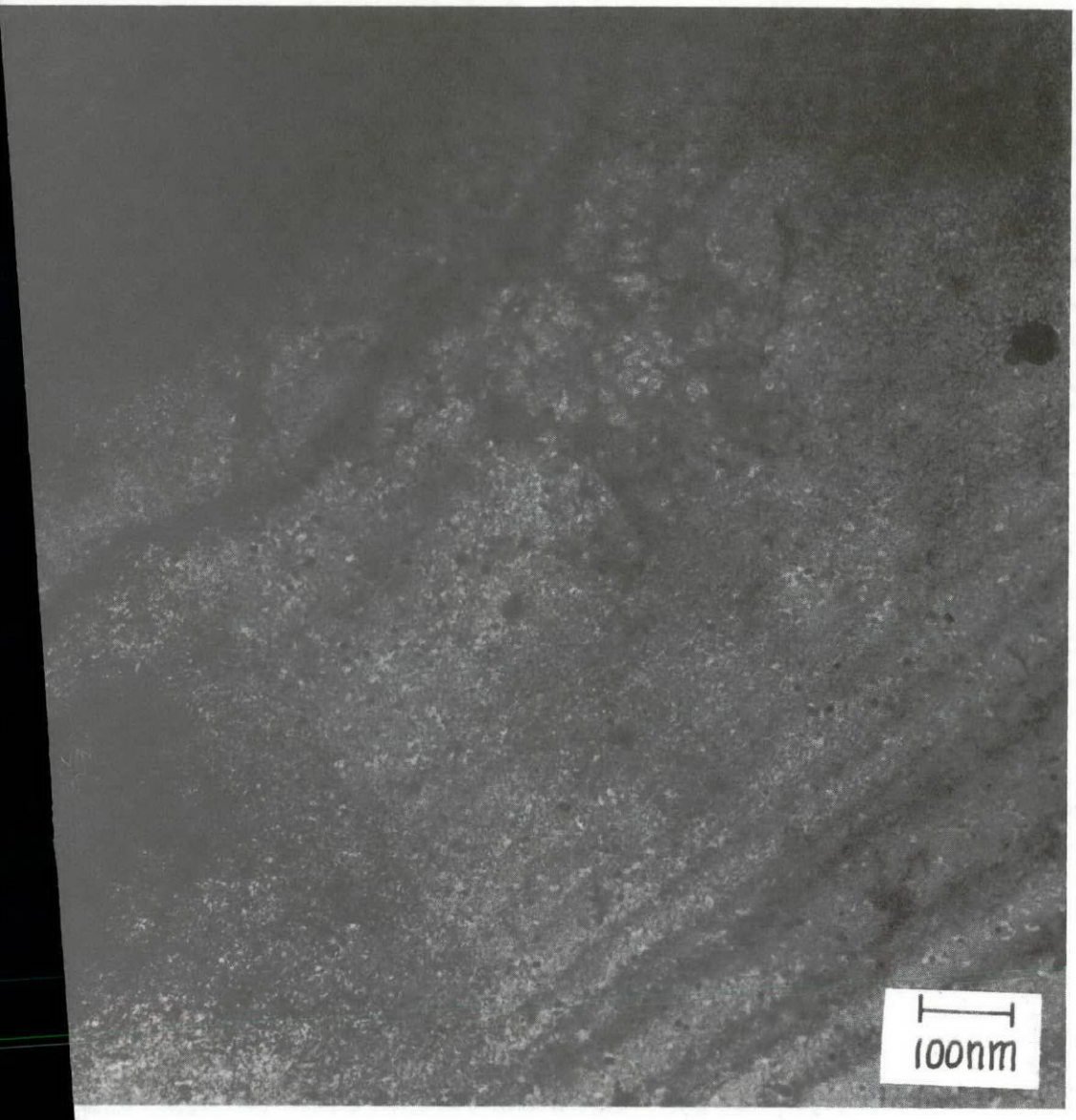


Figure 3a

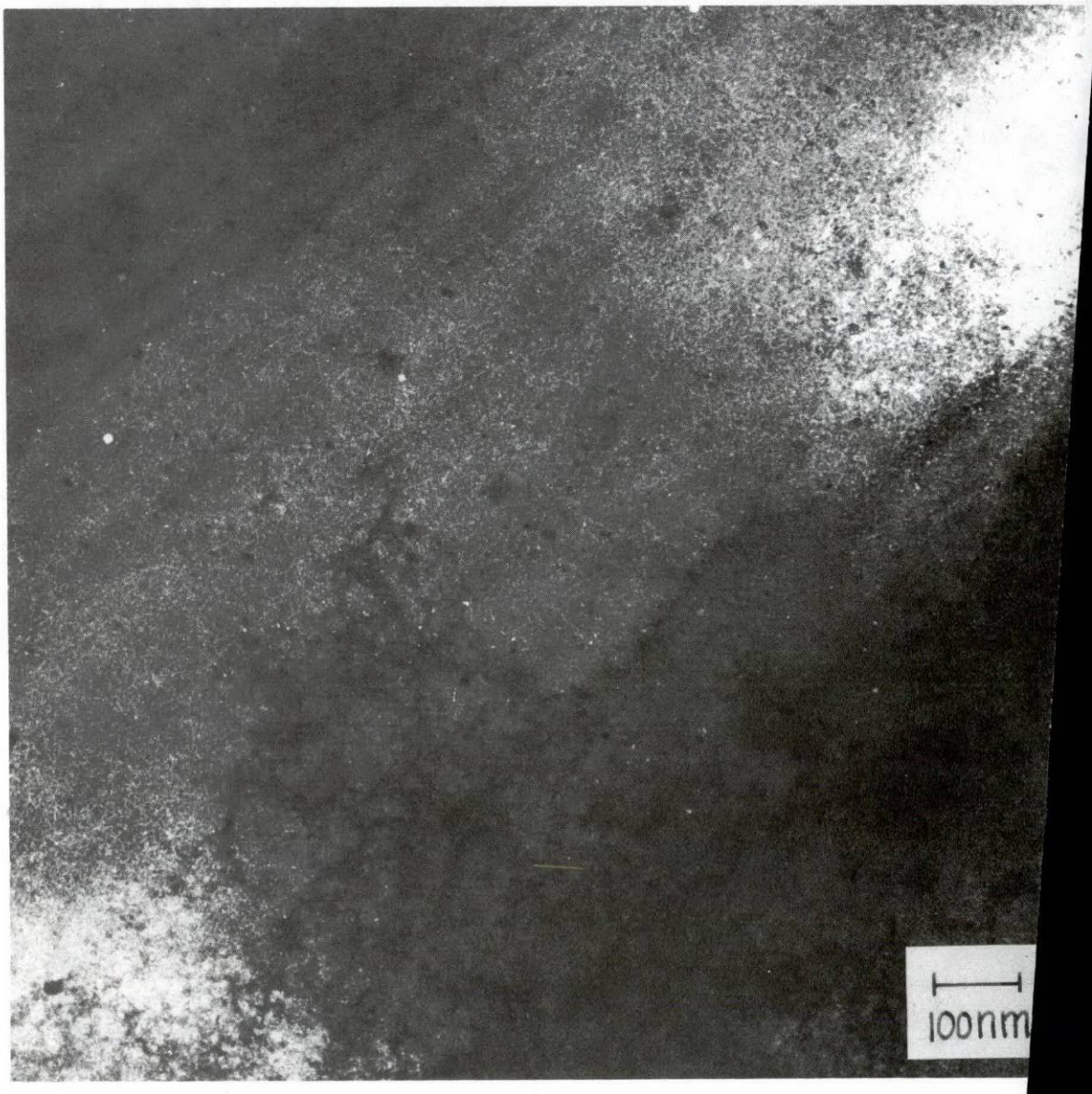


Figure 3b



Figure 3c

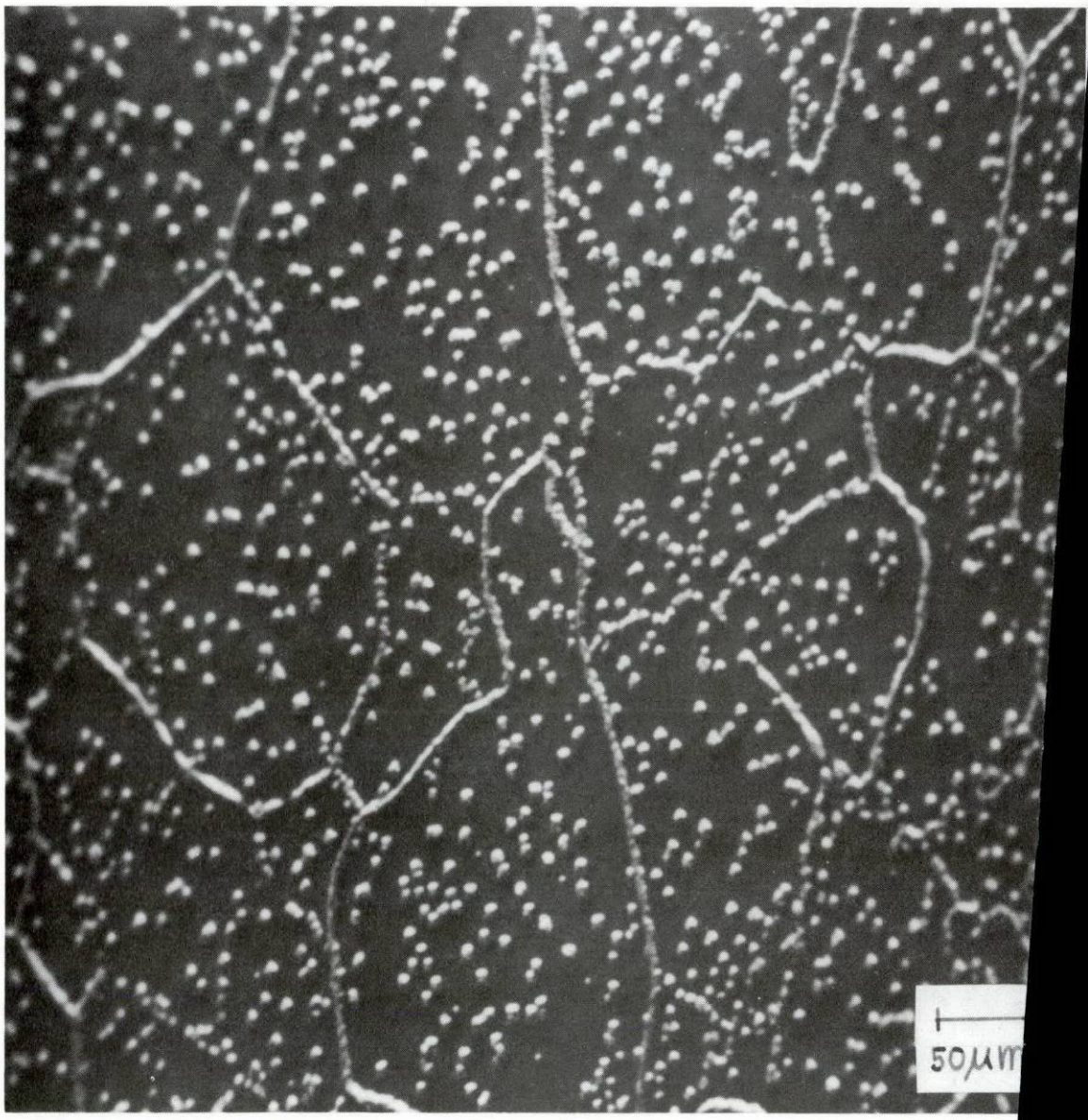


Figure 4a

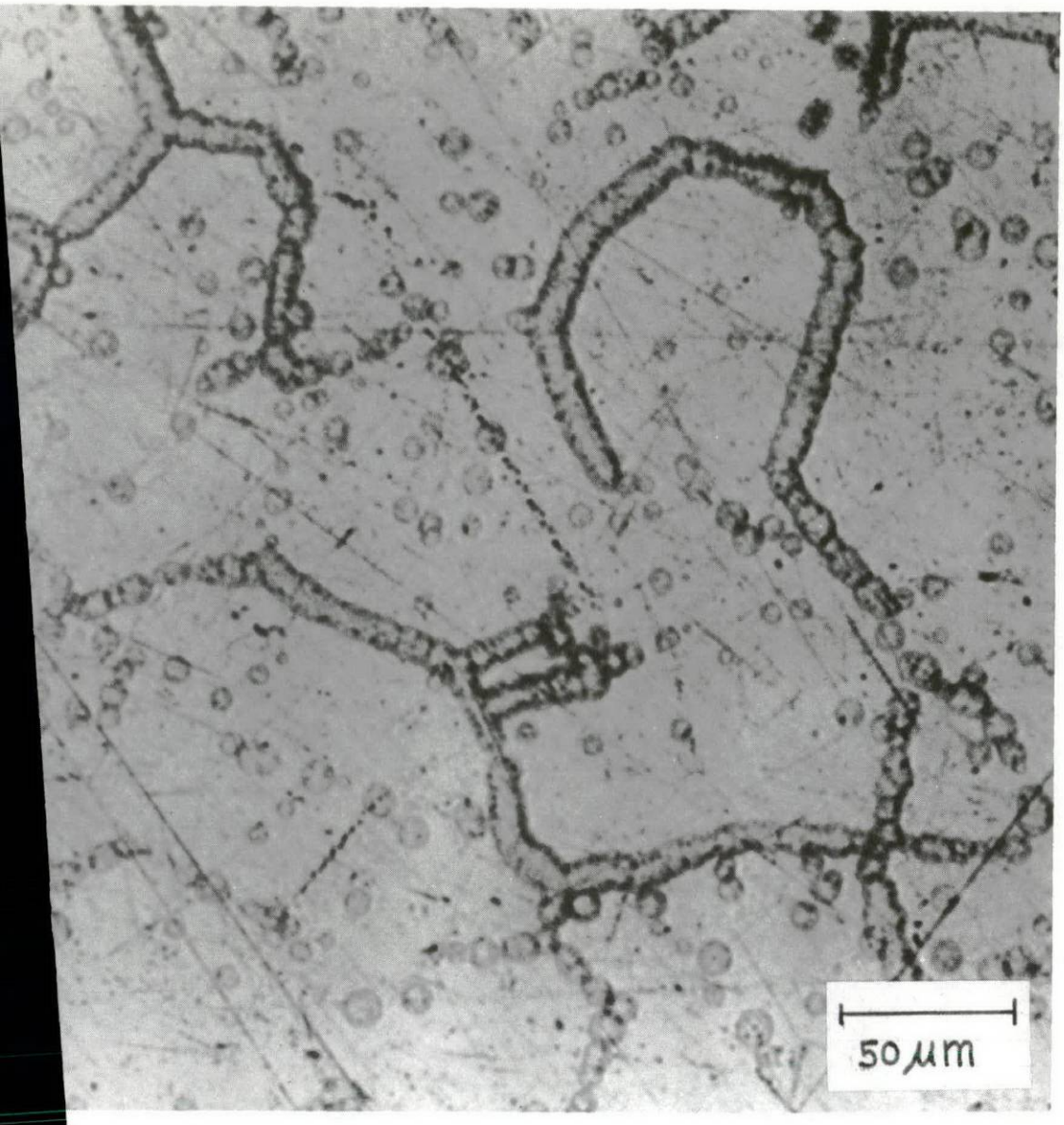


Figure 4b

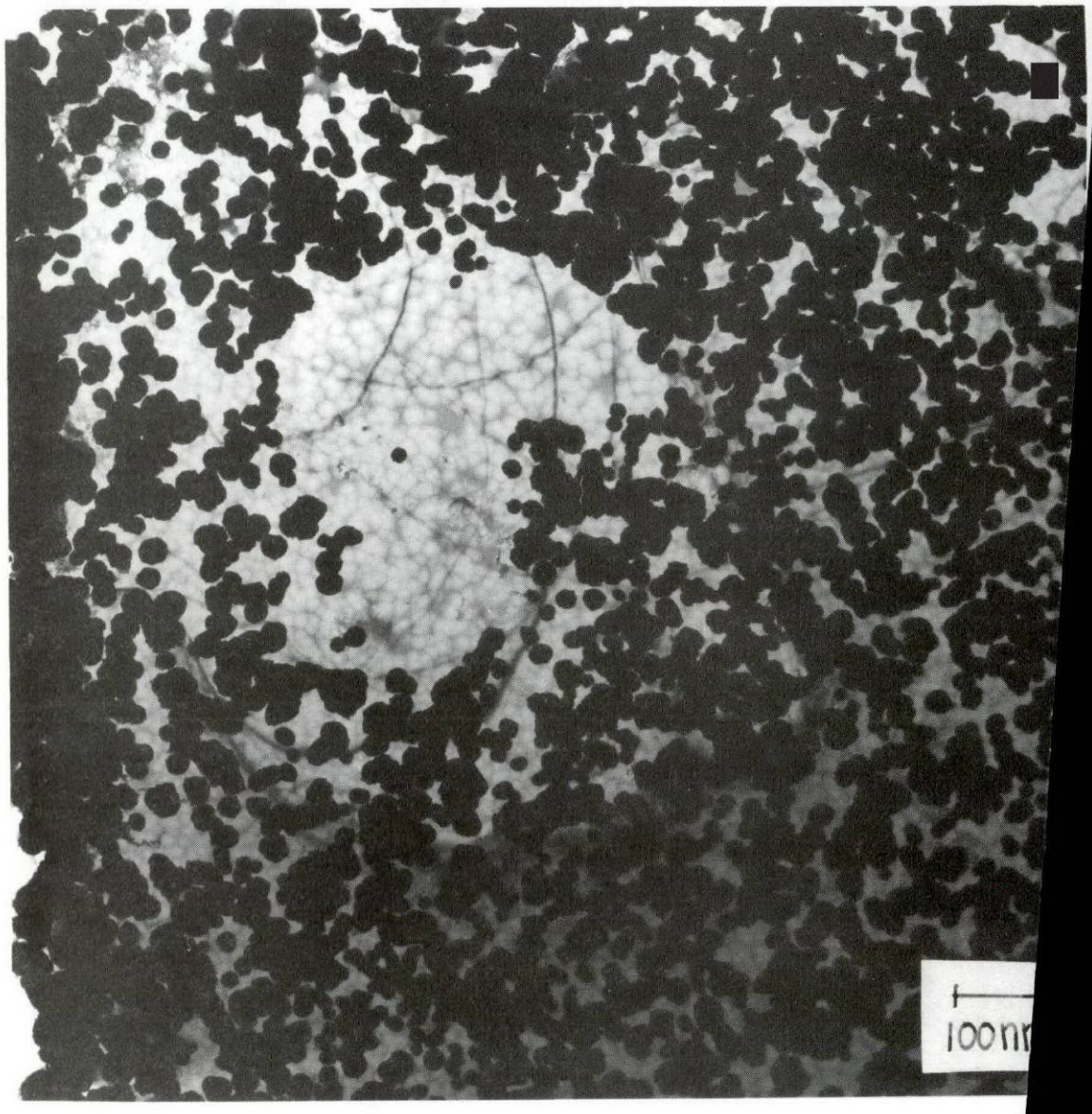


Figure 5a

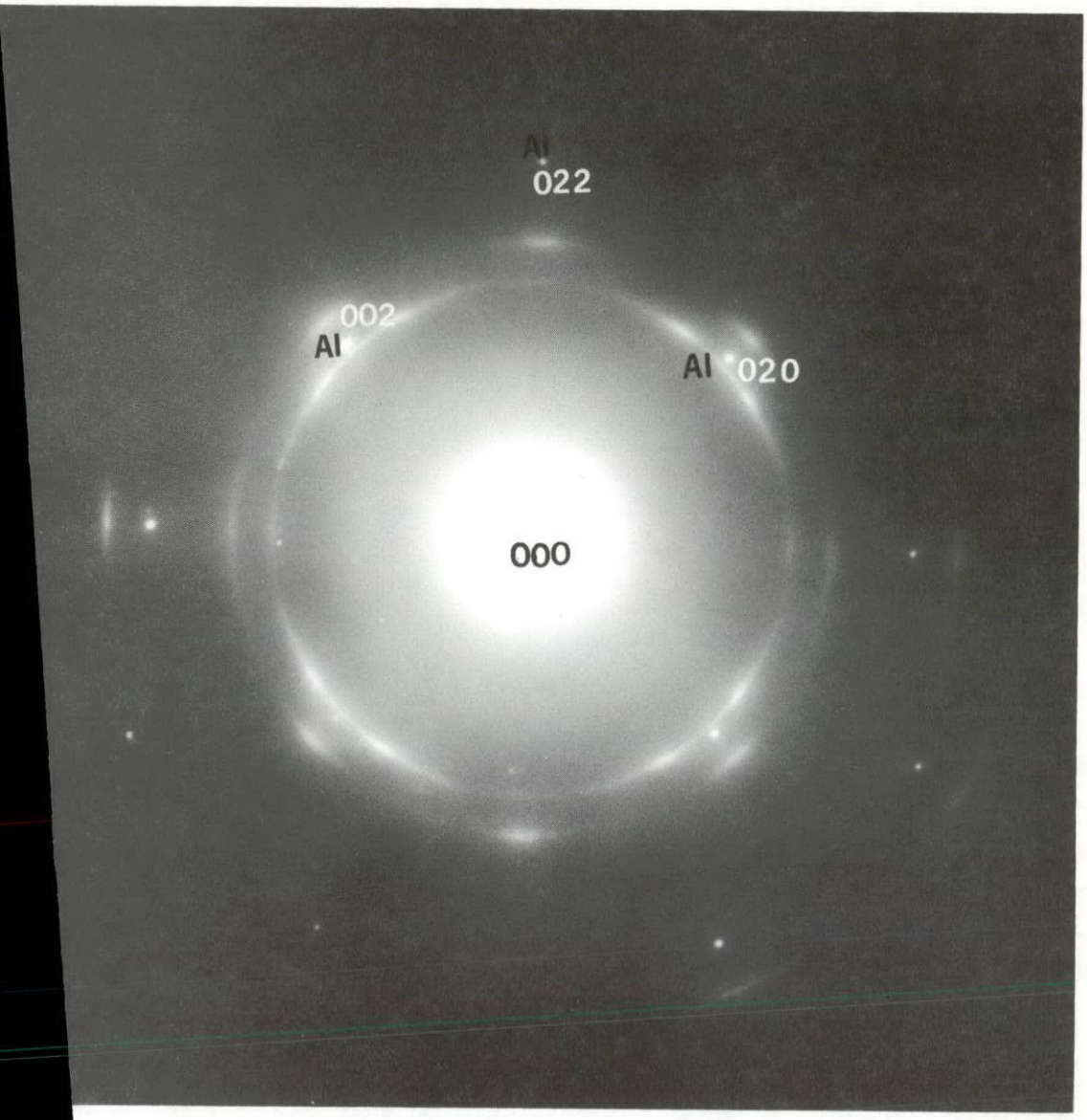


Figure 5b

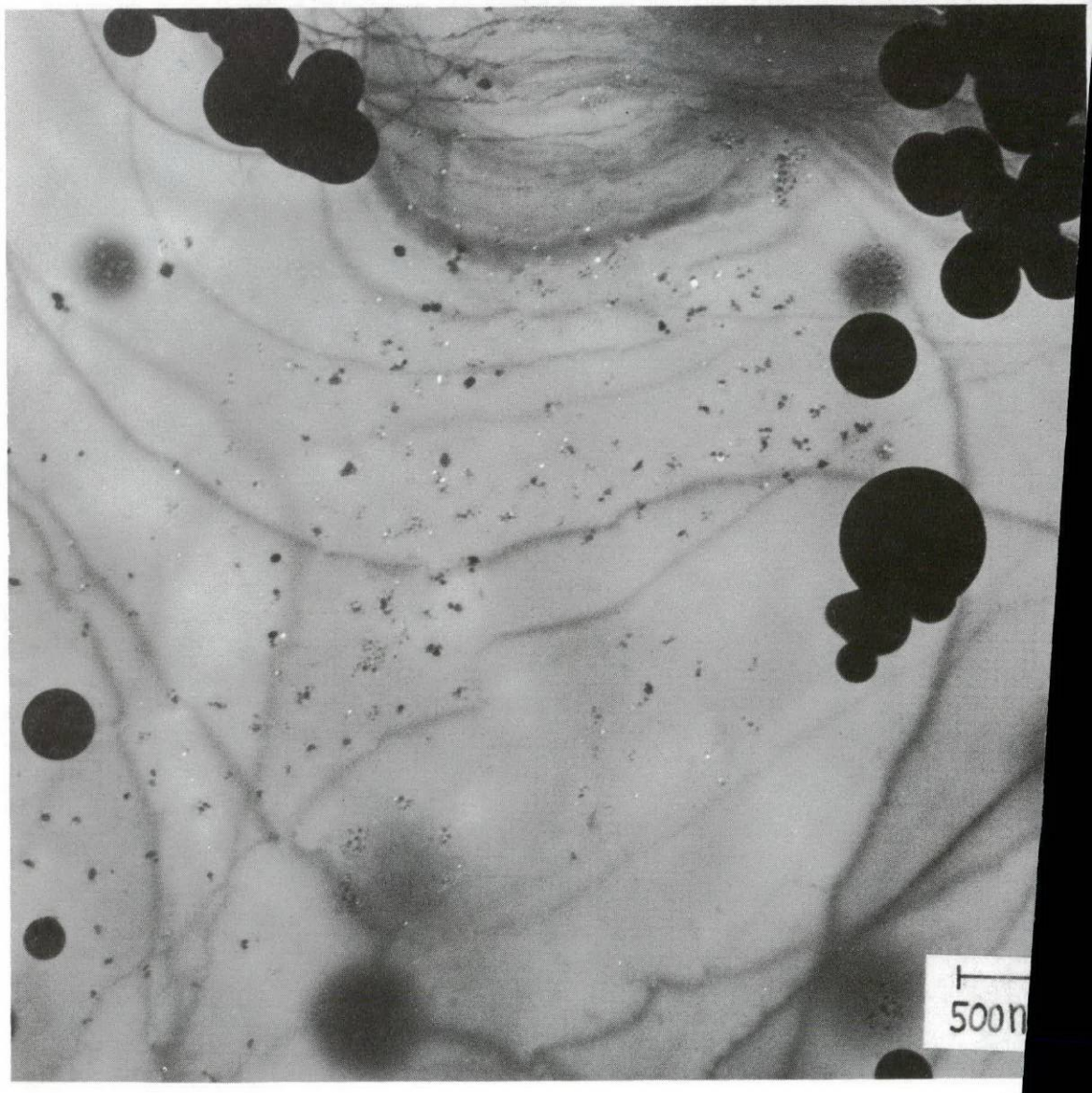


Figure 6

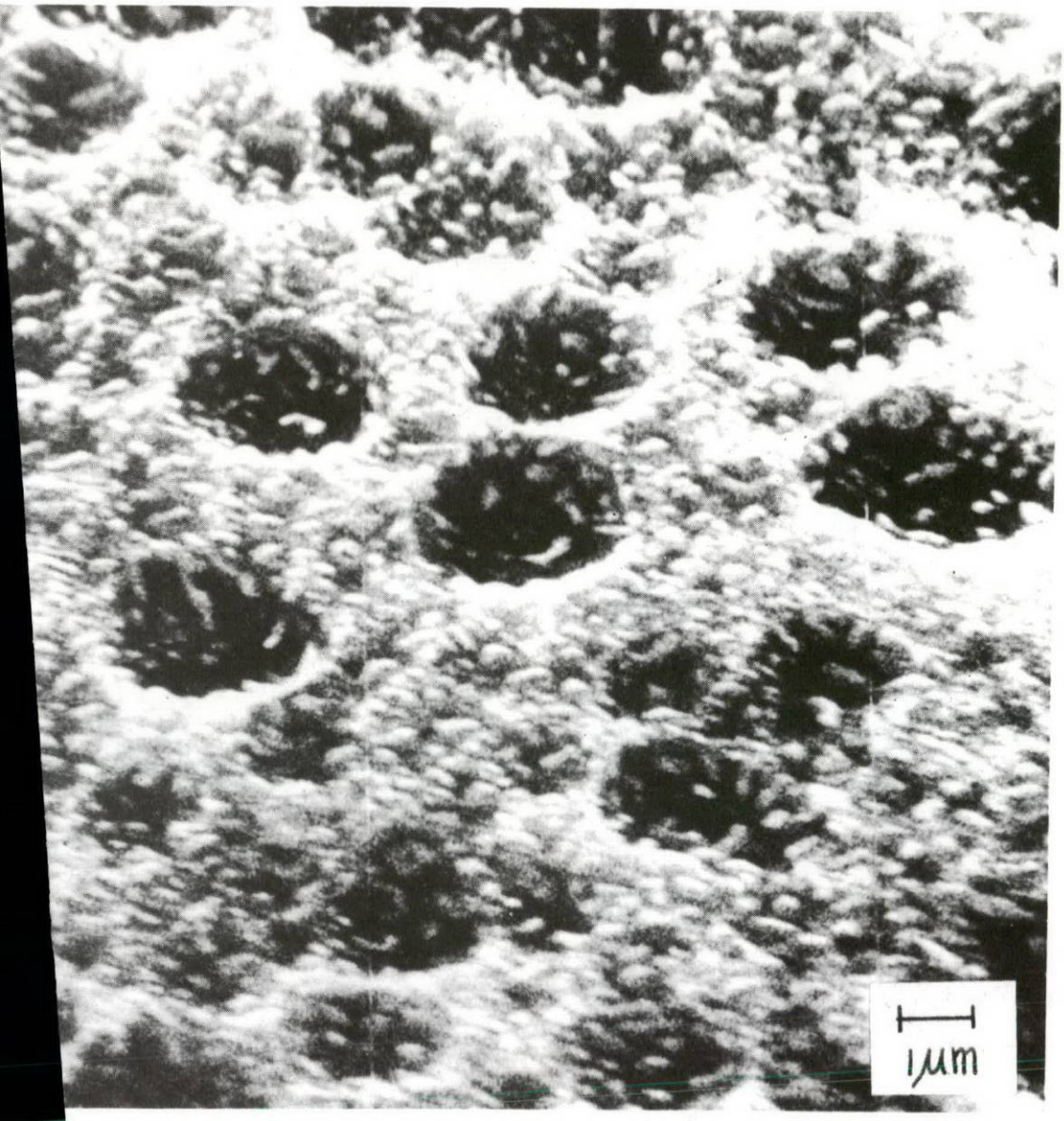


Figure 7



Figure 8a

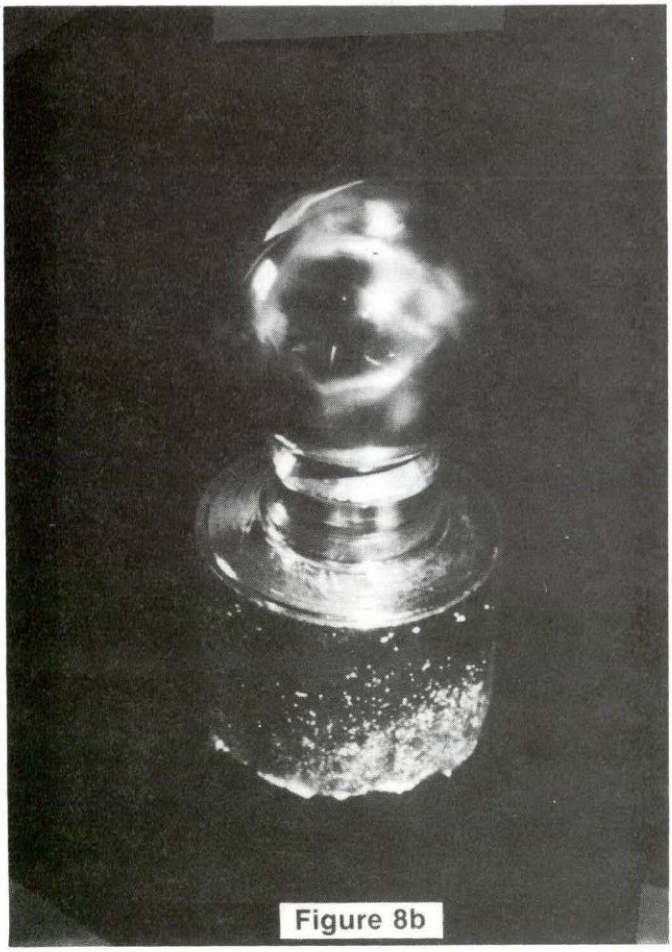


Figure 8b



Figure 8c

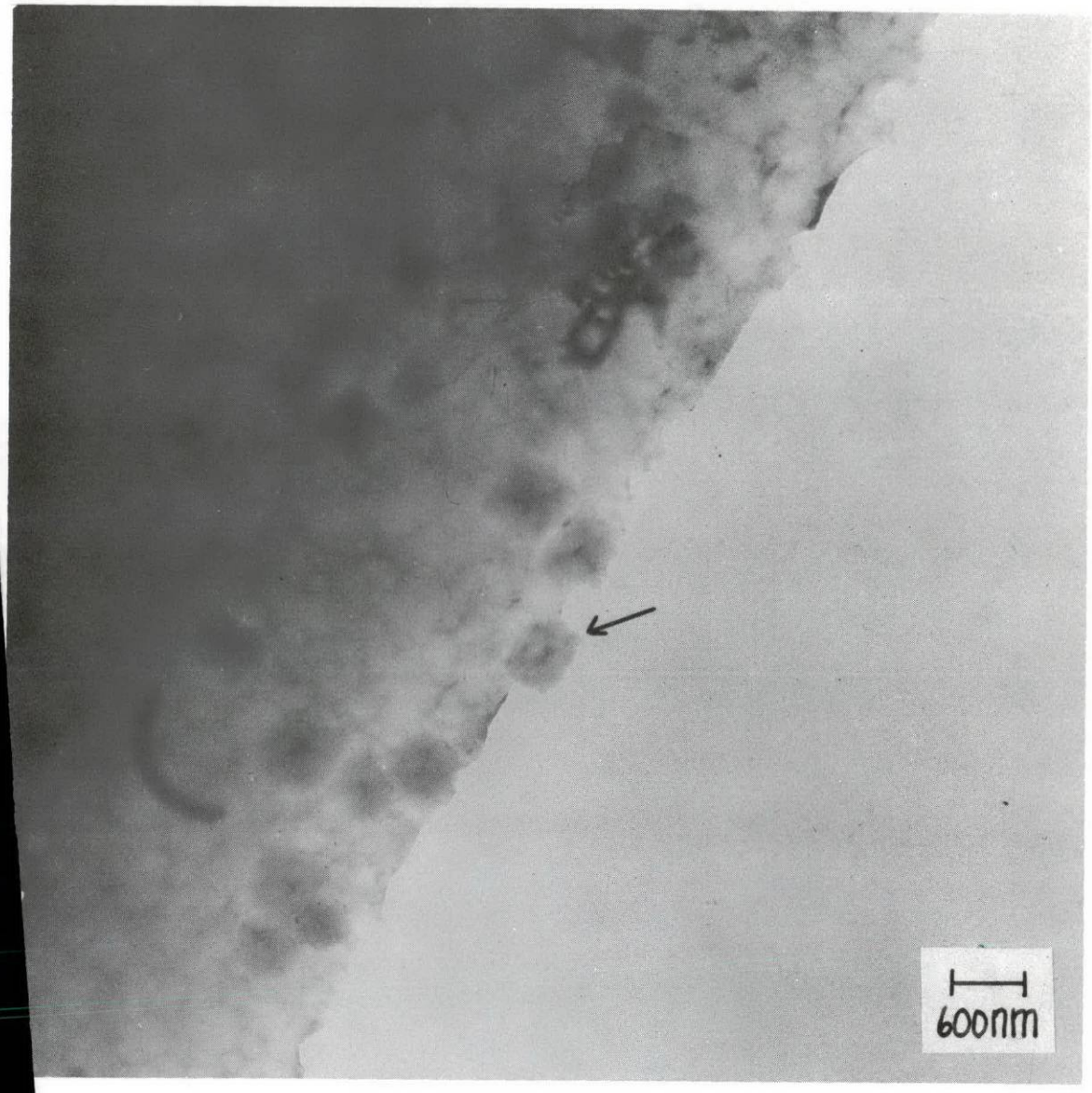


Figure 9

L-3

Research I
Session L

A Mini-Peel Test for Measuring Adhesion Of an Electroplate to ABS Substrate AES Research Project #42

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A MINI-PEEL TEST FOR MEASURING ADHESION OF AN ELECTROPLATE TO ABS SUBSTRATE

INTRODUCTION:

ASTM-B533-70[1] specifies a method of testing adhesion between a plastic substrate and an electroplated metallic coating. The method calls for standard specimens and is of value mainly for control of the processing solutions. ASTM-B533[2] describes a thermalcycle test for the evaluation of electroplated plastics. In commercial practice adequate adhesion is valuated almost exclusively by thermalcycling.

Project 42 is a study of the effect of molding, resin and etching on ermalcycling failure. Failures in this test typically occur at the edges, rting lines, or junctions of ribs. The development of a quantitative test pable of measuring adhesion on these areas was a prerequisite to the study. criteria for the test were:

a) The test not require a standard specimen.

b) The test be capable of measuring adhesion on very small areas.

s paper discusses the development of a test satisfying the above criteria.

Initially some time was devoted to developing a direct tensile joint ngth test utilizing a 1/8" diameter test piece. Electroformed nodules rejected as being too cumbersome and unpredictable. A number of adhesive niques were evaluated before we recognized the limitations of a direct le test. Attempting to utilize a diminutive sample piece in studying tially non-uniform surface would inevitably introduce an undesirable nt of uncertainty. Attention was therefore directed at developing a test le of providing an "adhesion profile" of a molded part.

fter several trials we finally settled on a modification of the Jacquet est utilizing 1/16" wide strips. The strip was formed by masking with ve vinyl tape and etching to remove the unwanted plate. With suitable and jigs the test should be capable of measuring the peel strength on any significant surface. For this study an Ingstrom Universal Testing ent, Table Model 1130, with a ten pound load cell certified as being e to within 1/4% of the range, was used. The test results were recorded rip chart for later evaluation.

DISCUSSION:

"The standard Jacquet peel test measures not pure adhesion but a com of factors." Among the known factors influencing the Jacquet values are:

1. The physical properties of the electrodeposited metal.
2. Aging of the electroplated sample.
3. The thickness of the electrodeposited metal.
4. The adhesion between the metal and the plastic which itself is a function of:
   a) The grade of resin.
   b) The molding conditions.
   c) The preplate process.

When studying peel test values we are interested in variations in Item 4 To be meaningful variations due to 1, 2 or 3 should be eliminated or a compensating correction applied.

Variations due to the physical properties of the electrodeposited may be eliminated by standardizing on bright acid copper of controlled ductility for the electroplate. Aging of the electroplated samples can controlled but it is not possible to control exactly the thickness of e deposits on complex moldings. It is, therefore, necessary to derive corre factors to compensate for this variable.

EXPERIMENTAL:

The part chosen as a test piece was a 2 1/2" diamenter x 2" high closed at one end. It consists of two relatively simple surfaces and major problem area. As the dimensions of the part are small, it was to process a large number of pieces at one time, thus eliminating con to unwanted variation in the processing conditions.

Preplate Procedure: Parts for testing were processed on our producti line utilizing the conventional steps of (1) chromic acid etch 10 mi (2) neutralizer 2 minutes, 130°F; (3) colloidal tin/palladium catalys accelerator; and (5) electroless copper.

Peel Test Procedure: Samples for peel testing were preplated, clean electroplated with bright, ductile acid copper. Except where specif "unbaked" the samples were oven baked for two hours at 180°F, then c room temperature. They were then stored in an air conditioned room required for peel testing.

The copper plated parts were cleaned by wiping with 1,1,1-Trichloroethane; masked with vinyl adhesive tape; the exposed copper was stripped in a 50% aqueous ferric chloride solution at 110°F and the parts were rinsed and dried. The masking tape was removed and a 1/4" tab lifted at the beginning of each strip. The strips were peeled from the plastic at a 90° angle at the rate of 2" per minute. The force required was recorded, automatically, on the chart.

ffect of the Electroplated Metal Thickness on Adhesion Values: The selected art was molded in Cycolac EP3510 (a plating grade of ABS manufactured by org-Warner Corporation) under optimized conditions and processed on a regular roduction line. Test bands showed uniform adhesion around the circumference the part and, with the exception of the base and top edge, at a 90° angle to e circumference. The parts used in developing the following data were from e same molding run. All parts were processed at the same time on our oduction electroless plating line and were electroplated (at the same current sity) to various thicknesses in a Bright Acid Copper tank. Parts were n baked for two hours and then aged for a minimum of two weeks at ambient perature before peel testing. Separate data was generated for each of two ities. The data for Cavity A is presented in Fig. I, that for Cavity B in II. Initial inspection of the data suggests that the relationship is truly linear but that it could be approximated by straight lines. Linear es were fitted to the data utilizing the method of least squares. The ulated curves were:

	Cavity A	Cavity B
For Thickness Range 1.0-6.0	y=0.5570 + 0.1345x	y=0.5365 + 0.1236x
	s=0.1069	s=0.1776
	r=0.8768	r=0.8371
For Thickness Range 1.0-3.0	y=0.3191 + 0.2498x	y=0.3092 + 0.2370x
	s=0.0393	s=0.0745
	r=0.9795	r=0.9060
or Thickness Range 3.0-6.0	y=0.9537 + 0.0421x	y=0.8236 + 0.0601x
	s=0.0843	s=0.1103
	r=0.4358	r=0.4332

s" is the standard error of the estimate an "r" is the coefficient of tion. The linear fit in the 1.0-3.0 mils range is very good, that in 6.0 mils is very poor. In the 1.0-3.0 mil thickness range the contribution ness to the peel test values was 0.2434 lbs/mil.

With plate thicknesses over 3.5 mils there was a noticeable undercutt in the ferric chloride etch. This resulted in a fine saw-thoothed effect the edge of the strip and was visible as tiny peaks and valleys on the cha of force versus displacement.

Effect of Variation in the Strip Width: When analyzing the data it was no that the actual strip widths varied by as much as ±30% from the target 1/1 rolls of nominal 1/16" vinyl tape had been consumed in preparing the sample and it was determined that the rolls were not of uniform width. Also, whe applying the tape it had been noticed that it tended to stretch under ten It was desirable to be able to express all results for a standard strip w To determine the legitimacy of this procedure, nine parts were masked alternately with 1/16" nominal and 3/4" nominal tape. The thirty-six str were peeled. The width of the 3/4" strips was 0.7205", that of the narro strips 0.06717". Values for the narrow strips were multiplied by 10.726 The values calculated from the narrow strips and the actual values for t strips are recorded in Fig. III. It would seem that the procedure of ad the actual values for the 30% variation in strip width is valid.

APPLICATION OF THE TEST:

The test part was molded, in a four cavity mold, from what was kno an unsuitable plating grade of ABS for this particular part. Thirty-fi parts were preplated using similar conditions to those used in the prio Fifteen parts were electroplated with copper, nickel and chromium and w through ten thermalcycles of 180°F to -30°F. Only one part survived al cycles; seven failed on the first cycle and four on the second cycle. failure was a raising of the electroplate around a section of the top actual location of the raised section varied by cavity. At the failur two significant surfaces meet at an angle of almost 270°. It was post that the thermalcycle failures could possibly be due to the interacti geometry of the part and the stresses induced by thermalcycling.

The remaining twenty parts were electroplated with approximately of acid copper. Two parts from each cavity were oven baked at 180°F hours and then cooled to room temperature. No lifting of the electro visible. All twenty parts were held in an air conditioned room for mately six months. Two parts from each cavity of the unbaked parts baked parts were peel tested; the peel test values, adjusted as prev

described, are listed in Table I. Strips 1, 2, 3, and 4 were peeled around the cylindrical surface at the bottom, 1/2" and 1" from the bottom and the top of the part respectively. Strip 5 was peeled around the mating edge of the top (flat) surface.

It is widely recognized that the "as plated" adhesion of electroplate to ABS is very low but that it increases rapidly at room temperature during the first 24 hours and gradually thereafter. Prior work had demonstrated that the accelerated aging procedure produced increases in adhesion values equivalent to that produced by aging for 30 days at room temperature. The question remained as to whether the minimal increased adhesion values attained during the six months aging at room temperature would be sufficient to offset the stresses produced by heating to 180°F. One part from each cavity of the ed parts was therefore baked at 180°F for two hours. Strip four was peeled om each part. The results, listed in column 4b, demonstrated that air aging fore baking did not improve performance.

MARY AND DISCUSSION:

The standard 1" Jacquet peel test has proved a powerful quantative estigative tool in the development and control of plastic plating processes. mitation of its utility is the 1" wide strip imposed by the test. Typical s of failure on commercial parts are edges, parting lines, and rib junctions. acilitating study of these areas the proposed test would extend the range eel test evaluations. Peel test values are known to be, in part, a function e thickness of the electrodeposit. It was demonstrated that while the ionship is not truly linear it can be approximated reasonably well by a r function over the thickness range 1.0 to 3.0 mils. In this thickness the contribution of metal thickness to the peel test values is 0.2434 1. However, this factor is valid only in the adhesion range studied, 0-1.0 pounds for a 1/16" strip. Prior experience with the standard 1" est suggests that alternative factors should be developed for other

ed Method of Testing: The following is the recommended testing procedure:

an the preplated part and electroplate with 1.5-2.5 mils of ductile ght acid copper.

n bake for 2 hours at 180°F, then cool to room temperature.

3. Wipe with degreaser solvent (1,1,1-Trichloroethane) and mask (in the desired pattern) with adhesive vinyl tape.
4. Strip the exposed copper in a 50% aqueous solution of ferric chloride at 110°F ±5°F. Rinse and dry.
5. Remove the masking tape and lift a 1/4" tab at the beginning of each strip.
6. Mount the part on the fixture. Pull the strip from the plastic at a 90° ±5° angle at the rate of 2" per minute. Record the required forc on the chart.

NOTE 1: Use an even force when applying the tape as it can stretch tension thus altering the width.

NOTE 2: The stripping rate of the ferric chloride solution decrease with use. The solution should be discarded if it does not completely strip the copper within 90 minutes. Unreasonab prolonged immersion time can produce a noticeable undercut at the edges of the strips.

NOTE 3: As the peel test values are very low an accurate tensile t machine must be used.

The proposed test would not appear to have any value in Quality Assura it (a) requires specially prepared samples and (b) is destructive. Th quality of commercial parts can best be assured by thermalcycling. In existing facility the chemical processing line is relatively fixed. C of the processing solutions can be controlled by analysis and testing the method specified in ASTM B-533. The primary utility of the propo would seem to be in the area of product development e.g., choice of R Grade, Molding Conditions, Optional Steps in an existing line and, wi limitations of the "product mix", the times and temperatures of the p solutions. In these areas relative rather than absolute values may all that is required thus avoiding the rather laborious task of appl several correction factors to the raw data.

REFERENCES:

1. ASTM-B-533-70 Measurement of Peel Strength of Metal Plated Plastics.

2. ASTM-B-533 Recommended Practice for Thermalcycling Test for Evaluation of Electroplated Plastics.

3. Edward B. Saubestre, Lawrence J. Durney, Juan Hajon and Erwin Bastenbeck. Paper presented at the American Electroplaters Society 52nd Annual Convention, New York, New York, July 13, 1965.

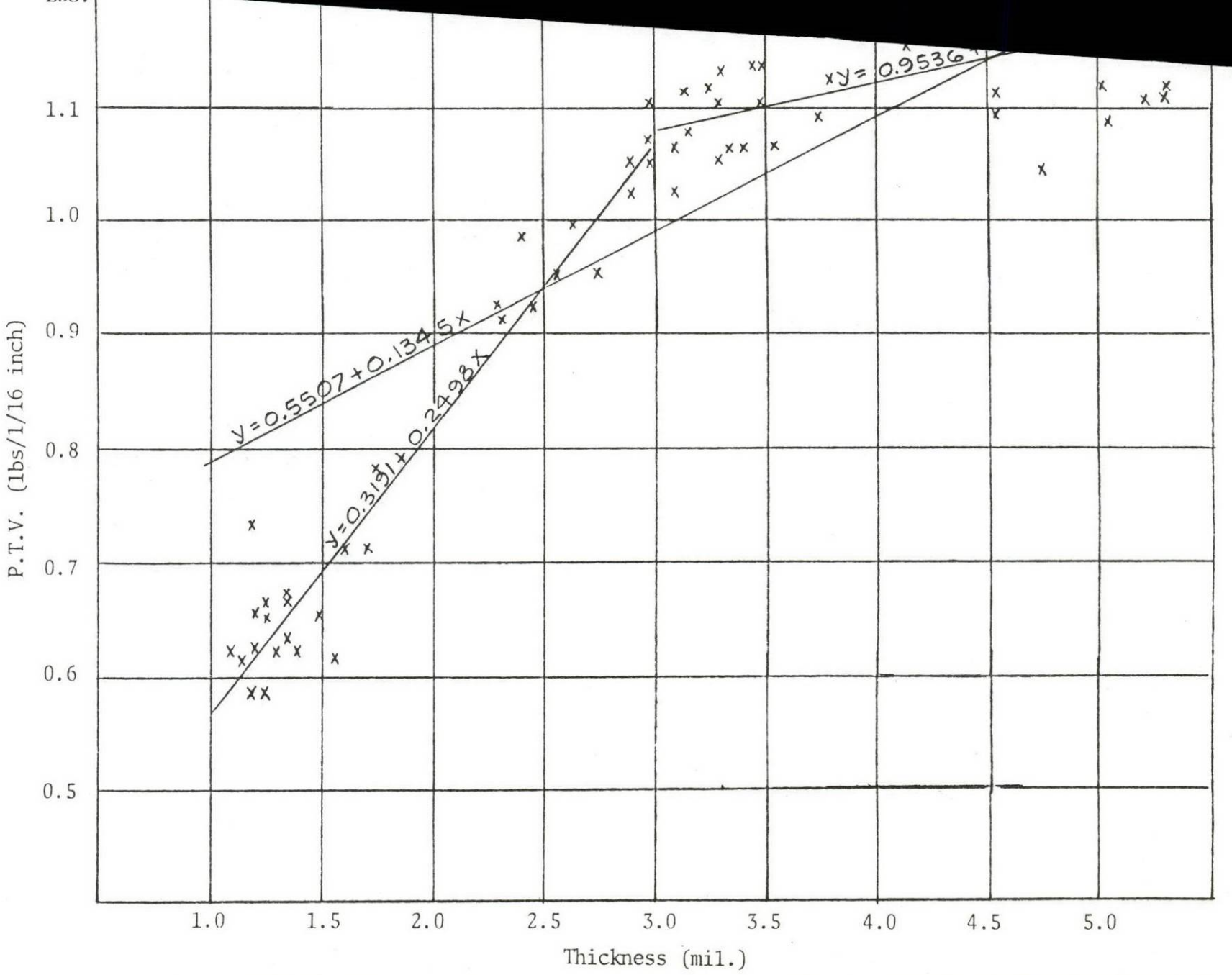

y=0.5507+0.1345x
y=0.3191+0.2498x
xy= 0.9536
P.T.V. (lbs/1/16 inch)
1.1
1.0
0.9
0.8
0.7
0.6
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
Thickness (mil.)

FIG. II. Peel Test Values vs. Thickness of Bright Acid Copper. Data for Cavity B.

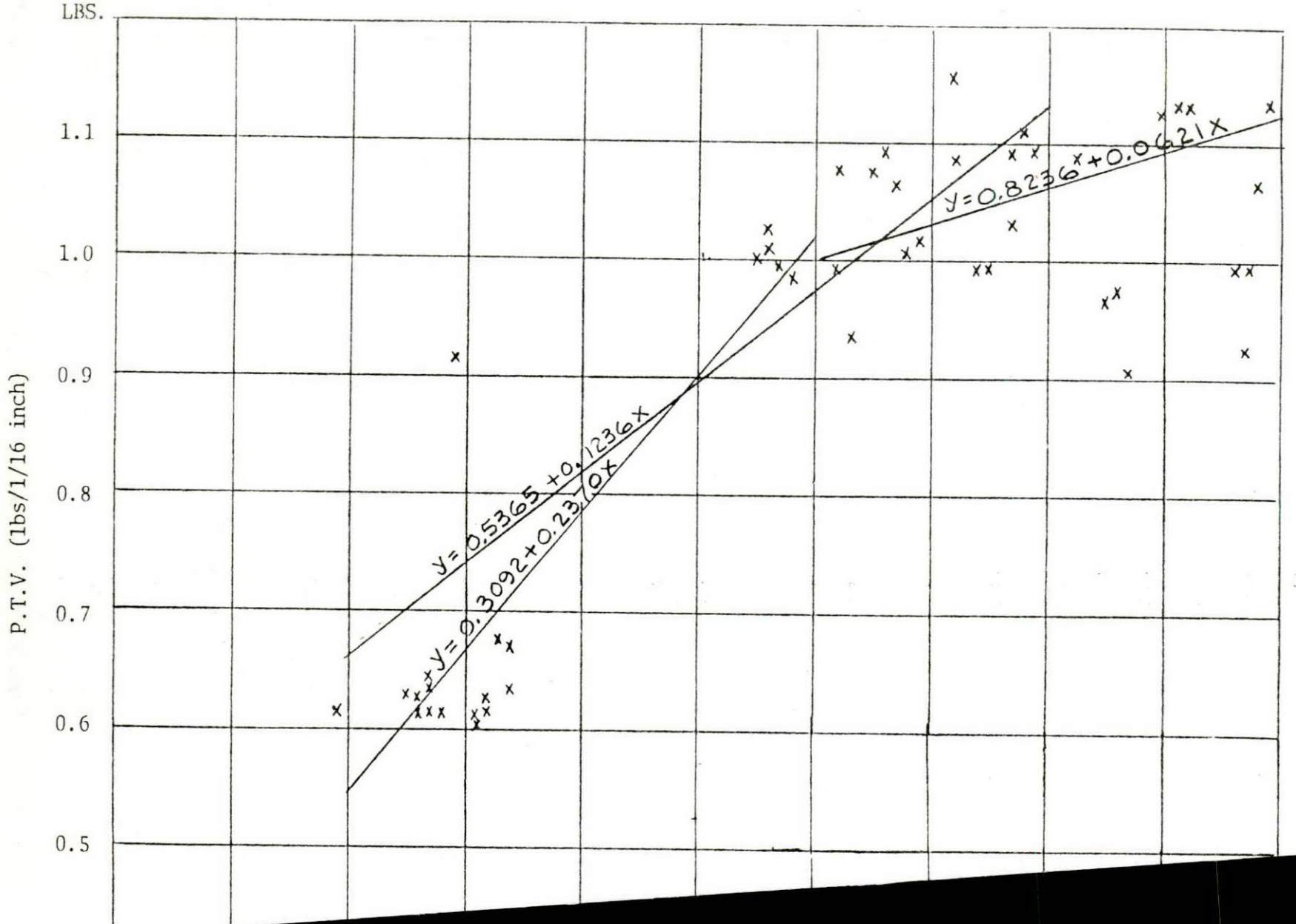
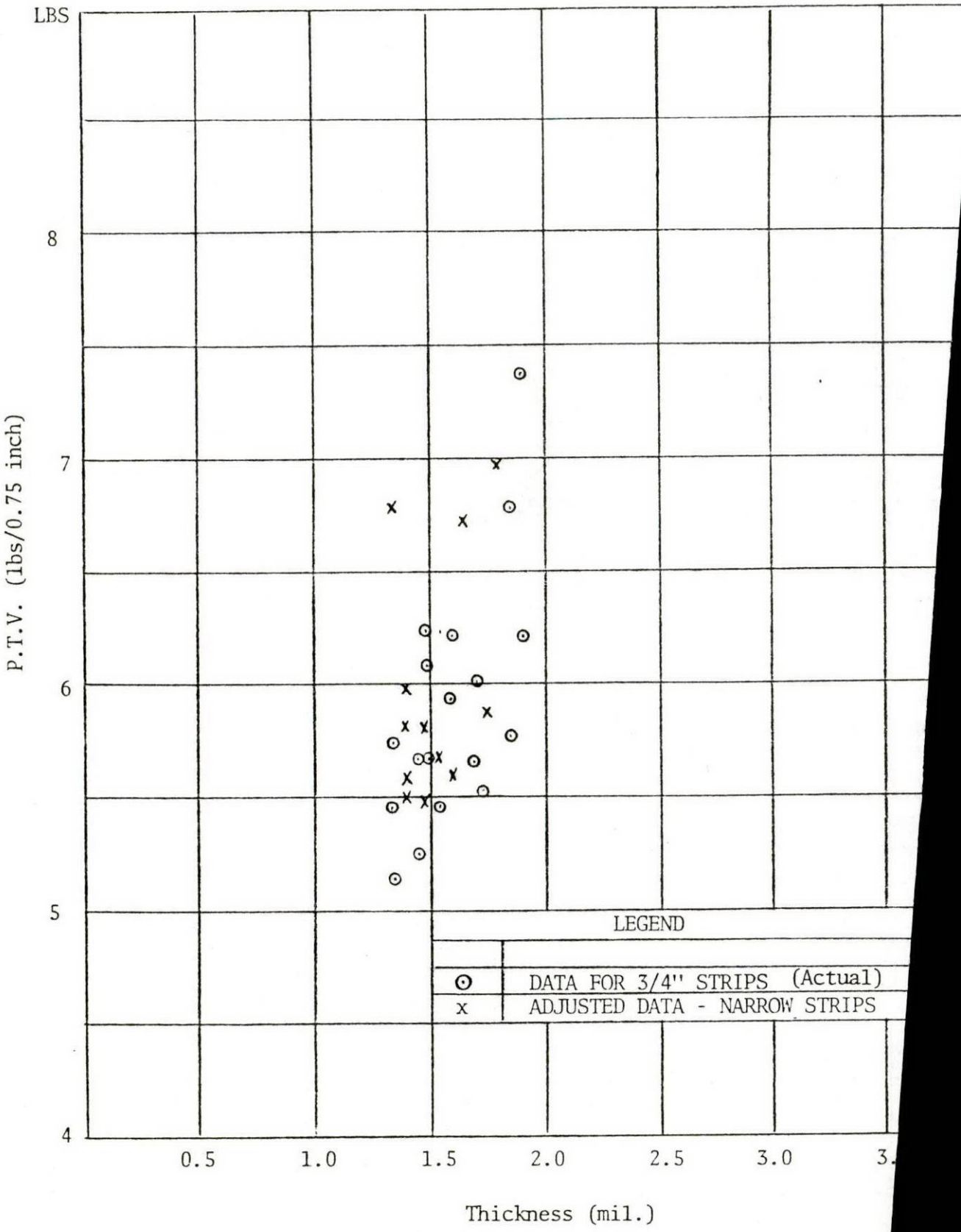


FIG. III Peel Test Values vs. Thickness of Bright Acid Copper. Data for 3/4" wide strips.



													4				5				4b	
	Unbaked		Baked		Unbaked		Baked		Unbaked		Baked		Unbaked		Baked		Unbaked		Baked		Baked After Air Aging	
Cav.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.
10	.593	.635	.528	.814	.845	.963	.749	.819	.814	.869	.782	.971	.450	.899	.015	1.092	.398	.787	.595	.757	0	1.12
10	.443	.776	.347	.636	.826	.863	.506	.530	.829	.855	.758	.794	.676	1.044	0	1.246	.526	.755	.639	.858		
11	.331	.690	.343	.597	-	-	.702	.770	.528	.529	.645	.788	.196	.780	0	1.077	.570	.721	.181	.736	0	1.25
11	.500	.691	.563	.731	.804	.830	.735	.820	.773	.869	.745	.841	.236	.947	.072	.971	.645	.699	.572	.622		
12	.281	.781	.227	.791	.651	.844	.638	.692	.504	.777	.598	.707	.014	.886	0	1.079	.258	.775	.421	.741	.212	1.097
12	.517	.741	.353	.722	.744	.768	.646	.773	.733	.833	.655	.696	.193	.962	0	1.056	.553	.653	.446	.715		
13	.477	.626	.339	.622	.681	.722	.738	.776	.685	.724	.699	.720	.122	1.071	0	1.067	.494	.863	.487	.663	0	1.538
13	.618	.676	.546	.712	.786	.804	.745	.801	.746	.757	.738	.814	.018	1.061	0	.995	.471	.788	.446	1.219		
Avg.	.470	.702	.406	.703	.760	.828	.682	.748	.701	.777	.702	.791	.163	.955	.011	1.073	.489	.755	.473	.789	.053	1.251

L-4

Research I
Session L

Reverse Osmosis Field Test: Closed Loop Recovery Of Zinc Cyanide Rinsewaters AES Research Project #45

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ABSTRACT

A field test was conducted to demonstrate closed-loop recovery of zinc cyanide rinsewater at a job shop plating facility. Since the zinc cyanide bath operates at room temperature with very little evaporation from the bath, reverse osmosis (RO) treatment of the rinsewater must be supplemented by evaporation in order to achieve the volume reduction necessary for return of a concentrate to the plating bath. The permeate from the RO unit was recycled to the first rinse after plating while the distillate from the evaporator was recycled to the second rinse after plating. Continuous, unattended operation of this system was demonstrated with no adverse effects on plating quality.

Spiral-wound PA-300 membrane modules were used in the RO unit. Periodic tests were conducted throughout the demonstration to characterize membrane performance under standard conditions. These tests indicated a gradual loss in membrane flux and rejection. After 3,000 hours of exposure to the rinsewater, the membranes were cleaned by flushing with a cleaning solution. The cleaning resulted in nearly complete restoration of flux and rejection. The gradual loss in membrane performance is thus attributable to fouling of the membrane by particulates in the rinsewater. Such fouling can be reduced by better pre-filtration and reversed by periodic cleaning.

The economics of the combined RO evaporation system were assessed for a system designed to provide rinsing equivalent to the present two-stage counter-current rinse at the demonstration site. The analysis showed that the total operating cost (including amortization) was somewhat less for the combined RO evaporation system than for evaporation alone. The minimum cost occurred for 90% water recovery in the RO system. However credits for rinsewater recovery were insufficient to completely off-set the total operating cost of the recovery system.

INTRODUCTION

Wastewater treatment technologies for the electroplating industry c be broadly classified as end-of-pipe destruction processes or in-plant r ery processes. The end-of-pipe destruction processes treat a total shop effluent to remove a mixture of heavy metals. At present it is neither nically nor economically feasible to recover and recycle metals from the of-pipe processes (1). On the other hand, in-plant recovery processes t rinsewater from a specific plating bath (or other operation) making it p sible to recover and return the heavy metals to the plating bath.

Because of the inherent disadvantage of end-of-pipe treatment -- lo of valuable plating chemicals, cost of treatment chemicals, cost of sluc disposal -- increasing attention has been focused on closed-loop recove methods. In many cases, the economics of closed-loop recovery have bee favorable resulting in rapid payback on the capital investment for reco equipment (2).

Aside from a few applications in which closed-loop recovery can be by countercurrent rinsing along, some technique must be used to remove solved plating chemicals from the rinsewater. Although other technique under development, evaporation, reverse osmosis (RO), and ion exchange the most commonly used processes for rinsewater recovery (1,3). Each techniques has particular advantages and disadvantages, and the best t or combination of techniques will depend on factors specific to each a cation.

A number of advantages can be cited for the use of RO in rinsewa recovery. These include low capital cost, low energy and operating c and minimal space requirements. However, there are also some limitat two major limitations for RO are:

1. The membrane modules deteriorate with time and require periodic replacement. The rate of deterioration depend on the type of membrane, the rinsewater pH and temperat and the concentration of other reactants in the rinsewa such as oxidants.

2. Reverse osmosis cannot produce a highly concentrated s for recyle to the plating bath. Thus for ambient temp baths, RO must be supplemented with some other concent technique, such as evaporation, in order to close the

To date, RO has been applied primarily to the recovery of nicke waters. For nickel, the rinsewaters are relatively mild in pH (4-6) in acceptable life for the conventional commercial membranes (cellu tate and aromatic polyamide). In addition, nickel baths operate at temperatures where substantial evaporation occurs, and closed-loop can be achieved with RO alone.

Several programs, jointly sponsored by EPA and AES, have been conducted to evaluate the applicability of RO to plating baths other than nickel (4,5,6). Laboratory tests were conducted with a variety of newly developed membranes and rinsewaters with extreme pH levels (6). These tests indicated that of the membranes tested, the PA-300 was superior to the other membranes for treatment of copper cyanide, zinc cyandie, and chromic acid rinsewaters. The PA-300 membrane has since been commercialized (currently designated TFC-PA; manufactured by Fluid Systems Division of UOP) and is available in a spiral-wound modular configuration.

A field test was undertaken to evaluate the PA-300 membrane module for recovery of zinc cyanide rinsewater under realistic conditions. Zinc cyanide was selected because of the large volume of zinc cyanide plating done by the industry and because the high pH of the rinsewaters would provide a "worst case" test of the membrane for resistance to alkaline conditions. Since the zinc cyanide bath operates at room temperature, it was necessary to use an evaporator to supplement RO treatment and achieve the level of concentration necessary for closed-loop operation. This paper presents and discusses the results of this field test.

METHODS AND MATERIALS

A mobile RO test system was leased from Abcor, Inc. and an evaporator was eased from Wastesaver Corporation for the duration of the field test. These wo units were installed on an automatic rack, zinc cyanide plating line at ew England Plating Co. in Worcester, Massachusetts. The overal schematic of he installation is shown in Figure 1. Feed to the RO system was withdrawn from inse Tank #1 and separated by the RO system into a permeate stream and a concentrate stream. For purposes of design, it was assumed that the RO system would roduce about 2 gpm of permeate and would operate at 90% conversion. (Conversion is defined as the ratio of permeate flow to feed flow.) Thus the RO system uld be fed at the rate of 2.22 gpm and would produce concentrate at the rate 0.22 gpm. The permeate was returned to Rinse Tank #1 and the concentrate s fed to the evaporator.

Since dragin and dragout were essentially identical for the plating bath the rate of evaporation was negligible, there was no room in the plating h for a concentrate stream. If the evaporator were fed only RO concentrate, would have to evaporate it to dryness in order to prevent eventual overflow the bath. In order to prevent precipitation of plating chemicals in the porator a 1 gpm purge stream was circulated from the plating bath through evaporator and carried the plating salts introduced with the RO concentrate k to the plating bath. That is, the evaporator concentrate was higher in centration than the plating bath by the amount added by the RO concentrate. distillate from the evaporator was collected in a holding tank and added controlled rate to Rinse Tank #2. A float valve operating off the level inse Tank #1 insured that the rate of RO concentrate production was exactly nced by the rate of distillate returned to Rinse Tank #2. A slight excess istillate was produced to insure that the holding tank would always remain ; and the excess was permitted to overflow into the plating bath (0.02 gpm). steam rate was cut back to minimize overflow from the holding tank.

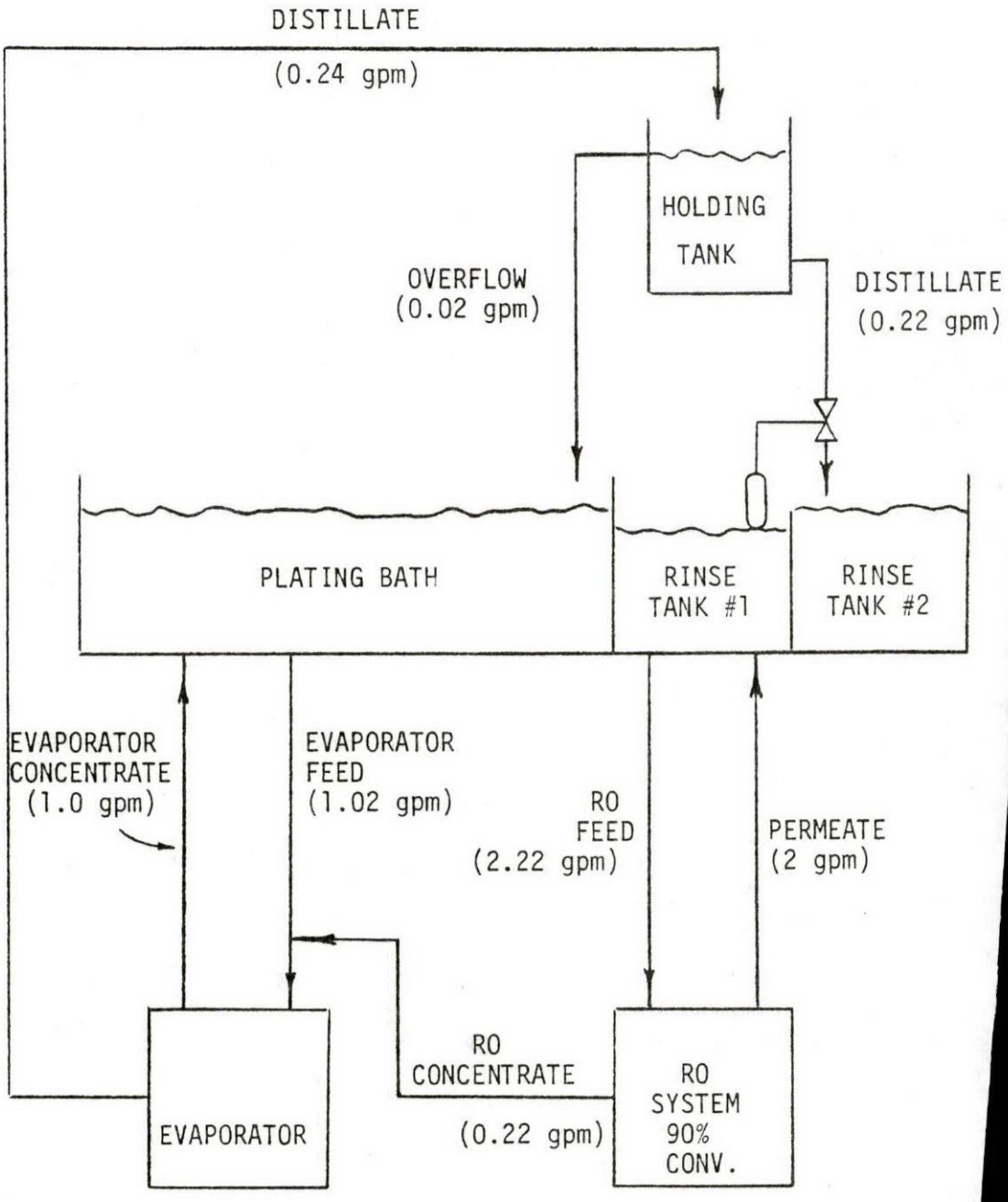


Figure 1. Overall Schematic of RO/Evaporator Operation

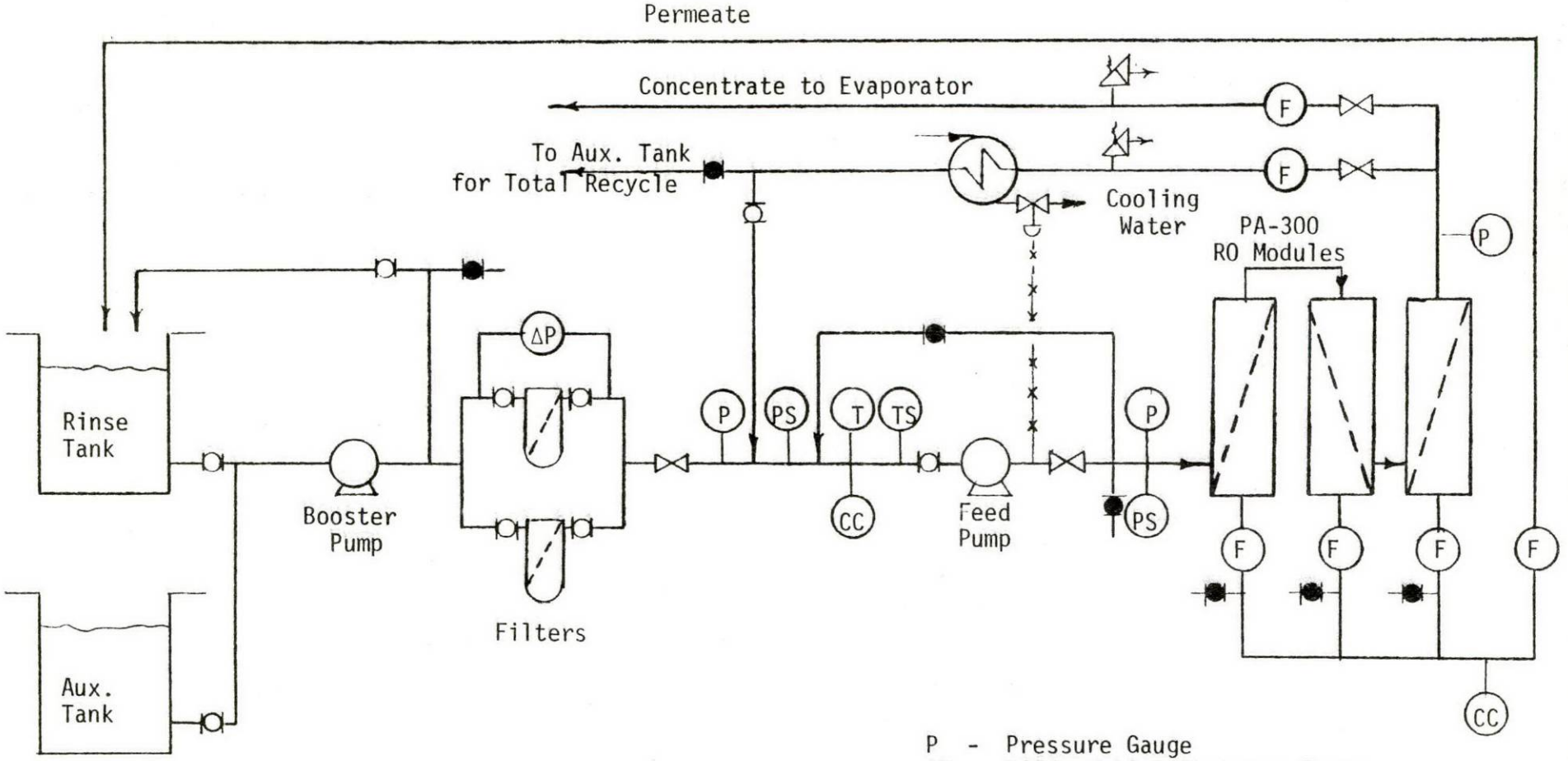
A flow schematic of the RO system is shown in Figure 2. Feed from the first rinse tank was withdrawn by a booster pump and passed through two string-would cartridge filters in parallel. Both 1-μ and 20-μ filters were used at different times during the field test. Excess flow from the booster pump was returned to the rinse tank. After pre-filtration, the feed was pressurized to 700 psi with a multi-stage centrifugal feed pump and passed through three 4-inch diamter, spiral-wound, PA-300 modules arranged in series. Most of the concentrate from the third module was recycled to the suction of the feed pump in order to maintain the required feed flow rate through the modules. A heat exchanger in the recirculation loop removed heat generated by the energy input of the pumps. A small flow of concentrate from the third module was fed to the evaporator (see Figure 1), and the permeate from the three modules was combined and returned to the first rinse tank. The instrumentation and controls for the RO system are shown in Figure 2.

In order to characterize membrane performance with a standard feed solution, the RO system was periodically operated in a total recycle mode using the auxiliary feed tank. For this mode of operation, the booster pump recycle line was closed off, the concentrate line to the evaporator was opened, and the permeate was returned to the auxiliary tank rather than the rinse tank. The standard solution (generally a portion of plating bath diluted to 10% by volume of original bath strength) was charged to the auxiliary tank and the system was operated with total recycle until steady state was achieved. At steady state, the permeate flow rate for each module was measured, and samples of the feed and permeate from each module were obtained for analysis.

Typical operating conditions for both closed-loop and total recycle were:

Feed Pressure	700 psi
Recirculation Flow Rate	10 gpm
Temperature	70-90°F
Concentrate Flow Rate	0.2 gpm (closed-loop only)

The flow schematic for the evaporator is shown in Figure 3. Steam was fed rough a pressure reducing valve to a tube bundle submerged in the boiler sec-on of the evaporator, and steam condensate was returned to the plant boiler. r most installations, a cooling tower is used to cool the water which is circulated through the condenser section of the evaporator. However, for is installation it was more convenient to use recirculated chilled water since was readily available at the installation site and the chiller had sufficient ess capacity. The evaporator was maintained under vacuum by circulating er through an eductor. Cooling water was added to the eductor tank to remove energy input of the eductor circulation pump. Feed to the evaporator was trolled by a level switch (LS) and solenoid valve. Upon low level signal, solenoid valve opened and feed was drawn by vacuum into the evaporator. distallate from evaporation of the feed condensed, was collected in a tray w the condenser, and was continuously pumped back to the second rinse after ing (see Figure 1). The concentrate from the boiler section of the evaporator continuously pumped back to the plating bath.



P - Pressure Gauge
ΔP - Differential Pressure Gauge
PS - Pressure Switch
T - Temperature Gauge
TS - Temperature Switch
F - Flow Meter
CC - Conductivity Cell

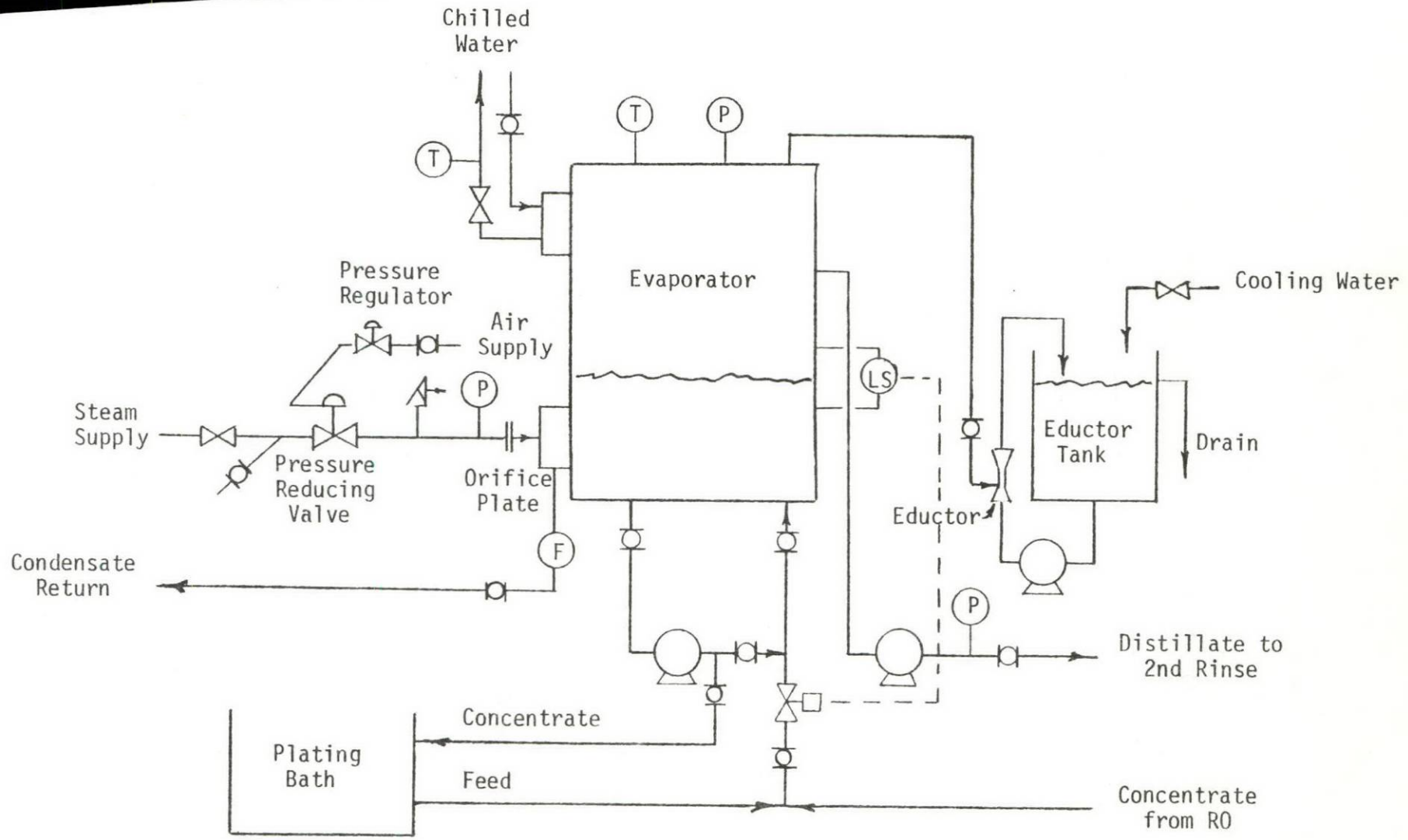


Figure 3. Flow Schematic for Evaporator

Typical operating conditions for the evaporator were:

Vacuum	26-27 in. Hg
Temperature	100-110°F
Steam Pressure	<5 psi
Concentrate Flow Rate	1 gpm

During the field test, the RO modules were cleaned using a cleaning sequence recommended by the membrane manufacturer. The modules were fir flushed with 50 gal of water to remove the plating chemicals. A 0.1% by volume solution of Triton X-100, a non-ionic surfactant, was prepared ar recirculated through the modules at a pressure of 700 psi, a flow rate o 10 gpm, and a temperature of 120°F for 45 minutes. After flushing with another 50 gallons of water, a 2% citric acid solution was prepared and adjusted to pH 3.0 with ammonium hydroxide. This solution was recircul through the modules at the same condions and for the same time as the T X-100. Following the citric acid cleaning the system was again flushed water and returned to treatment of zinc cyanide rinsewater. Since the 300 membrane is rapidly degraded by chlorine, all water used for flushi and preparing cleaning solutions was dechlorinated by the addition of s sulfite.

Samples collected during the field test were analyzed for zinc (a absorption), free cyanide (selective ion electrode), total solids (gra determination of residue), conductivity (conductivity bridge), and pH

The nominal composition of the plating bath was:

Zn (as metal)	20,000 mg/l	2.7 oz/gal
CN (as NaCN)	60,000 mg/l	8.0 oz/gal
Caustic	75,000 mg/l	10.0 oz/gal
Brightener (700 Special)	4 ml/l	4 gal/1000 gal

In addition to these compounds, polysulfide was regularly added to th purification, and the bath also contained a large quantity of carbona total solids concentration of the bath was in the vicinity of 350,00 (35% by weight).

RESULTS AND DISCUSSION

Field activities covered the months of June through December o During this time, the system was operated primarily in the closed-l shown in Figure 1. However, closed-loop operation was periodically to conduct total recycle tests on the RO system. The performance o is generally assessed in terms of the module flux (rate of permeate per unit membrane area) given in gallons per ft^2 per day (gfd) and (defined for a particular dissolved species as one minus the ratio to feed concentrations) given in percent. Since both flux and reje

on feed concentration, it is necessary to conduct RO performance tests at a fixed feed concentration in order to be able to accurately interpret trends in the flux and rejection data. During closed-loop operation the feed concentration to the RO system can vary considerably (depending on the parts being plated and their dragout); hence total recycle tests at a fixed feed concentration (10% of bath strength) were periodically conducted to accurately assess trends in the RO system performance. System performance was monitored less rigorously during operation in the closed-loop mode.

The total operating time for the field demonstration (time during which permeate was being produced) was approximately 1000 hours. The total exposure time of the modules to the rinsewater, however,was about 4,200 hours. The longer exposure time reflects the system down-time during which the modules were sitting in contact with the concentrated zinc cyanide rinsewater. Various factors contributed to the system down-time, including: electro-mechanical failure of various system components, high or low alarm shut-down of the system, various problems with the plating line (unrelated to the recovery system), and weekends and holidays. The total exposure time is probably more significant than operating time in controlling the degree to which the modules are attached chemically by constituents in the rinsewater (e.g., caustic). On the other hand, operating time is more significant in controlling the degree to which the modules become fouled with particulates in the feed. Correlations presented below are based on exposure time. However, the operating time was reasonably evenly spread over the test program, and correlations on an operating-time basis would be similar.

osed-Loop Operation

The RO/evaporator system was designed to operate continuously, with no erator attention, between start-up Monday morning and shut-down Friday afternoon. However, during most of the field test program, various electro-mechanical d other problems occurred which prevented unattended week-long operation. ch failure generally resulted in several days down time because of the logics of getting project personnel to the field site, diagnosing the problem, and plementing remedial action. Eventually these problems were solved and week-ng unattended operation was demonstrated.

During demonstration of the closed-loop system, no adverse effects were ed on the quality of the plated parts. However, the rinse tanks after zinc ting were followed by an acid dip, a flowing rinse, and other surface finish- steps before the parts were finally inspected. Therefore the degree of sing following zinc cyanide plating was probably not of critical importance quality control.

Both the RO system and evaporator were under-designed as a direct replace- for the two-stage countercurrent rinse at a nominal rinsewater flow rate gpm (see "Economics" below). The system design reflected limitations im- d on program costs, availability of PA-300 modules at the time the system fabricated, and lack of design data for the zinc cyanide application. Never- ess, the system was of sufficient size to obtain meaningful design and mic data.

RO performance during closed-loop operation was monitored by measurin the productivity of each module (rate of permeate production) and by monit the conductivity of the combined RO permeate. In general, the productivit during closed-loop operation was similar (but slightly higher) than the pr ductivity during the total recycle tests (see discussion below). The conc of the combined permeate generally ranged between 2,000 and 4,500 μ-mhos/c This is equivalent to a total solids concentration of approximately 1,000 2,000 mg/l.

The evaporator was operated at about one-half of its rated capacity gal per hour vs. a capacity of 25 gph). Samples of distillate and evapor concentrate were obtained and analyzed for zinc, free cyanide, total soli conductivity and pH. The results of these analyses are presented in Tabl During closed-loop operation at the time the samples were taken, a stream about 1.5 gpm from the bath was circulated through the evaporator and bac the bath in order to prevent precipitation of plating salts in the evapor Thus, the evaporator was operating on a feed very similar in composition bath and producing a concentrate which was more concentrated than the pl bath. (In addition, the plating bath during this test appears to be sig cantly higher in zinc than the nominal level given above). The quality tillate produced was quite good. Zinc and total solids concentrations w below their respective detection limits, but cyanide, conductivity, and xide ion were detectable. The rejections or removal efficiencies were high; particularly for zinc and total solids. The quality of distillate considered quite suitable for final rinsing.

Total Recycle Tests at 10% of Bath Concentration

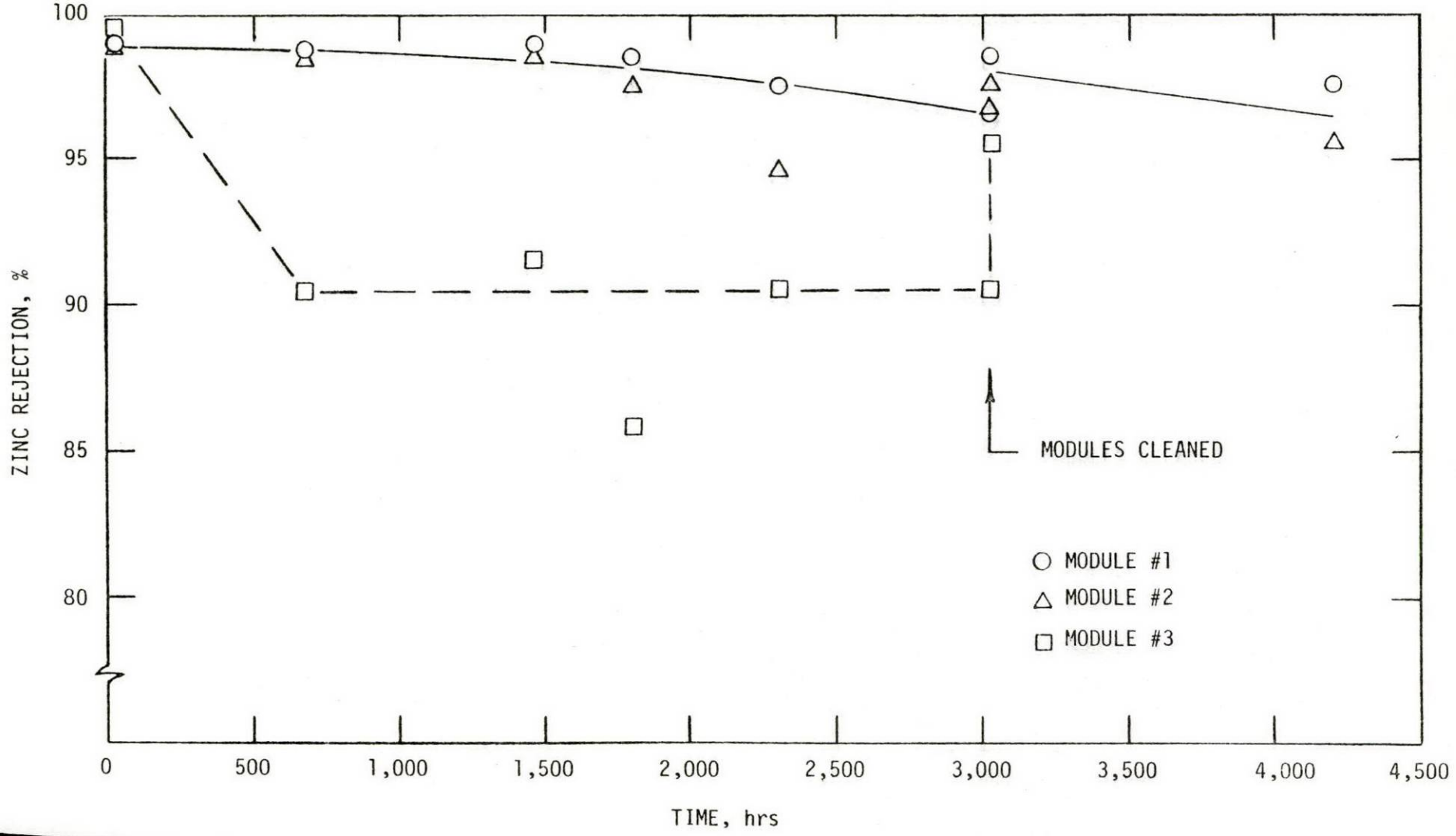
Total recycle tests were periodically conducted in order to evalua membrane module performance under well defined conditions of feed conce tration (10% of bath concentration),pressure (700 psi), temperature (75 85°F), and recirculation rate through the modules (10 gpm). Results fo as a function of time are shown in Figure 4. The flux was calculated the measured permeate flow rate using a surface area of 70 ft^2 per modu (Actual surface areas measured after the field test for Modules #2 and were 73 and 69 ft^2, respectively.) The data were corrected to 75°F us the inverse relation between flux and water viscosity.

For Modules #1 and #2 the flux levels were nearly identical throu the field demonstration. The flux gradually declined from 13 gfd to over the first 3,000 hours. Following cleaning at 3,000 hours, the f increased to 12 gfd, which is very close to the original level. Thus cleaning procedure employed was quite successful in restoring the flu It may therefore be concluded that the major reason for flux decline fouling of the membranes.

TABLE 1. REJECTION RESULTS FOR EVAPORATOR DURING CLOSED-LOOP OPERATION

	CONCENTRATE	DISTILLATE	REJECTION
Zinc	46,000 mg/l	<0.1 mg/l	>99.9998%
Cyanide	90,000 mg/l	35 mg/l	99.96%
Total Solids	409,000 mg/l	<5 mg/l	>99.999%
Conductivity	160,000 mg/l	300 mg/l	99.81%
pH	13.4	10.3	

NOTE: Operating conditions 104°F, 27 in Hg vacuum, 17% conversion.



exposure time as determined by total recycle tests at 10% of bath.

Results for Module #3 are also presented in Figure 4 (dashed line). The flux starts at a significantly higher level (20 gfd) but declines more rapidly to a value of 5 gfd at 3,000 hours. The cleaning procedure was ineffective in restoring the flux of Module #3. Because of its low flux and low rejections (discussed below) Module #3 was removed from the system at 3,000 hours.

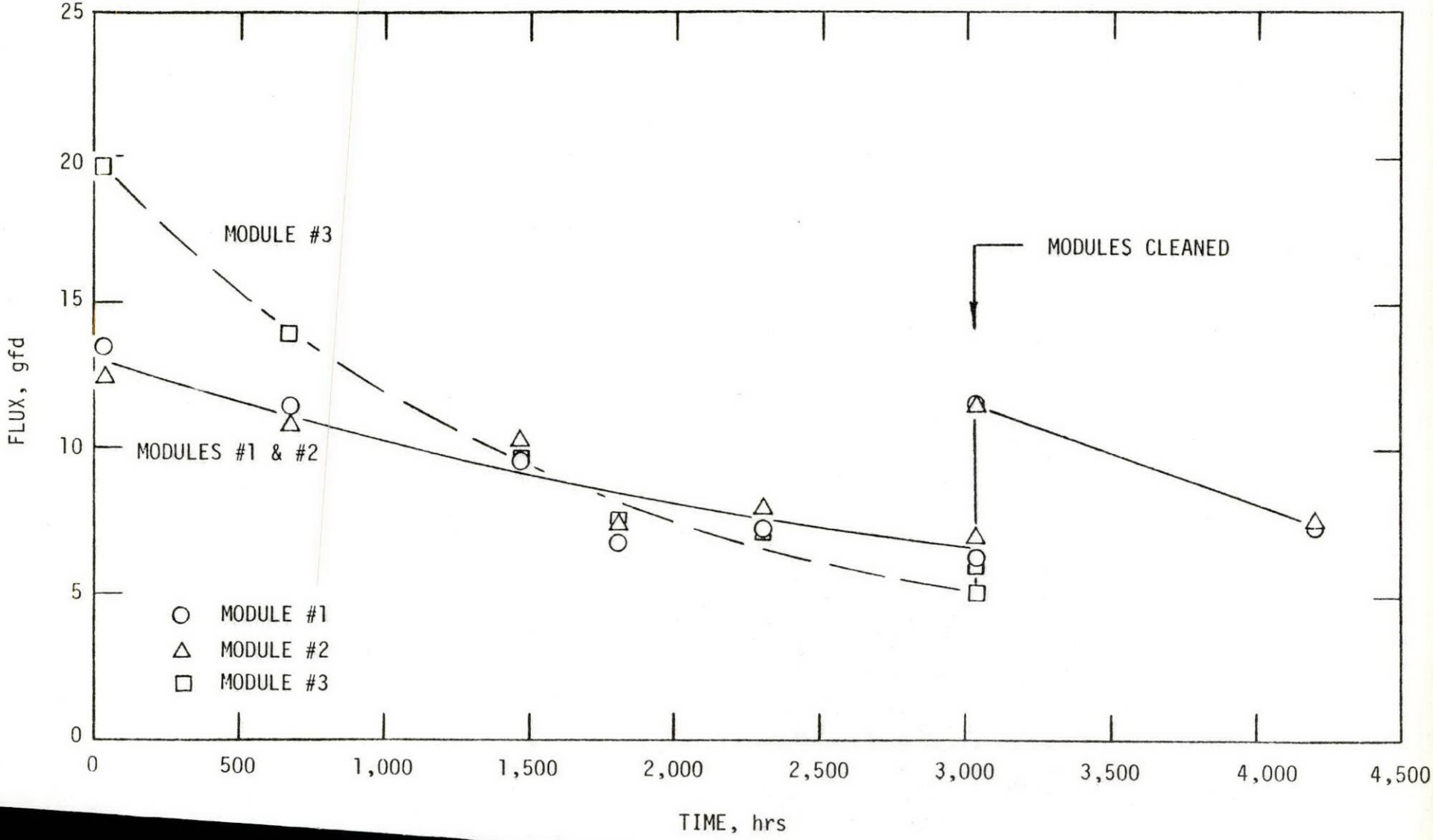
After cleaning, the system was returned to closed-loop operation on the actual rinsewater. During the next 1,200 hours the flux for Modules #1 and #2 declined to about 7 gfd. The rate of flux decline was more rapid during this time period since a coarser grade (20μ vs 1μ) cartridge filter was used to pre-filter the feed during this segment of the demonstration.

Results for zinc rejection during the field demonstration are shown in Figure 5. For Modules #1 and #2 the zinc rejections agree reasonably well and are correlated with a single curve (solid line). The zinc rejection declined gradually from an initial value of 99% to 97% after 3,000 hours. Upon cleaning, the rejection for Module #1 increased to nearly 99% while the rejection for Module #2 increased to about 98%. Thus the cleaning procedure was successful in restoring the zinc rejection. Therefore it is reasonable to conclude that the loss of zinc rejection is primarily the result of membrane fouling. After cleaning the rejection again declined as fouling occurred.

For Module #3 the zinc rejection dropped off rapidly to a value of 90% after only 700 hours and remained reasonably constant between 700 and 3,000 hours. Cleaning produced a significant increase in rejection (from 90 to 95).

The rejection of free cyanide is shown in Figure 6. Again the results for Modules #1 and #2 agree quite well throughout the test. For these modules the cyanide rejection declined slightly -- from 98% to 97% -- during the first 3,000 hours. Cleaning had little effect on the rejection level. However, because of the small loss in rejection, cleaning would be anticipated to have only a minor effect on rejection levels. Following cleaning, the cyanide rejection declined at a more rapid rate, probably as the result of increased rate of fouling.

The cyanide rejection results for Module #3 are also shown in Figure 6. As for zinc, the cyanide rejection dropped quite rapidly, from 99 to 85%, during the first 700 hours and appeared to stabilize at about 85% until 3,000 hours. The data point at 3,000 hours (93% rejection) indicates a potential recovery in rejection before cleaning. Since no similar recovery was observed for zinc and total solids rejections, it is possible that the cyanide rejections at 3,000 hours could be attributed to a sampling or analytical error.


25
20
15
10
5
0
FLUX, gfd
MODULE #3
MODULES CLEANED
MODULES #1 & #2
MODULE #1
MODULE #2
MODULE #3
0
500
1,000
1,500
2,000
2,500
3,000
3,500
4,000
4,500
TIME, hrs

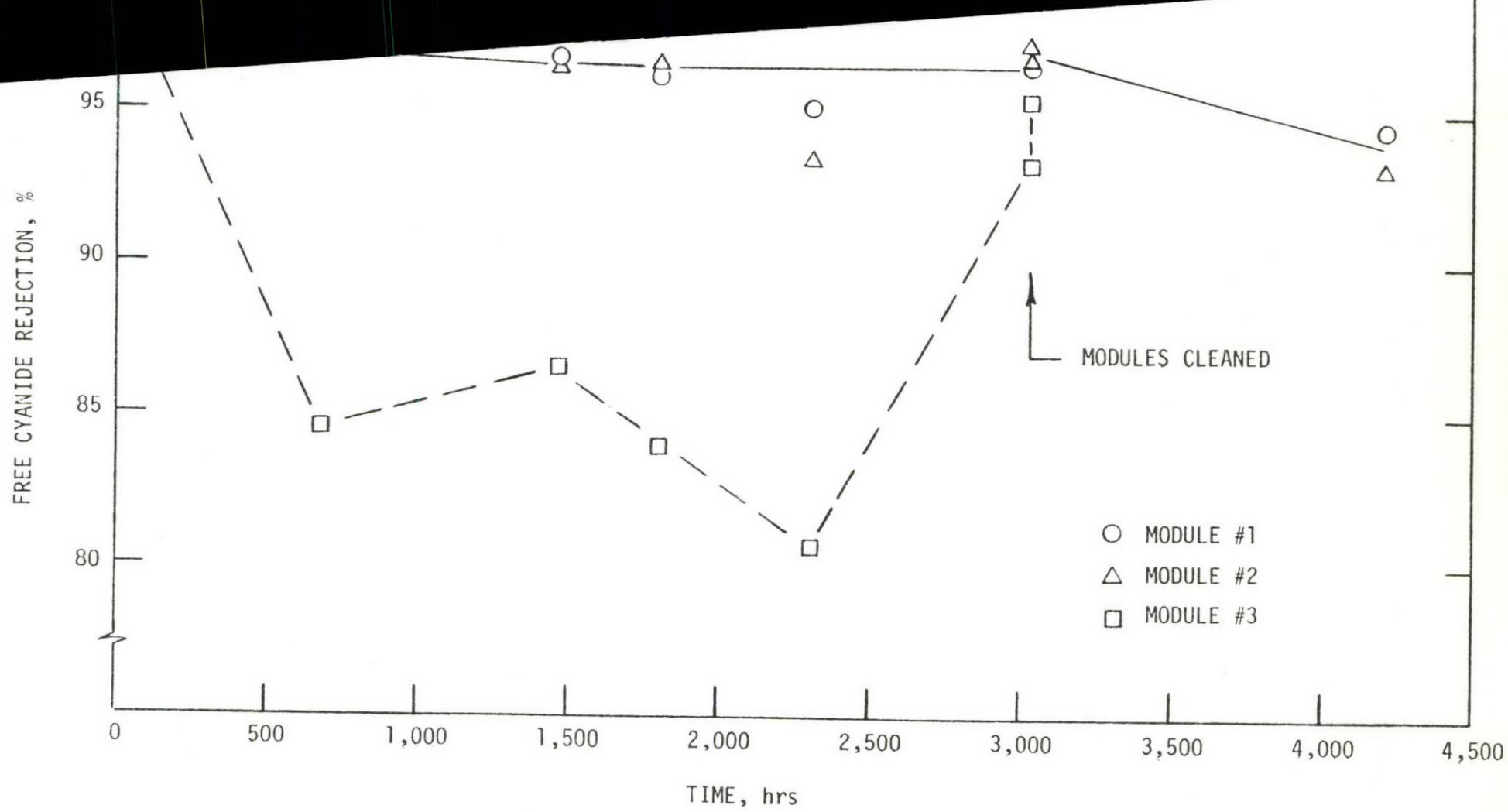


Figure 6. Free cyanide rejection vs. exposure time as determined by total recycle tests at 10% of bath.

Total solids rejections are presented in Figure 7. The results for Modules #1 and #2 are, as before, almost identical. There was a gradual loss in total solids rejection for Modules #1 and #2 from 95% initially to 90% after 3,000 hours. Cleaning at 3,000 hours produced an apparent loss in rejection. (A similar loss was also noted for conductivity rejection.) During operation after cleaning, the rejection increased to 90% -- the same level as before cleaning. Thus the loss of rejection upon cleaning was only temporary. Indeed, since the results of Figures 4-6 indicate fouling and a decline in membrane performance between 3,000 and 4,200 hours, it is reasonable to postulate that a similar decline in total solids rejection occurred during this period. By virtue of the fact that the rejection at 4,200 hours is the same as at 3,000 hours, it can be concluded that the cleaning actually improved the total solids rejection. The observed loss in rejection is probably the result of an interaction between the citric acid cleaning solution and the membrane surface. Similar results have been observed with citric acid in cleaning tests conducted by the manufacturer (7). These tests consistently showed a los in rejection after cleaning, but the rejection then increased over a rela tively short period (5-24 hours) to the level expected for a clean module The mechanisms of this interaction is not well understood, but the rejec loss appears totally reversible by extensive flushing or by returning th system to operation on the normal feed. Thus the most reasonable explanation of the total solids rejection behavior is that, when the system w returned to normal operation after cleaning, the rejection increased to level probably close to 95% within 24 hours and then decreased gradually to 90% at 4,200 hours as fouling of the module occurred.

The total solids rejections for Module #3 are quite similar to the zinc and cyanide rejections for this module. The rejection decreased f 95% to about 80% during the first 700 hours and remained at about 80% u the module was removed at 3,000 hours. Cleaning produced no significan change in total solids rejection for Module #3.

The close agreement between the results for Modules #1 and #2 wou be anticipated for two identical modules operated in series. By compar son the results for Module #3 are quite poor. Since the system conver per pass was low (high recirculation flow relative to permeate flow) t feed concentrations to the three modules were approximately the same; therefore a higher feed concentration would not account for the poor performance of Module #3.

A similar rapid loss in performance has been occasionally noted f some of the earlier PA-300 modules used in water desalination (7). Th problem was traced to a procedure used in manufacturing the modules. procedure has since been changed and the problem thereby eliminated. ever, the modules used in this field test were manufactured before th change, and it is believed that Module #3 was defective from the outs of the test.

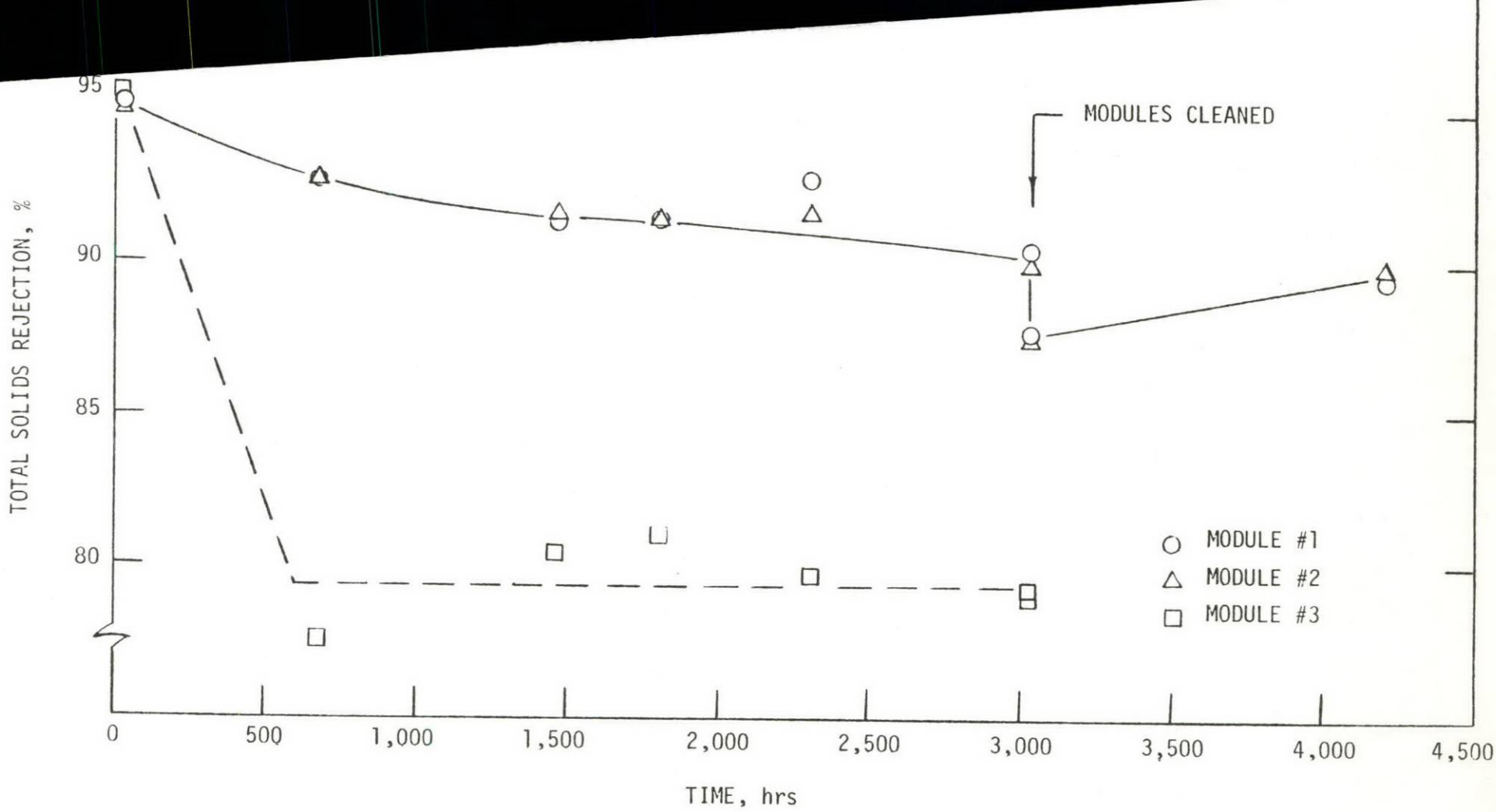


Figure 7. Total solids rejection vs. exposure time as determined by total recycle tests at 10% of bath

The level of suspended solids in the zinc cyanide bath was high comp to the levels observed for copper cyanide baths (5). A purifier (polysul was regularly added to the zinc cyanide bath and produced a mud-like sluc that was removed by filtration. Some of this sludge was carried over int the rinse tanks and thus into the RO system. During the first 3,000 hour the test, 1μ cartridge filters were used and had to be changed approximat once per week (assuming 100 operating hours per week). After about 3,000 hours, 20μ cartridge filter were used. The service time for the coarser filters was substantially longer (estimated service time = one month) but rate of fouling of the modules was greater with the coarser filters. It recommended that two cartridge filters in series -- a 20μ filter followed a 1μ filter -- be used for pre-filtration of zinc cyanide rinsewater.

Following the field test Module #2 was cut open and unwound for inspection. The membrane was fouled with a thin layer of sulfide sludge with the degree of fouling increasing toward the center of the module. layer could be very easily wiped from the membrane surface. During clea at 3,000 hours, a distinct odor of H_2S was noted during recycling of the citric acid solution. This is presumed to be the result of solubilizati some of the sulfide foulant. This suggests that the ammoniated citric a was the active ingredient in the cleaning procedure and that the Titron surfactant could be eliminated. Cleaning agents other than citric acid work as well or better and should be tested. Of particular interest wo be the use of oxidizing agents to oxidize the sulfide foulant layer. W the membrane is succeptible to rapid attack by some oxidizing agents su chlorine, it has been shown to be resistant to others such as chlorine dioxide and chromic acid (6,7).

In addition to fouling of the membrane, examination of the module ternals revealed some possible deterioration of the membrane backing material. Samples of the membrane and backing were returned to the ma facturer for examination, the finding of which confirmed that the back had been deteriorated, probably as a result of the high concentrations hydroxide ion in the rinsewaters (7). However, it is not clear what e deterioration of the backing would have on membrane module performance No gross effects on performance were observed during the field test. Substitute backing materials could be used, but a development program be required to commercialize the PA-300 on a more resistant backing.

Total Recycle Tests at Other Feed Concentrations

Following initial start up of the RO system, total recycle tests conducted to determine the dependence of flux and rejection on feed c tration. Tests were conducted at various dilutions of the plating ba ranging in nominal concentration from zero to 20% of the bath concent

Flux results as a function of the total solids concentration of feed are shown for Modules #1 and #2 in Figure 8. The results for t two modules are in very good agreement. (Results for Module #3 were

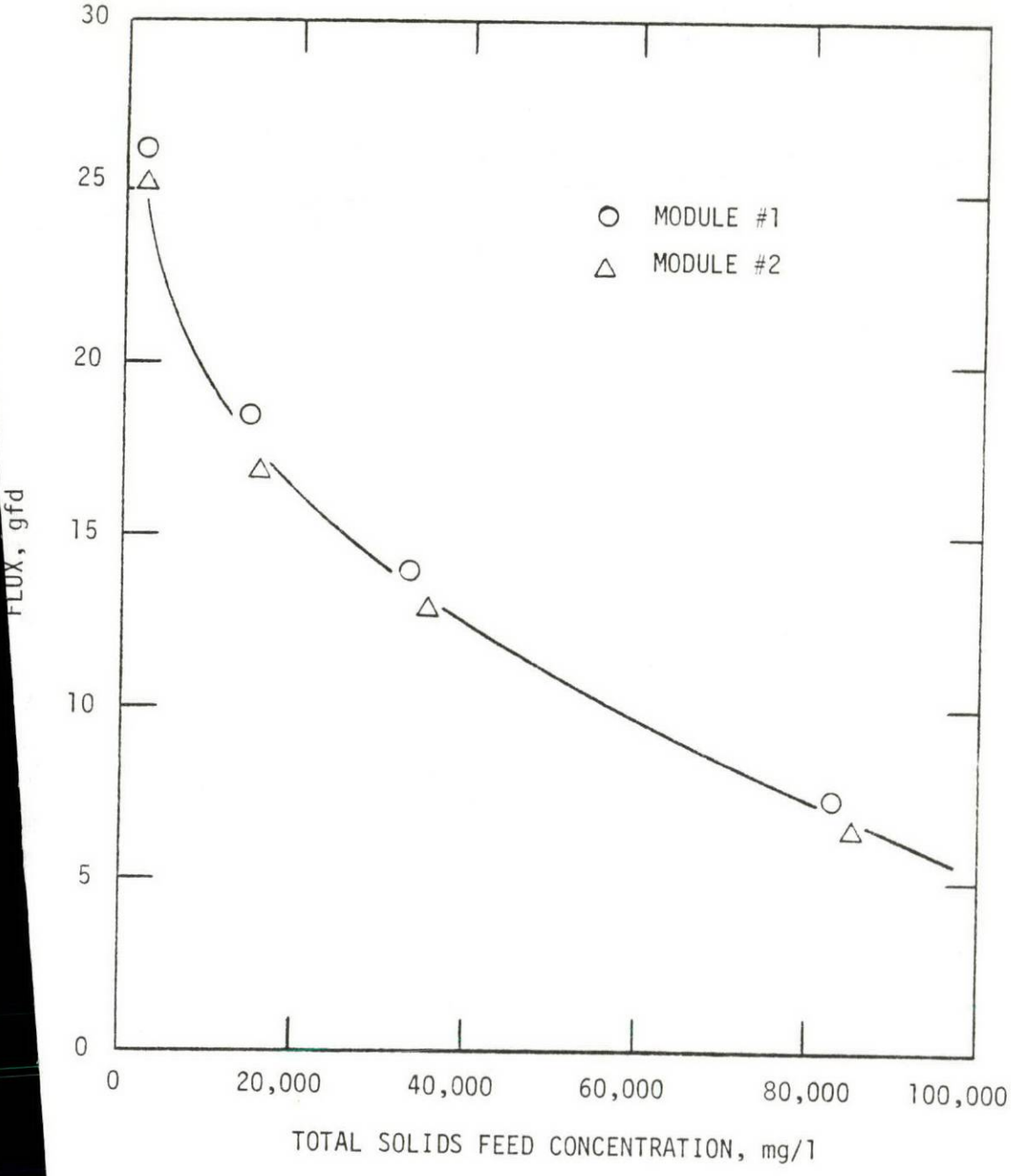


Figure 8. Dependence of flux on feed concentration.

consistent with those shown in Figure 8 and have not been included). As expected, the flux decreases with increasing feed concentration and approaches a level generally considered uneconomical at a feed concentrat in the vicinity of 100,000 mg/l. By comparison the bath concentration is approximately 350,000 mg/l in total solids. These data illustrate the problem of using RO to achieve very high concentrations. The data presen in Figure 8 can be used in optimizing the degree of concentration that should be obtained in the RO system prior to evaporation.

Rejection as a function of the total solids concentration in the fee is shown in Figure 9 for Modules #1 and #2. The zinc, cyanide, and total solid rejections remain essentially constant at 99%, 98%, and 95%, respec tively for feed concentrations below about 40,000 mg/l total solids. At higher feed concentrations the rejections drop off as expected.

Economics

One of the main objectives of conducting a field demonstration is t provide a basis for evaluating the economics of the process. Figure 10a shows the flow schematic for the original two-stage countercurrent rinsi system. The rinsewater flow rate was measured at 2.0 gpm. The rate of dragout from the bath was estimated by turning off the rinsewater and measuring the buildup of zinc and total solids in the first rinse as a function of time. The calculated dragout rate was 0.01 to 0.015 gpm. However the parts being plated during this determination were flat and free-draining and a somewhat higher dragout rate of 0.02 gpm was consid more typical for purposes of design. Given these flow rates and ideal mixing in the rinse tanks, the zinc concentration is reduced from 20,00 mg/l in the bath to 2.0 mg/l in the final rinse.

Figure 10b shows the flow schematic, flow rates (in gpm), and zinc concentrations (in mg/l) for an RO/Evaporator system designed to give the same zinc concentration in the final rinse. The flow rates given Figure 10b are for 90% water recovery in the RO system (ratio of syste permeate to system feed: 5.85/6.5 = 0.90). All of the concentrate fr the RO system is converted to distillate in the evaporator, and an equ flow (0.65 gpm) of plating bath is used to purge the concentrated chem from the evaporator and prevent precipitation. The stream returning the bath is about 3% higher in concentration than the bath, and precip in the evaporator would occur only if there were some constituent in bath (e.g., carbonates) at a concentration very close to its solubili limit. The permeate and distillate flow rates given in Figure 10b (5 0.65 gpm, respectively) are considerably greater than the correspondi flows in the system demonstrated (1-1.5 and 0.2 gpm, respectively).

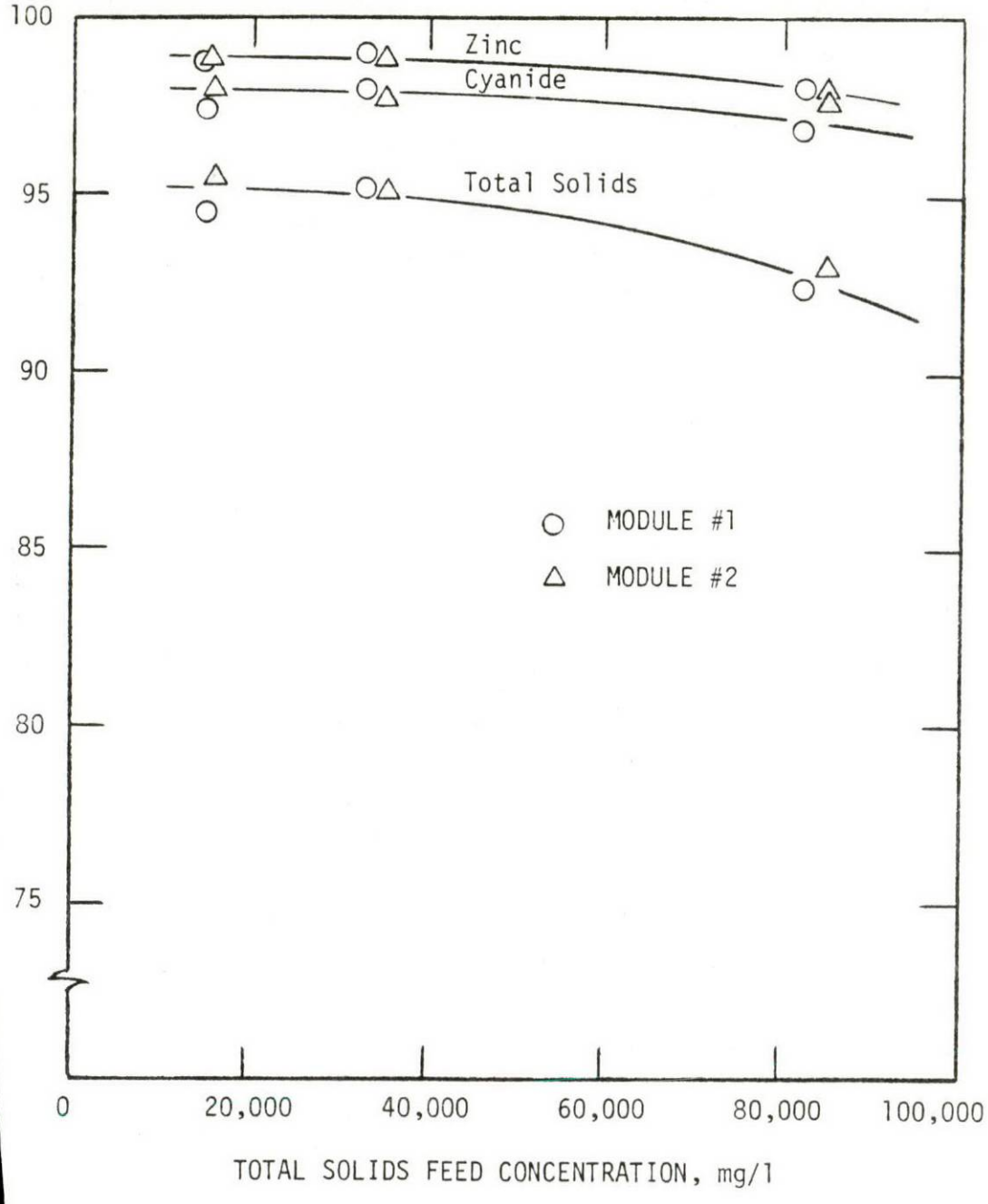
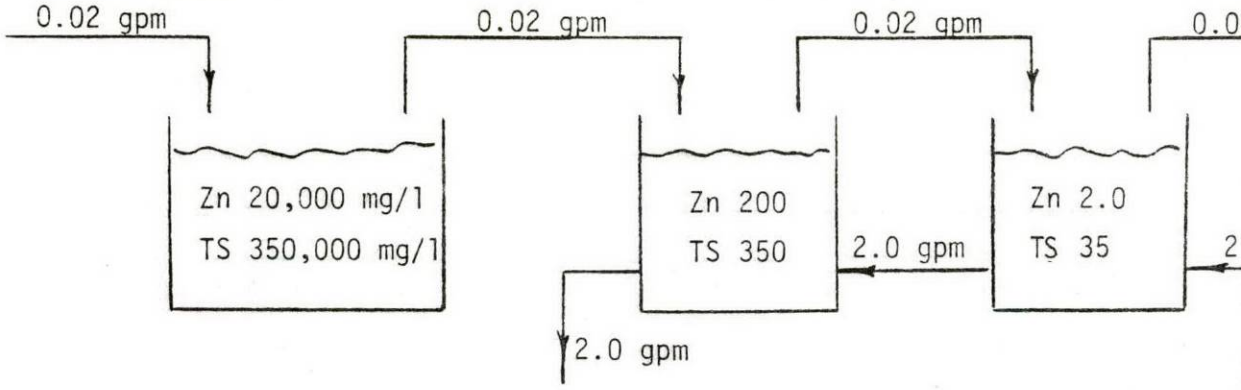
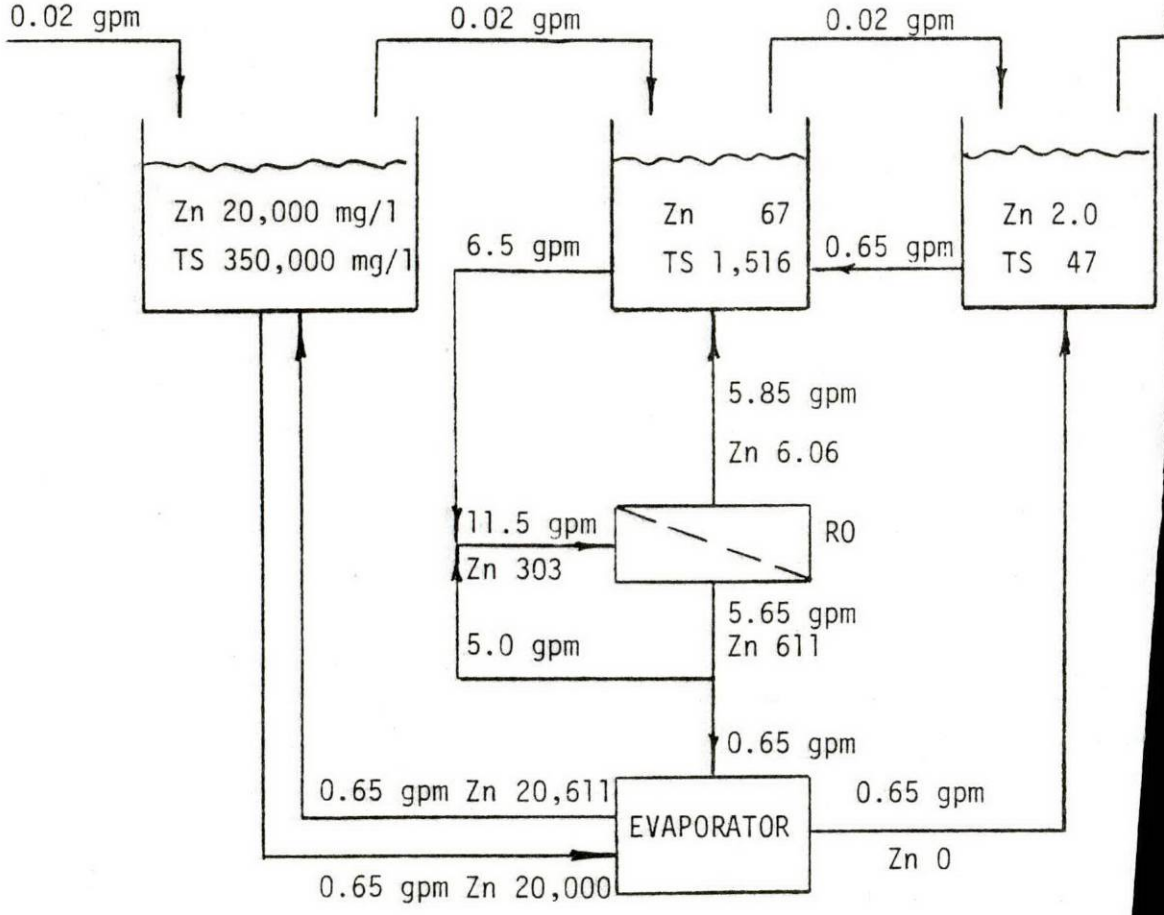


Figure 9. Dependence of rejection on feed concentration.



a. Present rinsing system



b. Closed-loop rinsing system

Figure 10. Flows and concentrations for open and closed-loop rinsi

One of the most important of design criteria is the flux for the RO system. The flux depends on the operating pressure, temperature, feed concentration, and the flow rate of concentrate from the module. The system would be designed to operate at 800 psi, maximum recommended operating pressure for the modules. The design temperature would be 77°F. At higher temperatures the flux would increase, and the rejection would remain essentially the same. Thus the performance of the RO system would improve with increasing temperature, although the membrane life may be shortened. For the design case shown in Figure 10b (i.e. 90% RO system conversion) the total solids concentration in the feed to the first RO module is calculated to be 5,500 mg/l and the concentrate withdrawn from the final module is 10,600 mg/l. Thus the average feed-side total solids concentration is about 8,000 mg/l. From Figure 8 the flux for a new module at this feed concentration would be about 20 gfd (at 700 psi and a recirculation flow rate of 10 gpm). From Figure 4 the flux declines to about half of its initial value over an operating period of about 700 hours (exposure time: 3,000 hours). Thus it would seem reasonable to design the system for a minimum flux of 10 gfd. At this flux the rate of permeate production is approximately 0.5 gpm for each module (area = 70 ft^2). Based on the recommended ratio of concentrate flow to permeate flow (10 to 1) the rate of recirculation for the RO system would be 5 gpm as shown in Figure 10b. This recirculation rate is only half of that used during the field demonstration and could result in a slightly lower flux than measured; however the higher operating pressure -- 800 vs 700 psi -- would compensate by increasing the flux.)

Rejection is also an important parameter in the design. Based on the results of Figure 9 at a total solids concentration of 8,000 mg/l, the zinc and total solids rejections would be 99% and 95%, respectively. From figures 5 and 7, fouling of the modules can be expected to result in a decrease in zinc rejection from 99 to 98%. Thus, for the design, the minimum zinc and total solids rejections were selected as 98% and 90%, respectively.

The RO system can be designed to operate at any desired conversion within reason. At low conversion the capital and operating costs are dominated by the evaporator; at high conversion, capital and operating costs are dominated by the RO system. At some intermediate conversion, the total operating cost should pass through a minimum. Material balance calculations were performed for the system of Figure 10b using various RO system conversions. (Results are shown only for the 90% conversion case.) Capital and operating costs were then developed for each conversion in order to determine the optimum.

Table 2 gives the capital costs for the RO unit, the evaporator unit, and the total system, for various RO system conversions. The material balance relationships and the RO module rejection were used to calculate the permeate flow and the evaporator capacity required to give a zinc concentration of 2 mg/l in the final rinse. At zero conversion in the RO system (i.e. no RO system) the entire treatment load is handled by the

TABLE 2. CAPITAL COSTS FOR VARIOUS RO SYSTEM CONVERSIONS

RO System Conversion	Required Permeate Flow gpm	Required Membrane Area[a] ft^2	Required No. of Modules[b]	Membrane Module Cost[c] $	Housing Cost[d] $	Total Cost for RO System[e] $	Required Evaporator Capacity[f] gph	Total Cost for Evaporator $	Total System Cost $
0							120	44,129	44,129
0.70	2.575	371	6	3,780	1,700	21,780	66.2	39,199	60,979
0.80	3.625	522	8	5,040	2,550	23,890	54.4	39,199	63,089
0.90	5.85	842	12	7,560	3,400	28,560	39.0	33,880	62,440
0.95	8.91	1,283	18	11,340	5,100	34,040	28.1	33,880	67,920

(a) Design flux = 10 gfd.

(b) Based on area of 70 ft^2 per module.

(c) Based on $630 per module (Abcor, Inc.)

(d) Based on $850 per 3-module housing (The Permutit Co., Inc.).

(e) Based on system cost of $15,000 (Osmonics, Inc.) for system W/O modules, housings, and high-pressure pump. Pump/motor cost = $1,300 for <4 gpm permeate; $2,600 for >4 gpm permeate (Wanner Engineering, Inc.).

(f) Double effect evaporator with cooling tower package. Based on rated capacities of 200 gph ($44,129), 100 gph ($39,199), and 50 gph ($33,880).

evaporator. For this case the evaporator must produce 2.0 gpm in order to provide the same degree of rinsing as the original 2-stage countercurrent system. Cost details are noted at the foot of Table 2. The lowest capital cost occurs when the evaporator is used to handle the entire treatment load. For RO system conversion between 70 and 90%, the total system cost remains at about $62,000.

Total annual operating costs were also calculated for each RO system conversion. The breakdown of operating costs for a conversion of 90% is shown in Table 3. Specific costs and assumptions are noted at the foot of Table 3. The costs are based on operation 100 hours per week (Monday morning through Friday afternoon) and 50 weeks per year for a total of 5,000 operating hours per year. Similar operating costs were developed for other RO system conversions.

The electrical costs for the RO system are strongly dominated by the requirements for the high pressure pump. The use of a positive displacement pump was assumed with a combined pump/motor efficiency of 75%. In addition, since a new (or clean) module would produce twice the design flux, the RO system could be operated at half the design pressure (i.e., 400 psi). As fouling occurs the operating pressure would be increased to maintain the design flux, and the system would be cleaned when the operating pressure reached 800 psi. Thus an average feed pressure of 600 psi was used in calculating the power costs of Table 3.

When operating with the 1μ cartridge pre-filters, it was necessary to change the two parallel cartridges after about 100 hours of operation. With the 20μ filters, the pressure drop was still quite low (<3 psi) even after 400 hours of operation. With two parallel passes each having a 20μ and a 1μ cartridge in series, it is estimated that the four filters would last for about a month (400 hours). Monthly replacement was therefore assumed for the economic calculations.

With 1μ pre-filtration, cleaning was required after about 700 hours of operation. During this time three modules were in use. However for the design cases shown in Table 2, anywhere from 6 to 18 modules would be used. It is reasonable to postulate that the extent of fouling would vary inversely with the membrane surface area. Thus a cleaning frequency of once every four months (1600 hours) was assumed.

Membrane life is a very important parameter in the economics. As mentioned above, chemical attack of the membrane or other module components would be expected to depend on total time of exposure to the rinsewaters rather than operating time per se. The two field demonstration modules were exposed to the rinsewaters for a total of 4,200 hours. This is close to the 5,000 hours operating time per year taken as the basis for calculating the operating costs. If the system were designed to purge the modules with distillate on shut-down, the effective exposure time would also be about 5,000 hours. Thus a membrane life on one year would

TABLE 3. TOTAL AND NET OPERATING COSTS FOR 90% RO SYSTEM CONVERSION (5,000 OPERATING HOURS PER YEAR)

Item	RO System $	Evaporator System $	Total System $
Capital Amortization (a)	2,100	3,388	5,488
Direct Operating Costs			
Steam @ $3.50/1000 lbs (b)	-	3,760	3,760
Electrical @ $0.0474/kw-hr (c)	1,008	1,100	2,108
Operation & Maintenance @ $10/hr including fringe benefits (d)	960	960	1,920
Cartridge Filters & Cleaning Chemicals (e)	240	-	240
Membrane Replacement (2-year life)	3,780	-	3,780
Total Direct Operating Cost	5,998	5,820	11,808
Total Annual Operating Cost	~~8,088~~ 8,098	9,208	17,296
Credit for Bath Recovery @ $0.47/gal (f)			(2,820)
Credit for Water Recovery @ $0.45/100 ft^3			(361)
Credit for Cyanide Destruction @ $4.05/lb CN (g)			(6,440)
Credit for Solid Waste Disposal @ $29/drum and 25% solids in sludge (h)			(354)
Total Annual Credits			(9,975)
Net Annual Operating Cost			$7,321

(a) Straight-line depreciation over 10 years with zero salvage value.

(b) Based on actual cost for No. 4 fuel oil of $0.393/gal, heating value of 140,000 Btu/gal, and a boiler efficiency of 80%.

(c) Based on actual cost for October 1978.

(d) Based on actual maintenance labor rates.

(e) Four cartridge filters changed once per month at average cost of $4.68 eac Cleaning three times per year with 6 lbs citric acid per cleaning at $0.82 per pound.

(f) Chemical costs: zinc $0.445/lb; sodium cyanide $0.51/lb; caustic $0.185/ brightener $6.792/gal.

(g) Based on 8 lbs NaOCl per lb of CN with no addition of caustic (already pr in rinsewater). Cost for 15% NaOCl solution = $0.665/gal.

(h) Based on sludge centrifuged to 25% solids and hauled in lots of 80 55-gal drums.

be virtually assured. However, it is likely that the membrane life would be considerably longer than one year. During the field demonstration the modules produced only a fraction of the permeate flow that would be produced by a system designed to meet the rinsing constraints of Figure 10b. Thus the feed concentration to the field demonstration modules was considerably greater than would be seen by a larger capacity system. Furthermore, during periods when the demonstration system was not operating, the concentration across the membranes equilibrated resulting in very high concentrations on the permeate side. This situation would accelerate attack of the membrane backing material and other peremate-side components. Purging the system on shut-dhow would largely eliminate this source of module deterioration. Considering these factors, it is not unreasonable to project a two-year membrane life as assumed in Table 3.

Operating and maintenance labor for the RO system was assumed to require 1 day per month. This would include system start-up on Mondays, shut-down on Fridays, cartridge filter replacement, membrane cleaning, and other maintenance as required.

Steam consumption for a double effect evaporator operating as shown in Figure 10b with temperatures of 130°F and 110°F in the first and second effects, respectively was calculated to be 0.66 lbs steam/lb distillate. Electrical requirements for operation of the cooling tower, evaluation of the evaporator, pumping the various output streams, and miscellaneous usage were obtained from the manufacturer (4.64 kw, 8.64 kw, and 16.64 kw for double effect capacities of 50, 100, and 200 gph, respectively). As for RO, operation and maintenance for the evaporator was assumed to require one man-day per month.

As shown in Table 3, the direct operating costs (excluding amortization) are about $6,000 per year each for the RO system and the evaporator for a total of about $12,000. The total annual operating cost including amortization is $17,300. Table 3 also gives the breakdown of credits resulting from recovery of the rinsewater. The largest credit results from a reduction in the amount of cyanide to be destroyed. The credit for sludge disposal is calculated on the basis of the weight of zinc hydroxide produced by precipitation of the dragout and is probably significantly less than for plating shops which do not have solids dewatering equipment. The total annual credit for rinsewater recovery is about $10,000, which leaves a net operating expense of $7,300 per year for the recovery system.

Operating costs were also determined for other RO system conversions and are shown in Figure 11. For conversions ranging from 70% to 95% the RO operating costs increase and the evaporator operating costs decrease. The total operating cost passes through a minimum at an RO system conversion of 90%. Using an evaporator alone for rinsewater recovery (zero percent RO system conversion) the total annual operating cost including amortization is about $20,900. For the optimum combination of RO and evaporation, the total annual operating cost is approximately $17,300 which represents an annual savings of $3,600.

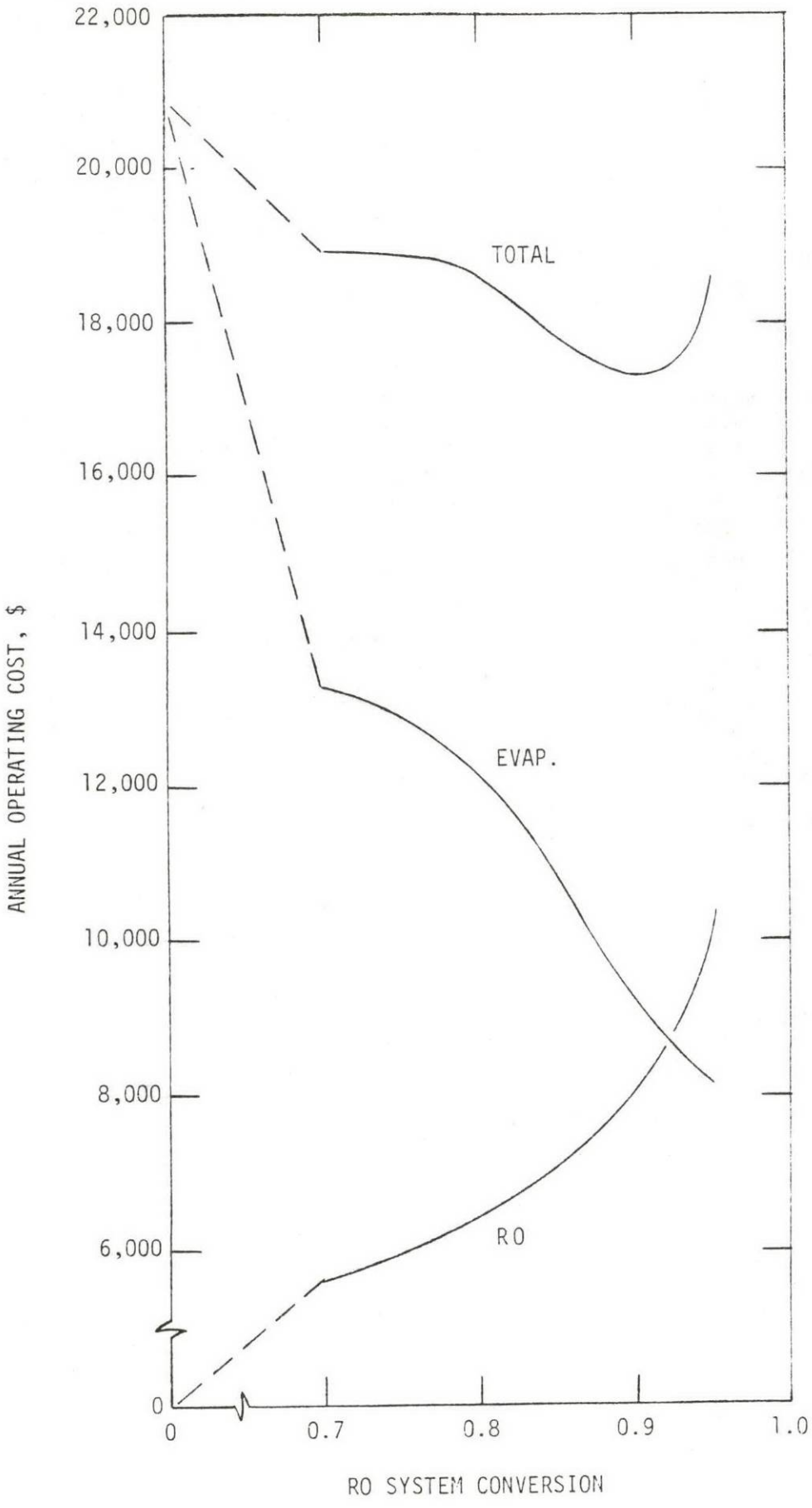


Figure 11. Annual operating costs for various RO conversion

In considering the impact of these numbers it should be emphasized that the recovery system was designed to meet a given rinsing criteria for a two-stage countercurrent rinsing system. Recovery system costs could be reduced significantly by using more rinsing stages. For manual operations, additional rinse tanks could be inserted in the line, and for automatic operations, over-the-tank spray rinses could be used. In addition, consideration should be given to working with higher rinse concentrations where rinsing is not critical. The costs for recovery provide a substantial incentive for reducing the rinsewater flow by simple, inexpensive techniques.

Acknowledgements

The authors gratefully acknowledge the cooperation and support of Bruce Warner, president of New England Plating Co. in providing the field site for the demonstration, support personnel to assist in installation, and cost information for operation and waste treatment at New England Plating Co. Financial support for the program was provided by EPA (Grant No. R805300) and AES (Research Project No. 45). Technical support during the program was received from the EPA Project Officer, Mary Stinson, and from the AES Project Committee: Jack Hyner, Joseph Conoby, Charles Levy, James Morse, and George Scott.

REFERENCES

1. Skovronek, H. S., and M. K. Stinson, Advanced Treatment Approaches for Metal Finishing Wastewaters (Part II). Plating and Surface Finishing, 64 (11): 24-31, 1977.

2. Anon., Recovery Pays! Plating and Surface Finishing, 66 (2):45-48, 1979.

3. Hall, E. P., D. J. Lizdas, and E. E. Auerbach, Plating and Surface Finishing, 66 (2): 49-53, 1979.

4. Donnelly, R. G., R. L. Goldsmith, K. J. McNulty, and M. Tan, Reverse Osmosis Treatment of Electroplating Wastes, Plating. 61 (5): 432-422, 1974.

5. McNulty, K. J., R. L. Goldsmith, A. Gollan, S. Hossain, and D. Grant, Reverse Osmosis Field Test: Treatment of Copper Cyanide Rinse Waters. EPA-600/2-77-170, U. S. Environmental Protection Agency, Cincinnati, Ohio, 1977. 89 pp.

6. McNulty, K. J., P. R. Hoover, and R. L. Goldsmith, Evaluation of Advanced Reverse Osmosis Membranes for the Treatment of Electroplating Wastes. EPA-600/8-78-010, Environmental Protection Agency, Cincinnati, Ohio.

7. Personal Communications, Dr. Robert L. Riley, Fluid Systems Division of UOP, San Diego, CA.

L-5

Research I
Session L

Effect of Electroplating Wastewater Sludge As an Admixture on the Physical Properties Of Concrete

AES Research Project #49

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Bronx, New York

ABSTRACT

EFFECT OF ELECTROPLATING WASTEWATER SLUDGE AS AN ADMIXTURE ON THE PHYSICAL PROPERTIES OF CONCRETE

Robert J. Spinna, P.E. - Principal Investigator
Walter P. Saukin, Ph.D., - Assistant Investigator

The electroplating industry has a major environmental problem with the sludge which results from treatment of wastewater from their various chemical processes. The sludge consists, to a large extent, of heavy metal hydroxides, silicates and phosphates. It is a difficult material to dispose of in a manner which does not seriously contaminate the environment.

It has been suggested that the sludge, which is 20% to 30% by weight solids, might react favorably in a concrete mix to produce insoluable compounds similar to many natural materials. If this can be done in a manner which does not lower the quality of the resulting concrete and which does not permit subsequent leaching of the sludge constituents into the environment, large amounts of the sludge could be disposed of at concrete batching plants located in many places through the country.

Wastewater sludge was collected from electroplating plants in the New York area and then these sludges were added in varying amounts to standard concrete mixes. The resulting concrete was subjected to a number of tests to evaluate the effect of the sludge on the physical properties of the resulting concrete.

Among the concrete tests were: compression (standard cylinder tests), plasticity (slump), leaching (solubility during curing and after) and bar pull-out tests.

In addition to these tests on the concrete mixes, tests of the chemical composition of the sludge and resulting concrete were performed. X-ray diffraction patterns of the sludge were obtained. Analysis of these patterns indicate the presence of crystallinity in the sludge and its composition in terms of such compounds. It also indicates the formation of compounds between the concrete and the metalic constituents of the sludge. Any variation of the diffraction pattern of normal concrete helps to elucidate the nature, durability and resistance to deterioration.

Also chemical techniques were also employed to elucidate the extent of the leaching of the sludge consistituents into the curing water and, after curing, into water in which concrete samples have been submerged.

The research data leads to tentative conclusions concerning the possibility of disposing of sludges by admixing with concrete.

The physical properties of the concrete were not adversely affected and the resulting compounds appear insoluble. Additional extensive testing is required to confirm the results of this preliminary study and develop design criteria.

M-1

Chromium II
Session M

Chromispel—A New Process For High Speed Chromium Plating

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Hebrew University, Jerusalem, Israel
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at T. J. Watson Research Center, IBM Corp.
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Paper not available at time of printing of proceedings.

M-2

Chromium II
Session M

Anodes for Chromium Plating

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Paper not available at time of printing of proceedings.

M-3

Chromium II
Session M

Pulse Plating of Wear Resistant Coatings

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PULSE PLATING OF WEAR RESISTANT COATINGS

T. A. Eckler
B. A. Manty
P. L. McDaniel

Abstract

Techniques have been developed for pulse plating a chromium-molybdenum alloy onto titanium and steel alloy substrates. "On" and "off" pulses were varied from 0.1 to 99.9 milliseconds (ms). Cathode efficiency and percent molybdenum in deposits were measured. A Scanning Electron Micrscope (SEM) was used to show the differences in the topography of the chromium-molybdenum deposits at various pulse durations. Wear and hardness tests were used to evaluate the beneficial effects afforded by the coating.

Background

Problems limiting the use of titanium in advanced gas turbine and airframe components have been analyzed by many chemists, metallurgists, and engineers in recent years. Over the past three decades, continued investigation has led to the development of ever-improving coatings and surface treatments. The most persistent problem areas have been wear, erosion, and corrosion. Although these problems have been alleviated for many environments, the high temperatures encountered in certain sections of gas turbine engines are still too severe for current titanium parts.

Early in our program, it was established that a chromium-molybdenum coating can be applied to various titanium alloys as a solution to these three major problems (Reference 1). Also, because of the compatibility of the solid solutions formed by the chromium-molybdenum-titanium system, the effects of the coating process on the mechanical properties of titanium were minimal. In addition, it was demonstrated that plating with current interruption can have a marked effect on the coating composition, increasing the molybdenum content (Reference 2).

The wear resistance of the various electrodeposits was evaluated on a Falex wear testing machine (Reference 2). The results of this testing showed that the chromium-molybdenum coatings substantially improved the wear life. In fact, the chromium-molybdenum coating plated directly on steel pins improved the wear resistance by a factor of three over a conventional chromium plate. The steel pins pulse-plated with a chromium-molybdenum coating showed a fivefold increase in wear resistance over a conventional chromium plate and a twofold increase in the wear protection afforded by the direct current-plated chromium-molybdenum.

Experimental and Results

In the pulse plating studies described in this report, a Nova Tran Corporation Model 10-5-10 pulse current source was used. Specimens were plated using a self-regulating plating bath containing 300 g/l Unichrome* and 75 g/l ammonium molybdate. Before plating they were grit blasted with an aluminum oxide slurry and etched in a 20 g/l sodium chromate solution containing 2 mls/l hydrofluoric acid.

AMS 4916 (Ti-8Al-1Mo-1V) was used in all these studies. Although the deposits obtained in this manner did not demonstrate adequate "as-deposited" adhesion, they were in intimate contact with the substrate material. This allows subsequent diffusion of the coating into titanium by heating at a temperature of from 650 to 900°C for a short period of time as described in References 1-3. The results described in this paper were all on undiffused coatings.

*Chromium, SRHS CR 110

Pulse Time Effects

The influence of current pulse duration on the cathode efficiency, composition and surface morphology was investigated by varying the "on" and "off" times from 0.1 to 99 milliseconds (ms). An average current density of 3 ASI was used and continued until 90 amp-minutes was accumulated on a specimen with 0.5 in^2 surface area.

With both the "on" and "off" times set equal, the changes in surface morphology with pulse duration are shown in Figure 1. The influence of these pulse changes on both the cathode efficiency and concentration of molybdenum in the deposit is shown in Figure 2.

Since the maximum molybdenum content was obtained using a 3 ms "on" and "off" time, another set of tests was run with a fixed "on" time of 3 ms and an "off" time of from 0.1 to 30 ms. Theoretically, the "off" time is more critical than the "on" time because it determines whether or not the solution at the cathode reaches equilibrium before the next "on" time. SEM photos of the coatings are shown in Figure 3 while the cathode efficiencies and molybdenum contents as a function of "off" time are plotted in Figure 4. Figure 4 also shows the normal optimum range for pulse plating (between 10 and 70% duty cycle). This is further explained in the discussion.

Another set of experiments was run with the "off" time fixed at 3 ms and the "on" time varied from 0.6 to 99.9 ms. Figure 5 illustrates the appearance of surfaces produced, and the effect on cathode efficiency and molybdenum content is shown on Figure 6.

Similar studies were conducted holding either the "on" time or the "off" time at 99.9 ms while the corresponding "off" or "on" time was varied. All of the specimens tested with an "on" time of 99.9 ms had a nodular topography similar to that shown in Figure 3 with an "off" time of 0.5 ms. The results of these tests are shown on Figures 7-9.

Electrolyte Composition Effects

The influence of electrolyte concentration changes on the deposits formed was studied by varying the ammonium molybdate concentration over a range of 75 g/l to 135 g/l. Concentrations below 75 g/l were previously shown to deposit less molybdenum in the plate (Reference 2) and concentrations above 135 g/l reduced the cathode efficiency to less than 20%. A pulse time of 40 ms "on" and 40 ms "off" was used, and the results are shown on Figures 10 and 11. Likewise, the effects of varying the chromium trioxide (Unichrome) concentration in the plating bath were studied using concentrations from 150 g/l to 375 g/l. Pulse times were 40 ms "on" and 40 ms "off." Figure 12 shows these results.

Temperature Effects

A solution was prepared using 300 g Unichrome and 75 g ammonium molybdate; "on"/"off" times were both set at 40 ms. Figure 13 shows the SEM photos obtained in this study. Cathode efficiency and molybdenum content are plotted against solution temperature in Figure 14.

Discussion

Pulse Time

The results obtained in these studies showed that pulse plating can be used to produce crack-free deposits with up to five times the molybdenum content of direct-plated coatings. Also it was found that, by varying the duration of the pulses, the molybdenum content of the coating can be controlled.

To facilitate the evaluation of the results, the concept of the duty cycle was used. The duty cycle is defined as the "on" time divided by the cycle time ("on" time plus "off" time). Most applications of pulse plating use a duty cycle between 10 and 70%. Most samples plated at a duty cycle greater than 70% had a nodular topography, a cathode efficiency greater than 33%, and a molybdenum content of 0.7% or less. Within the recommended range, however, a myriad of grain structures resulted, few of which were nodular. Also, most of the molybdenum contents were 0.7% or greater.

The "off" time is apparently more critical than "on" time, as borne out by the results shown in Figures 4, 6, 7, and 9. For the studies in which the "off" times were varied (see Figures 4 and 7), changes in cathode efficiency were usually accompanied by an inverse change in molybdenum content. In studies with varying "on" times (Figures 6 and 9), however, the cathode efficiencies showed very little variance with changes in "on" time.

Figure 15 is a plot of cathode efficiency vs "off" time with curves drawn in for selected "on" times. The change in form of the curves between 10 ms "on" and 60 ms "on" indicates that a change in the deposition mechanism takes place at some point between these two values.

Another evaluated characteristic was the hardness of the coating. The results are shown in Figure 16. For a given "on" time, the hardness decreases with increasing "off" time. Further, the rate of this decrease becomes less pronounced as the "on" time is increased. Earlier studies showed that the softer the deposit, the better the wear resistance of the Cr-Mo coatings (Reference 2). The values reported in Figure 16 were obtained before heat treat. All samples plated with an off-time of 99.9 ms have a Vickers hardness number between 210 and 240; this suggests the hardness values approach a value independent of "on" time as the "off" time is increased. This independence of "on" time again confirms that the "off" time is more important than the "on" time.

Electrolyte Composition

Varying the concentrations of the constituents of the plating solution showed that the bath ed in previous studies was well-suited for chromium-molybdenum plating. The variation of the mmonium molybdate concentration produced a series of coatings consisting of randomly-shaped atelets (Figure 10). Figure 11 shows that when the ammonium molybdate concentration was reased, the molybdenum content of the deposit increased at the expense of the cathode iciency. This was expected, since the molybdate in solution occupies more and more space at cathode as its concentration increases. This prohibits some of the chromium in solution from ng plated. The molybdenum is actually co-deposited with the chromium ions. This explains the cathode efficiency steadily decreases with increasing molybdate concentration. These ings show that coatings with high molybdenum content can be obtained by increasing the monium molybdate concentration of the solution, but that the possible benefits must be hed against the decrease in cathode efficiency.

The coatings produced by varying the Unichrome concentration of the solution were posed mainly of fine grains. No drastic changes in surface topography occurred as the hrome concentration was increased. Figure 12 shows high molybdenum contents were ned at Unichrome concentrations of 150 g/l (6.05%) and 175 g/l (3.01%). This agrees with the ous findings. The molybdate concentration in solution was relatively high compared to the ium ion concentration. Consequently, the cathode efficiencies at these concentrations were ow. At 225 g/l, the molybdenum content started to level out, but major improvement in le efficiency occurred until the Unichrome concentration reached 275 g/l. At greater trations, the cathode efficiency also leveled out. Beyond 300 g/l, no significant changes ed, suggesting that the saturation point of Unichrome was reached.

Temperature

SEM photos (Figure 13) reveal that a uniform coating was produced at all five temperatures tested. The physical appearance of the samples indicated that the deposition process was proceeding unsatisfactorily at temperatures of 54°C (130°F) and 71°C (159°F); cathode efficiencies at these temperatures were also quite low. At 43°C (109.5°F), however, the appearance of the coating was good, the molybdenum content relatively high, and the cathode efficiency over 20%. Figure 21 shows a steady decrease in cathode efficiency and an increase in molybdenum content between 13 and 54°C.

Conclusion

For chromium-molybdenum plating, variations in pulse time, plating solution composition, and temperature have a drastic effect on the coating produced. These variations result in a wide variety of grain structures and help to determine the efficiency of the deposition process and the properties of the coating produced, including molybdenum content, hardness, and wear resistance.

REFERENCES

1. Manty, B. A. and H. R. Liss, "Wear Resistant Coatings for Titanium Alloys," Final Report, Pratt & Whitney Aircraft Group, FR-8400 under Contract N00019-76-C-0342, March 1977.

2. Eckler, T. A. and B. A. Manty, "Wear Resistant Coatings for Titanium," Final Report, Pratt & Whitney Aircraft Group, FR-10239 under Contract N00019-77-C-0330, June 1978.

3. Eckler, T. A. and P. L. McDaniel, "Wear Resistant Coatings for Titanium Alloys," Quarterly Progress Letter No. 1, Pratt & Whitney Aircraft Group, FR-11123 under Contract N00019-78-C-0489, January 1979.

LIST OF ILLUSTRATIONS

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2. Influence of Pulse Time on Molybdenum Content of Deposit and Cathode Efficiency Using Equal "On" and "Off" Times

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4. Influence of "Off" Time on Molybdenum Content and Cathode Efficiency ("On" Time = 3 ms)

5. Effect of Pulse Duration on Surface Morphology Using "Off" Time of 3 ms

6. Influence of "On" Time on Molybdenum and Cathode Efficiency ("Off" Time = 3 ms)

7. Influence of "Off" Time on Molybdenum Content and Cathode Efficiency ("On" Time = 99.9 ms)

8. Effect of Pulse Duration on Surface Morphology Using "Off" Time of 99.9 ms

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10. Effect of Ammonium Molybdate Concentration on Surface Morphology Using "On" and "Off" Times of 40 ms

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13. Pulse Plated Specimens (40 ms "On," 40 ms "Off") Showing Effect of Temperature on Deposition

14. Effect of Solution Temperature (Unichrome)

15. Cathode Efficiency vs "Off" Time for Selected "On" Times

16. Hardness vs "Off" Time (Before Heat Treat)

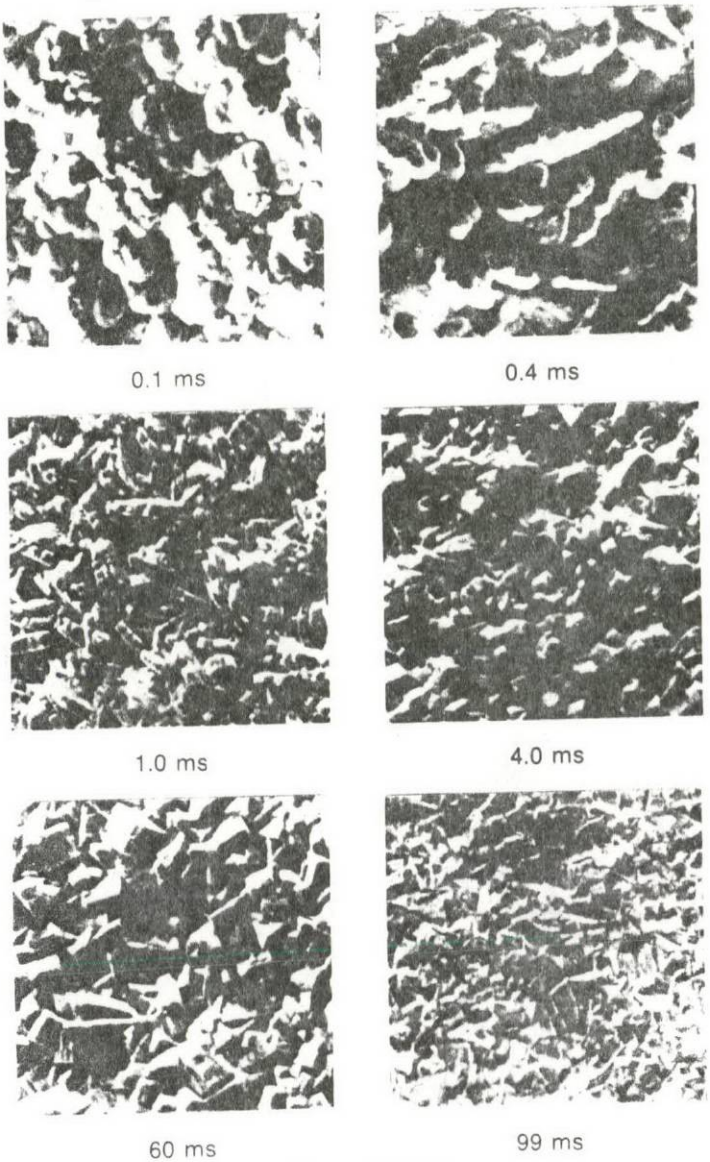


Figure 1. Effect of Pulse Duration on Surface Morphology Using Equal "On" and "Off" Times

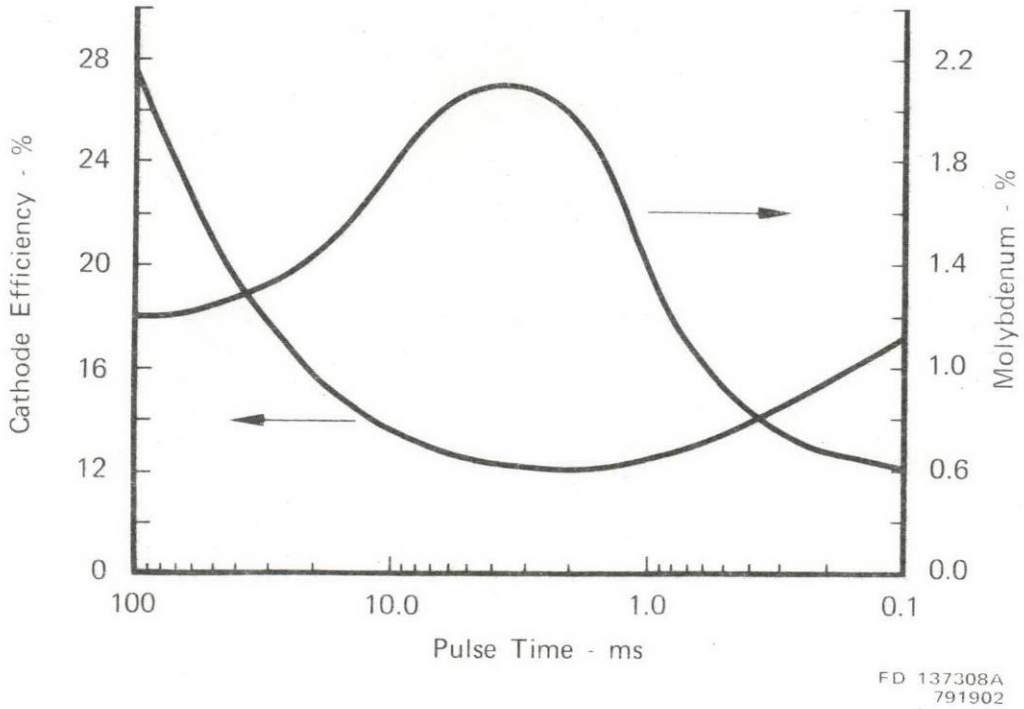


Figure 2. Influence of Pulse Time on Molybdenum Content of Deposit and Cathode Efficiency Using Equal "On" and "Off" Times

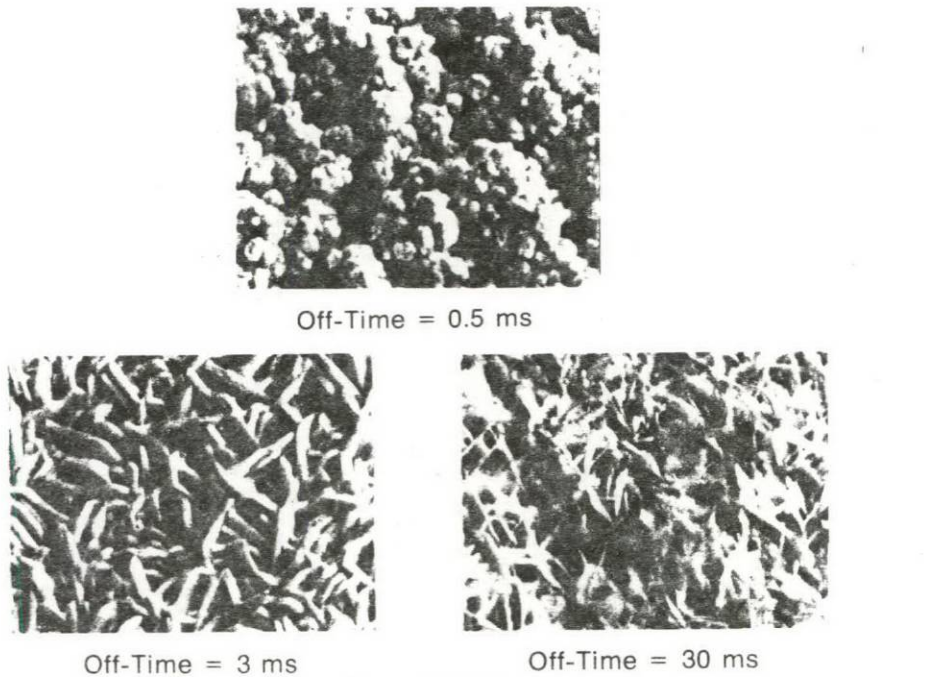


Figure 3. Effect of Pulse Duration on Surface Morphology Using "On" Time of 3 ms

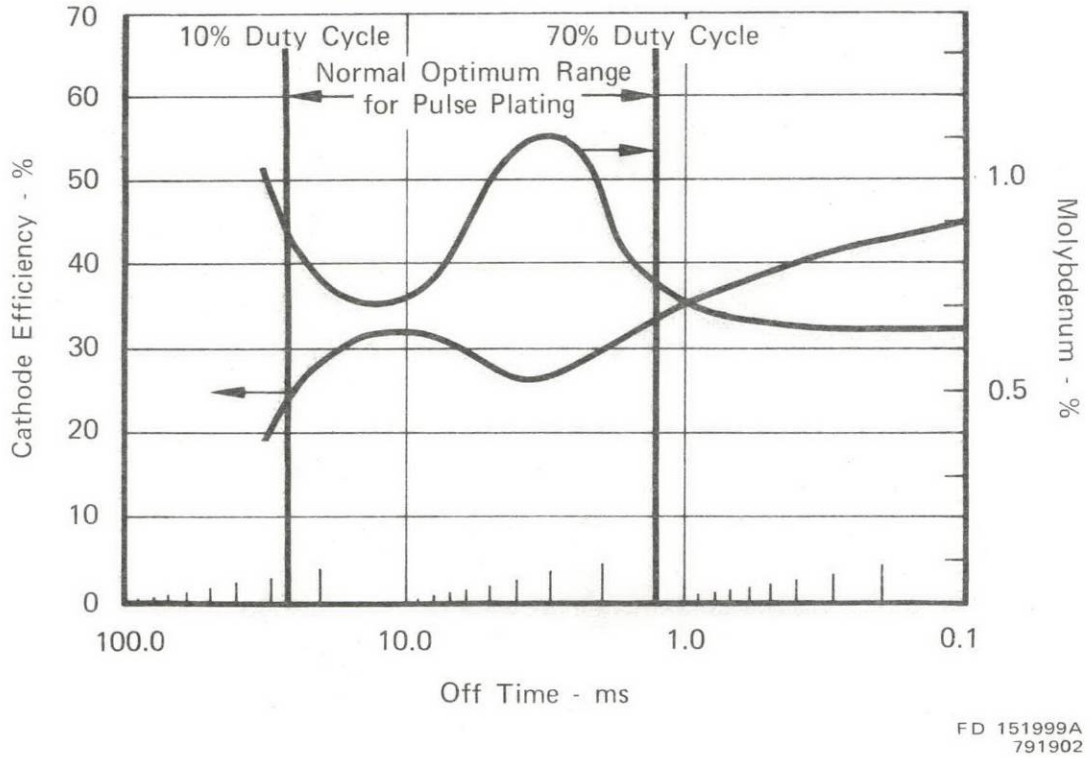


Figure 4. Influence of "Off" Time on Molybdenum Content and Cathode Efficiency ("On" Time = 3 ms)

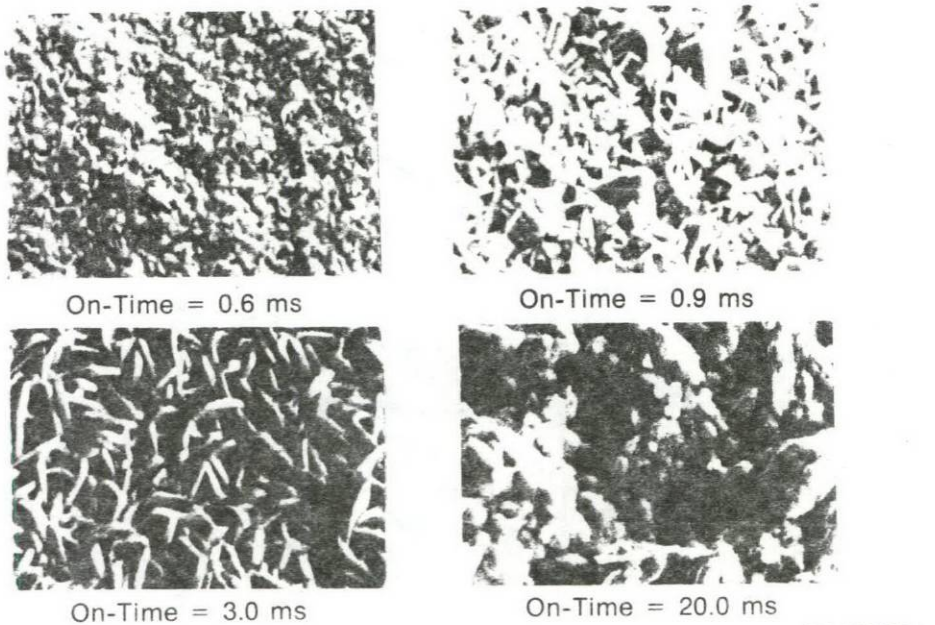


Figure 5. Effect of Pulse Duration on Surface Morphology Using "Off" Time of 3 ms

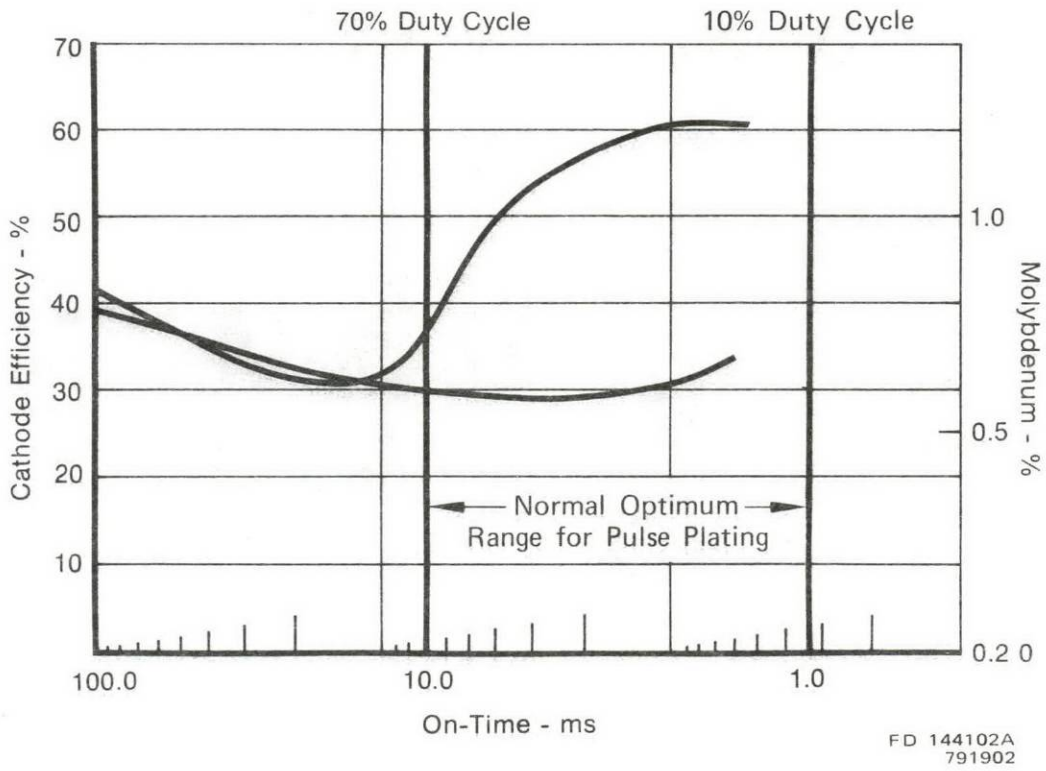
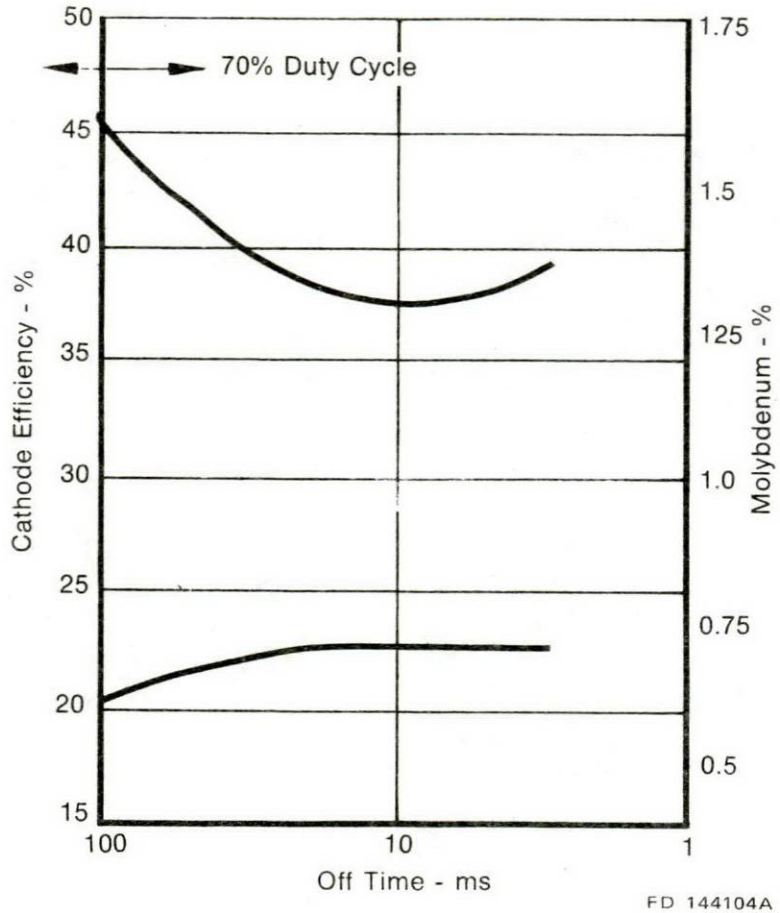


Figure 6. Influence of "On" Time on Molybdenum and Cathode Efficiency ("Off" Time = 3 ms)


50
45
40
35
30
25
20
15
70% Duty Cycle
Cathode Efficiency - %
1.75
1.5
1.25
1.0
0.75
0.5
Molybdenum - %
100
10
1
Off Time - ms
FD 144104A
791902

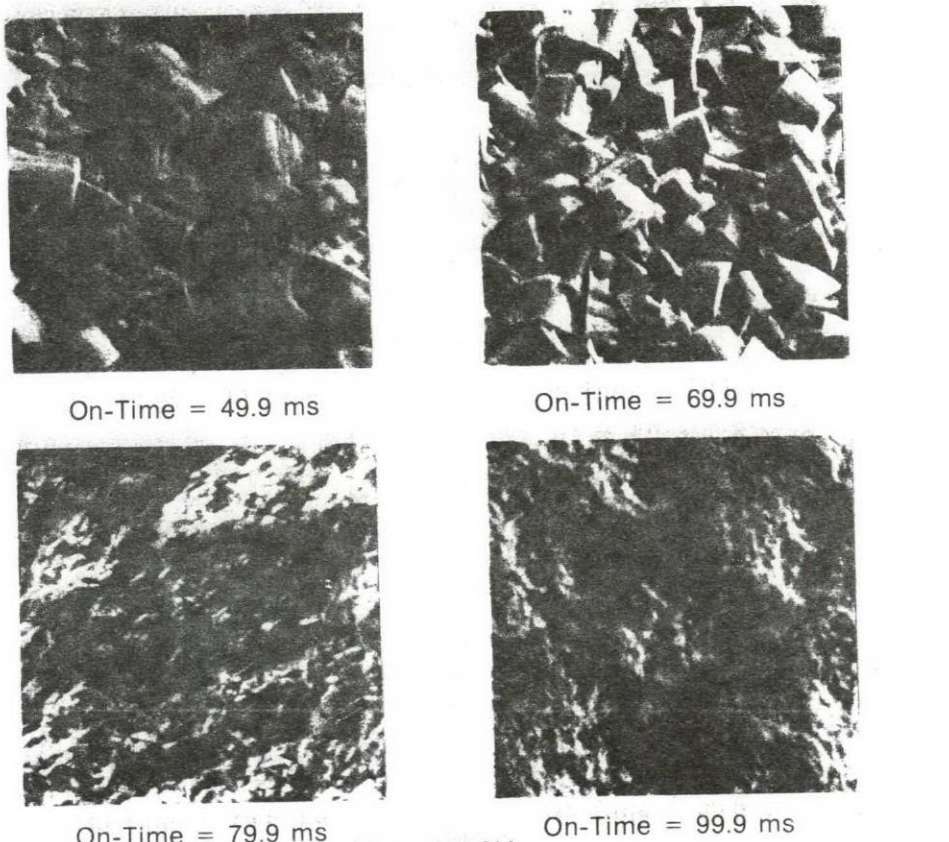


Figure 8. Effect of Pulse Duration on Surface Morphology Using "Off" Time of 99.9 ms

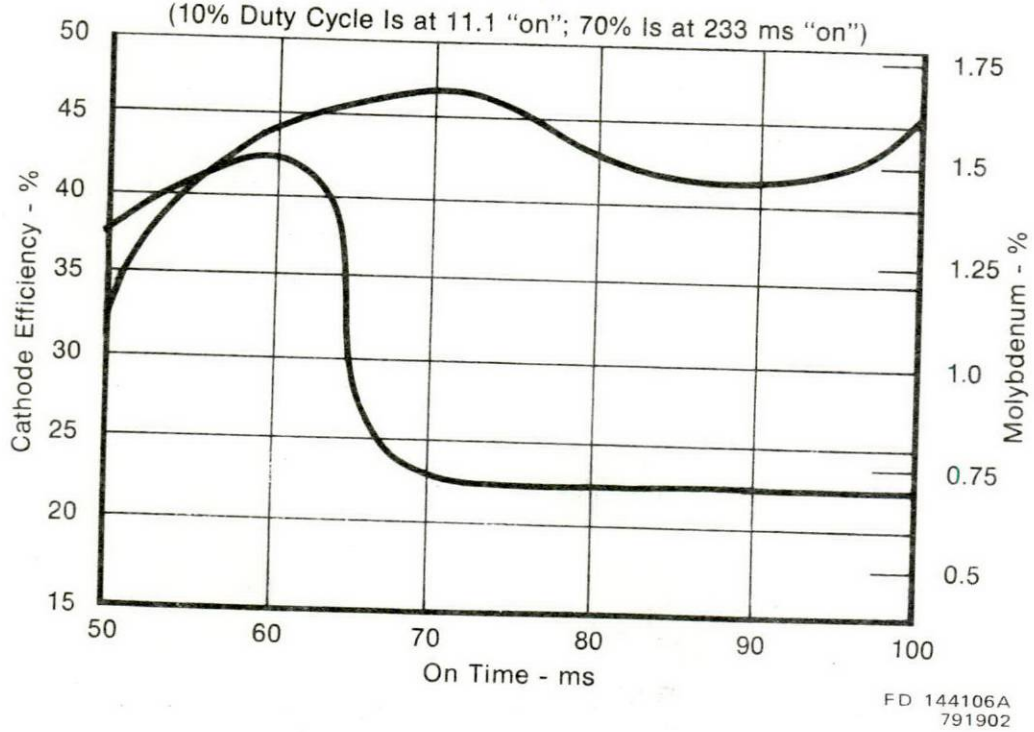


Figure 9. Influence of "On" Time and Molybdenum Content and Cathode Efficiency ("Off" Time = 99.9 ms)

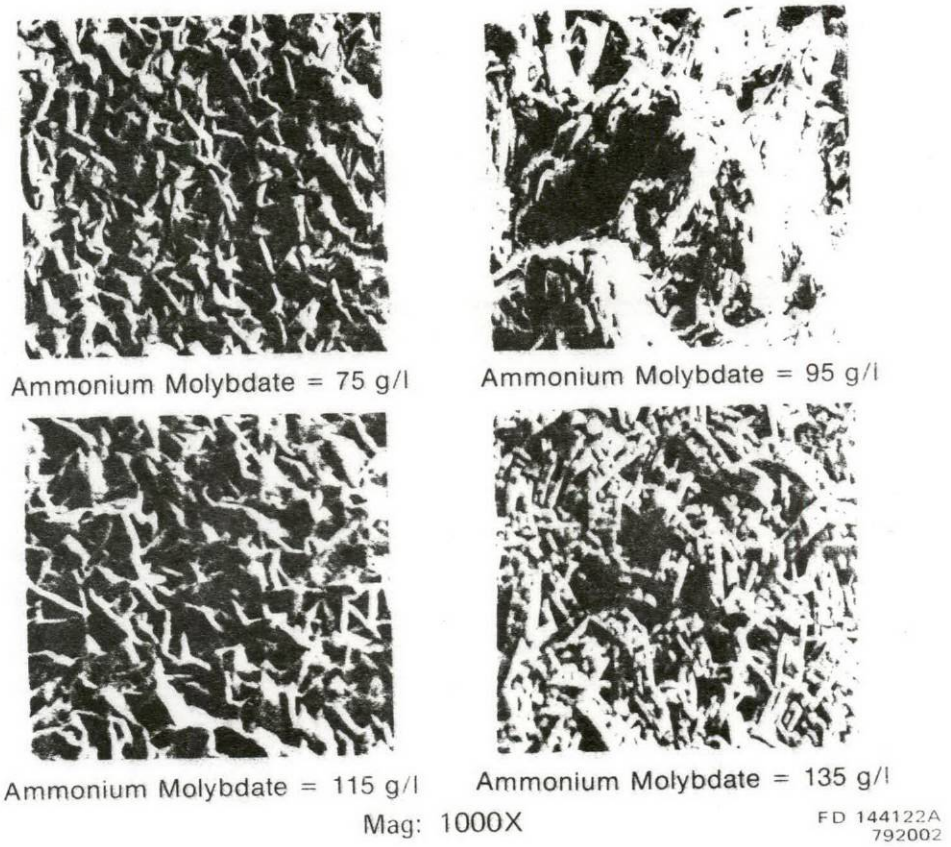


Figure 10. Effect of Ammonium Molybdate Concentration on Surface Morphology Using "On" and "Off" Times of 40 ms

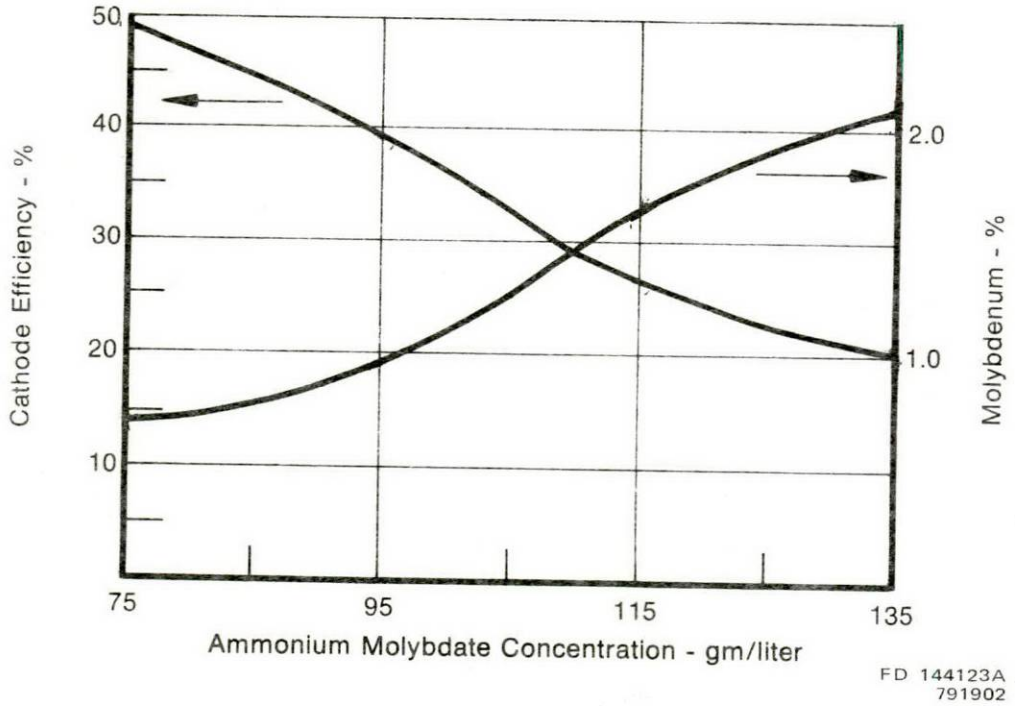


Figure 11. Effect of Increasing Ammonium Molybdate Concentration in Solution Using an "On" and "Off" Time of 40 ms

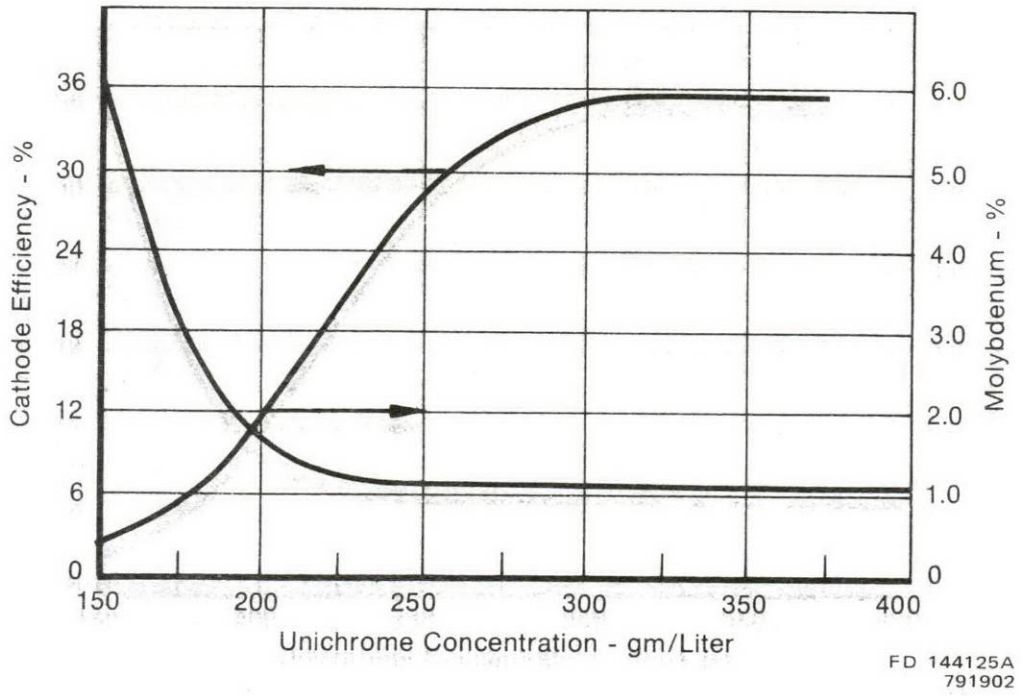


Figure 12. Effect of Increasing Chromic Acid Concentration in Solution Using "On" and "Off" Times of 40 ms

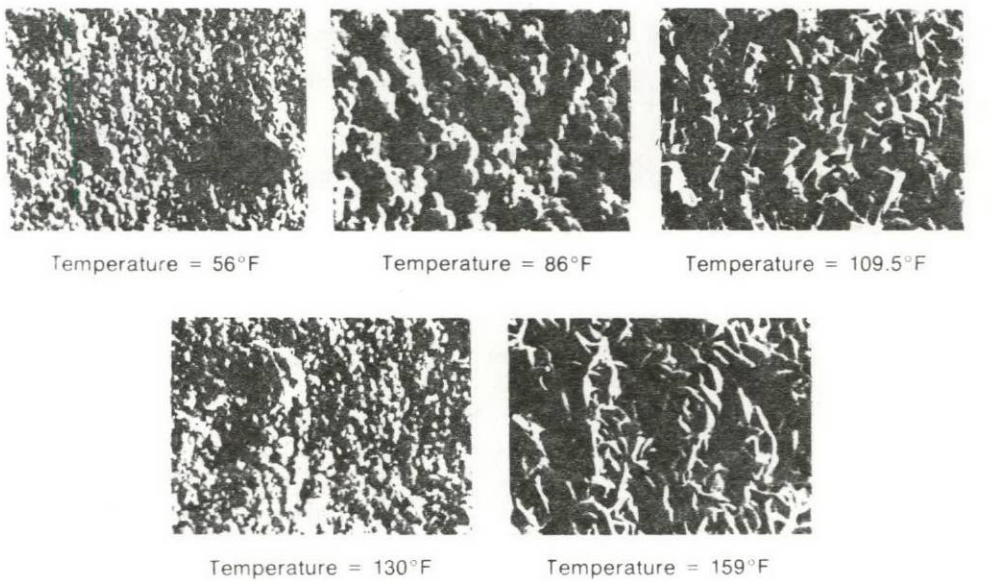


Figure 13. Pulse Plated Specimens (40 ms "On," 40 ms "Off") Showing Effect of Temperature on Deposition

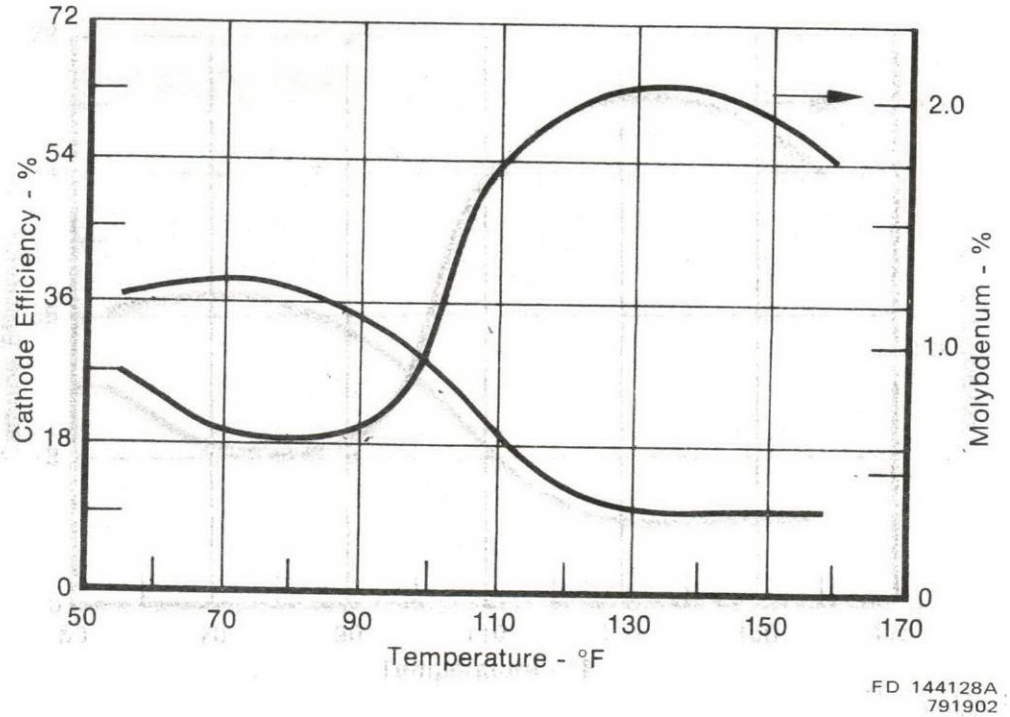


Figure 14. Effect of Solution Temperature (Unichrome)

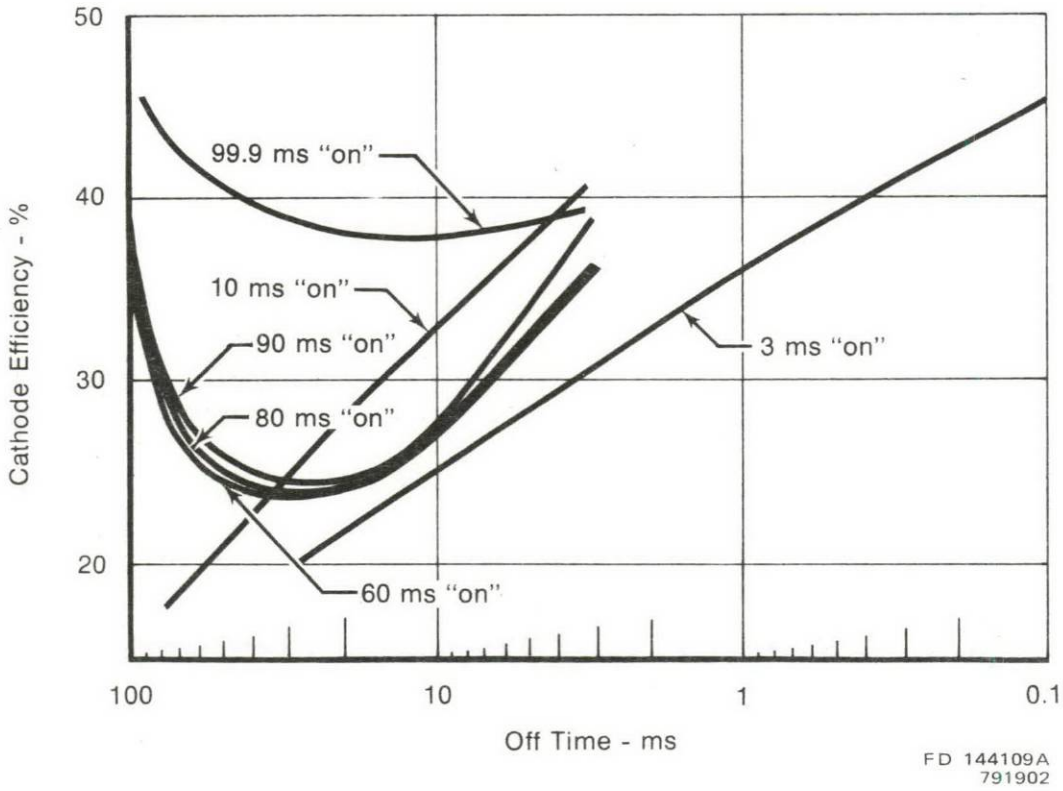


Figure 15. Cathode Efficiency vs "Off" Time for Sub

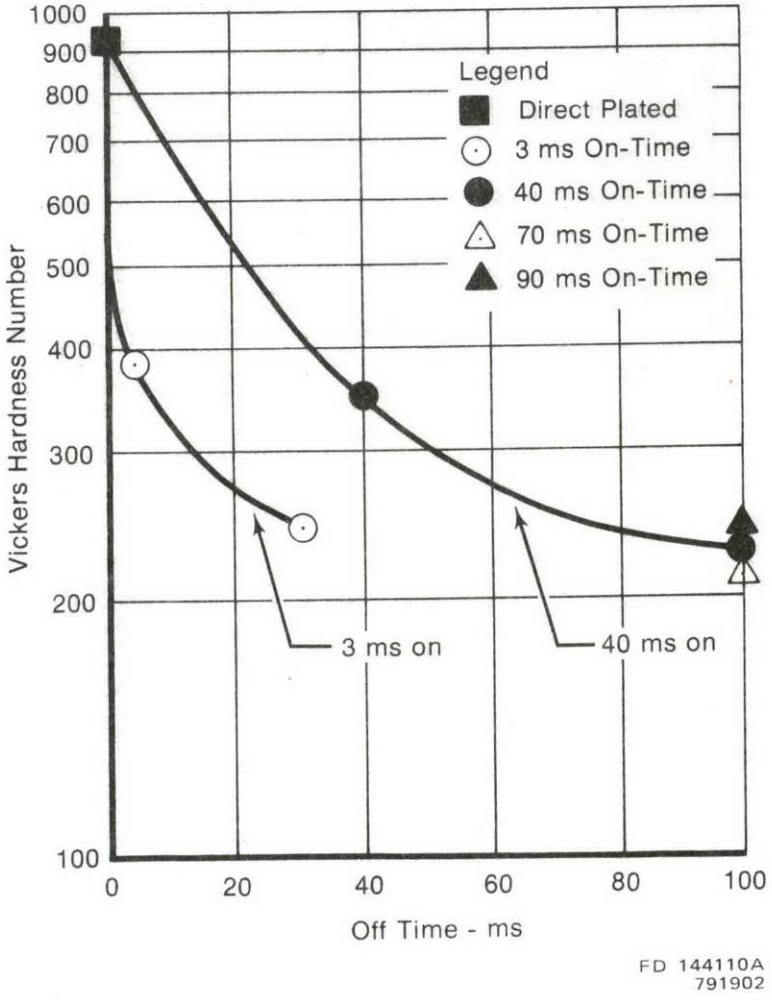


Figure 16. Hardness vs "Off" Time (Before Heat Treat)

M-4

Chromium II
Session M

Electrodeposition of Chromium-Iron Alloys From Trivalent Chromium Baths

T. Hayashi and A. Ishihama
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Japan

Electrodeposition of Chromium-Iron Alloys from Trivalent Chromium Baths

Tadao HAYASHI* and Akira ISHIHAMA*

Abstract

Chromium-iron alloys containing 20-40% Chromium are obtained from a bath composed of 0.5-0.6 M $CrCl_3$, 0.2-0.3 M $FeCl_2$, 1 M HCOONa, 0.5 M NH_2CH_2COOH, 0.15 M NH_4Br, 1 M NH_4Cl, 1 M KCl and 0.6 M H_3BO_3.

Cathodic polarzation and current efficiencies of the electrodeposition of chromium, iron and chromium-iron alloys were measured in order to elucidate the mechanism of the electrodeposition of chromium-iron alloys.

Composition of the Cr-Fe alloys can be varied in the range of 20-40% Cr using the above bath with the current densities of 100-300 $mA \cdot cm^{-2}$ at 30°C.

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Electrodeposition of Chromium-Iron Alloys from Trivalent Chromium Baths

By Tadao Hayashi* and Akira Ishihama*

Introduction

Electrodeposited alloys of chromium and iron group metals such as Fe, Ni and Co possess the good corrosion resistance, high strength and hardness and also retention of strength at high temperatures.[1)]

One of the series of the study of electrodeposition of Cr-Ni-Fe alloys, an attempt was made for establishing the bath parameters in the electrodeposition of Cr-Fe alloys which would lead to the formation of Cr-Ni-Fe alloys (18Cr-8Ni).

The electrodeposition of Cr-Fe alloys (85Cr-15Fe) has been reported by Faust et al. using a chrome alum bath containing a glycine as a buffer.[1-a)]

We have already reported the electrodeposition of Cr-Ni (10-80% Cr) and also Cr-Fe (10-60% Cr) alloys from a dimethyl formamide (DMF) bath containing $CrCl_3$ and $NiCl_2$ or $FeCl_2$ as a main constituent.[2a,2b)]

However, the toxity of the DMF bath seemed to be unfavorable for the practical use in industry.

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Recently, a new trivalent chromium plating bath[3),4)] using carboxylic acids as a basic electrolyte was develope and achieved some commercial acceptance.[5)] Chromium plating baths using organic acid complexants were also studied by Bersin[6)] and Barde.[7)]

In the present paper, the factors affecting Cr-Fe al deposition, the mechanism of alloy deposition and also th quality of the alloy deposits were studied in the electro deposition of Cr-Fe alloys from the formate baths.

Experimentals

The electrolyte used for the electrodeposition of Cr-Fe alloys were prepared from the special grade chemicals(Wako Pure Chemical Industries, Ltd.) and deionized water.

The composition of the electroplating baths studied are shown in Table 1.

Table 1.

The plating cell and the measuring circuit used in the present study are shown in Fig. 1.

Fig. 1

Electrodeposition of alloys was carried out by using a platinum cathode (1.0 mm ø, 0.45 cm^2) for the polarization measurement and also for the analysis of alloy deposits. A copper disk electrode (1.0 cm^2 x 0.5 mm thickness) was also used as a cathode for the evaluation of the deposits. In this case, one side of the copper disk electrode was coated with an insulating resin (Fullontex, Furuto Sangyo Co.) and the copper electrode was electropolished in 50 % phosphoric acid solution for 20 min and rinsed with deionized water before electroplating of the Cr-Fe alloys.

Insoluble graphite anodes were separated from the cathode

compartment by a sintered glass diaphragm in order to avoid the contamination of anode products.

The cathode potentials of the test electrodes during th electrolysis was measured against a saturated calomel electr (SCE). Each experiment was carried out by using an aged electrolyte.(2 days).

Chemical analysis of Cr and Fe in the alloy deposits was carried out by the absorption spectroscopy and also by the volumetric method.

The cathode current efficiency was obtained from the weight determination of the alloy deposits and an amount of electricty required for the electrolysis providing that the ionic valence of Cr is 3 and that of Fe is 2 for the electr deposition of Cr-Fe alloy.

Results and discussion

1) Composition of alloy deposits

Since the standard electrode potential of iron is -0. as compared with -0.74 V for chromium, iron is 0.30 V more noble than chromium. Therefore, iron should be deposited preferentially from the solution containing the simple sa of both metals.

Fig. 2 shows the chromium content in the Cr-Fe alloy deposits and the metal percentage of chromium in the bath

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Fig. 2

The curves of alloy composition always lay below the composition-reference line, and thus clearly indicate that iron is more readily depositable in the bath. The chromium content in the Cr-Fe alloy deposits increases with an increase of the percentage of Cr in the bath.

Influence of the bath composition on the Cr content in the Cr-Fe alloy deposits was examined by the use of various metal ratio Cr/Fe in the bath, and the most promising bath for the electrodeposition of Cr-Fe alloys which have the higher content of Cr was considered to be the F-1 bath among the baths listed in Table 1.

2) Effect of current density

In general, the content of the less noble metal in the alloy deposits increases with an increase of the current density.

Fig. 3 shows the variation of chromium content in the Cr-Fe alloy deposits and the partial- and total current efficiencies in the electrodeposition of Cr-Fe alloys from the F-1 bath (pH 2.8, 30°C) as a function of current density.

Fig. 3

With increasing the current density, the deposition rate the less noble metal, Cr becomes relatively high compared h the noble metal, Fe and hense, the content of Cr in the

alloy deposits increased.

Variation of the partial current efficiency of chromium can be estimated from the chromium content in the alloy deposi With increasing current density, the partial current efficien for the iron deposition decreased particularly in the range of 100 - 150 mA/cm².

3) Effect of pH and temperature

The effect of pH on the composition of the electrodeposi alloys is complicated and usually unpredictable.

The effect of pH on the chromium content in the alloy deposits was shown in Fig. 4 for the F-1 bath at 30 °C.

Fig. 4

The chromium content in the alloy deposits increased w an increase of pH at a current density of 50 mA/cm². On other hand, it decreased with an increase of pH at 200 mA/c

The partial current efficiency of iron deposition doe not seem to be affected by the pH of the alloy plating bat Therefore, the effect of pH on the electrodeposition of Cr alloy seems to be mainly on the deposition of Cr rather th Fe.

Fig. 5 shows the effect of temperature on the chromi content in the alloy deposits for the F-1 bath at pH 2.8.

Fig. 5

3a) Influence of prolonged electrolysis

Influence of the prolonged electrolysis on the deposition of Cr-Fe alloys seemed to be significant.

In the electrolysis of Cr-Fe alloy bath containig 0.6 M Cr^{3+} and 0.2 M Fe^{2+} at a c.d. of 150 $mAcm^{-2}$ (30°C), the current efficiency for the electrodeposition of Cr-Fe alloys decreased from 78% (15 μm) to 62% (150 μm) with the prolonged electrolysis as shown in Fig. 5a.

The Cr content in the alloy deposits also decreased from 48% (15 μm) to 40% (150 μm) with an increase of the thickness of the deposit. However, the current efficiency for the deposition of Fe does not seem to change with the duration of the electrolysis up to about 150 μm.

The smooth bright surface with a small granulate growth was obtained up to about 15 μm, however, the granulate growth covered the almost all surface in the thickness of 15-25 μm, and the large nodular growth prevails all over the electrode surface at about 30 μm.

From the practical point of view, the Cr-Fe alloy deposit containing ca. 45% Cr up to about 25 μm can be obtained from the formate type Cr-Fe bath containg 0.6 M Cr^{3+} and 0.2 M Fe^{2+} at a c.d. of 150 $mAcm^{-2}$ and 30°C.

The chromium content in the alloy deposits decreased with an increase of the temperature of the bath regardless of the current density studied.

4) Cathodic polarization

The cathodic polarization curves and also the partial currents for the Cr and Fe estimated from the current effici in the electrodeposition of Cr-Fe alloy were shown in Fig. 6

Fig. 6

The alloy deposition commences at about -1.0 V just be the partial current of Cr increased. The partial current the Cr deposition always increases in the potential range less noble than that of Fe. The current for alloy deposit increases at -0.5 V accompanying the evolution of hydrogen

The coverage of the electrode with hydrogen gas was observed in the potential range from -0.5 to -0.9 V, howev an abrupt increase in the current was observed above the potential of -0.9 V accompanying hydrogen evolution. Unde these conditions, the electrodeposition of metals has not detected in these potential range. Therefore, the main reaction at the platinum electrode seemed to be the evolu hydrogen. At a potential of -0.9 V, the partial current the electrodeposition of Fe increased. Thus, the deposi of Fe is predominant with a depression of hydrogen evolu to give the minimum value of the total current in the

polarzation curves. An increase in the partial current for Cr at -1.1 V gave the significant increase in the total current for the electrodeposition of Cr-Fe alloys.

Fig. 7 shows the cathodic polarization curves for the Cr-Fe alloy deposition as a function of Cr/Fe ratio in the baths.

Fig. 7

The partial current for the deposition of Cr or Fe in the alloy deposition was plotted against the electrode potential. The value of i_{Total} always located in the intermediate region between the polarization curve of Fe and that of Cr, and i_{Total} increased with a decrease of the Cr/Fe ratio in the baths.

The effect of pH on the cathodic polarization curves for the electrodeposition of Cr-Fe alloy and also for the partial current for Cr or Fe was shown in Fig. 8.

Fig. 8

The partial current for the deposition of Cr decreased with an increase of pH at -1.3 V. On the other hand, no influence was observed for the deposition of Fe, therefore, the total current for the electrodeposition of alloy increased with an increase of pH in the potential range more noble than -1.3 V. On the contrary, it decreased with an increase of pH

in the potential range less noble than -1.3 V.

The effect of temperature on the partial current of Cr or Fe as well as the cathodic polarization curves of the electrodeposition of Cr-Fe alloys was shown in Fig. 9.

Fig. 9

As might be expected, the cathodic polarization decreas with an increase of temperature and the current increased in the noble potential range. However, the partial current fo the Cr deposition increased with a decrease of bath temperat and the i_{Fe} also decreased at 20-40 °C.

These results coincided with the temperature dependenc of the Cr content in the alloy deposits as shown in Fig. 5.

5) Quality of the Cr-Fe alloy deposits

Fig. 10 shows the photomicrographs of the surface str of the alloy deposits obtained from the F-1 bath (pH 2.8, 30 °C) as a function of current density (50, 150 and 300 mA/cm^2).

Fig. 10

In the current density region below 50 mA/cm^2, a gra deposits with 1-4 μm diameter was obtained. Under these conditions, Cr content in the alloy deposit is ca. 20 % a the deposits have a gray metallic lustre. With increas

current density,a compact grayish white deposit with metallic lustre was obtained and a full bright deposit at the current densities of 100-200 mA/cm^2.

Fig. 11 also shows the photomicrographs of the Cr-Fe alloy deposits obtained from the F-3 and F-5 baths. Color of the alloy deposits changed from grayish white to brown, and finally to black with an increase of the metal ratio of Cr/Fe in the bath and the cracks were observed in the deposits obtained at above 150 mA/cm^2.

Fig. 11

The Cr-Fe alloy deposits obtained from the F-3 bath at the current densities of 50-150 mA/cm^2 had the smooth surface, however, large cracks were found in the same type deposits obtained at 300 mA/cm^2.

The Cr-Fe alloy deposits obtained from the F-5 bath with a current density of 50 mA/cm^2 had black metallic lustre and a granulat growth (15-20 μm diameter) was also found in the deposits.

The effect of pH on the surface appearance of the Cr-Fe alloy deposits obtained from the F-1 bath is shown in Fig. 12.

Fig. 12

Current densities suitable for the formation of bright

deposits moved towards the lower current densities with an increase of pH, that is, current density, 300-500 mA/cm² for pH 2.0 and 50-100 mA/cm² for pH 3.6-4.0.

The Cr-Fe alloy deposits obtained from the F-1 bath at 50 mA/cm² at pH 2.0 exhibited a brown metallic lustre with a nodular growth. The alloy deposits obtained from the same bath at 150 mA/cm² gave the large cracks and some peeling was observed along the crack lines. At a current density of 300 mA/cm², the alloy deposits exhibited a relatively smooth gray metallic lustre with a small nodular growth.

The effect of pH on the formation of the Cr-Fe alloy deposits can be explained in the following sequences. The formation of the granular deposits in the lower current den range in the low pH baths such as pH 2.0 would be due to th burning of Fe deposit owing to the lower concentration of F ion in the bath. In the higher current density range, Cr deposition seemed to be predominant, therefore, the alloy exhibited a compact metallic lustre similar to pure Cr dep

6) X-ray diffraction analysis

An x-ray diffraction analysis of the Cr-Fe alloy depo obtained from the F-1 bath(pH 2.8) at 30 °C, revealed tha the alloy deposits have a fine non-crystalline form which no detectable x-ray diffraction lines corresponding to th Fe or Cr-Fe crystal lattice. The alloy deposits obtaine at 50 mA/cm², however, gave the specific diffraction peal $2\theta = 43°$ corresponding to the α-Fe crystal lattice (110

Summary

Cr-Fe alloy are electrodeposited from the formate bath containing $CrCl_3$ and $FeCl_2$ as a main constituent with a total concentration of 0.8 M.

The cathodic polarization measurements in the electrodeposition of the Cr-Fe alloys as well as Cr and Fe revealed that the deposition of Cr occurs at less noble potentials compared with Fe and hydrogen, and the Cr-Fe alloy deposition commences only at above 10 mA/cm^2.

The Cr content in the alloy deposits is always less than the percentage of Cr in the bath, and it increased with an increase of the metal ratio Cr/Fe in the bath.

The Cr content in the alloy deposits also increased with an increase of pH of the bath in the lower current density range below 50 mA/cm^2, however, it decreased with an increase of pH in the higher current densities.

The Cr content in the Cr-Fe alloy deposits decreased with an increase of temperature of the bath regardless of the current density.

The Cr-Fe alloys containing 20-40% Cr are obtained from the formate bath composed of 0.5-0.6 M $CrCl_3$ and 0.2-0.3 M $FeCl_2$ as a basic constituent at pH 2.4-3.2 and 20-40 °C in the current density range from 100 to 300 mA/cm^2.

The Cr-Fe alloy deposits exhibit good adherence to copper and have the gray semi-bright to grayish white metallic lustre.

References

1) W. H. Safranek, 'The Properties of Electrodeposited Metals and Alloys', New York, American Elsevier Pub. Co., Inc. (1974)

1a) L. D. McGraw, J. A. Gurklis, C. L. Faust, J. E. Bride, J. Electrochem. Soc., 106, 302 (1959)

2a) T. Hayashi, H. Nishikawa, J. Metal Finishing Soc., Ja 25, 660 (1974)

2b) N. Furukawa, T. Hayashi, ibid., 29, 301 (1978)

3) Anon, Product Finishing, 28, 30 (1975)

4) J. C. Crowther, S. Renton, Electroplating and Metal Finishing, 28, 6 (May 1975)

5) Anon, Chemical and Engineering News, 53, 16 (1975)

6) T. Berzins, U. S. Pat. 3,021,267 (1962)

7) J. E. Bride, Plating, 59, 1207 (1972)

Table 1 Composition of baths

Bath	$FeCl_2 \cdot 4H_2O$(M)	$CrCl_3 \cdot 6H_2O$(M)	HCOONa(M)	NH_2CH_2COOH(M)	NH_4Cl(M)	NH_4Br(M)	KCl(M)	H_3BO_3(M)
F-1	0.2	0.6	1	0.5	1	0.15	1	0.6
F-2	0.3	0.5	"	"	"	"	"	"
F-3	0.4	0.4	"	"	"	"	"	"
F-4	0.5	0.3	"	"	"	"	"	"
F-5	0.6	0.2	"	"	"	"	"	"
F-6	0.8	0	"	"	"	"	"	"
F-7	0	0.8	"	"	"	"	"	"

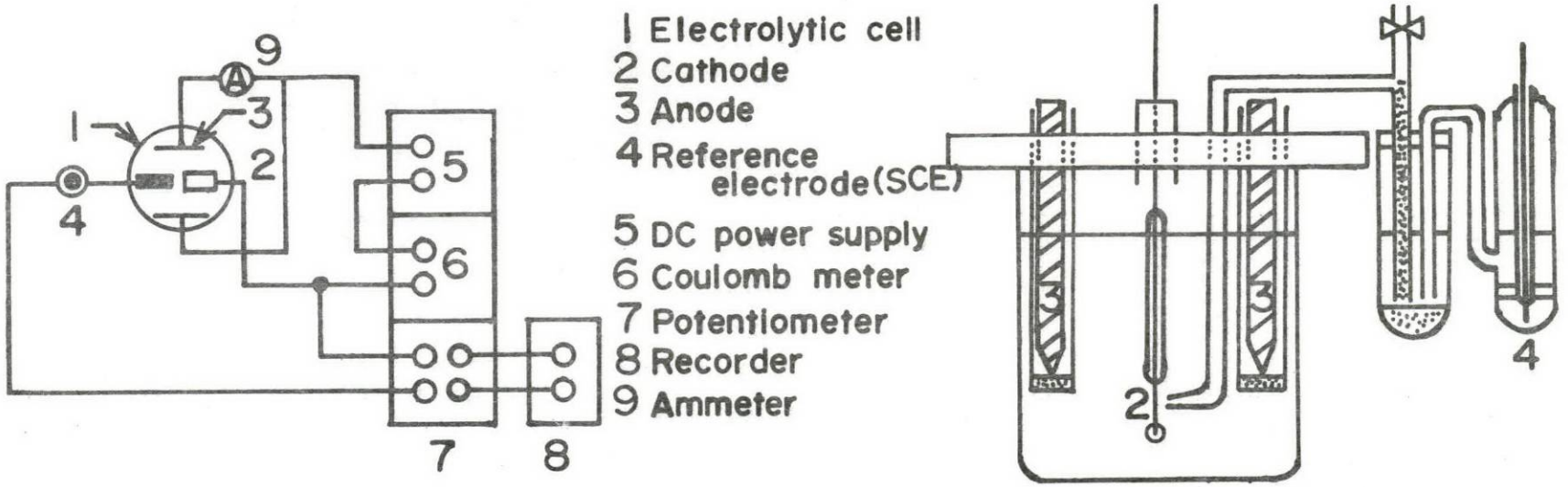


Fig. 1 Electrolytic cell and galvanostatic circuit

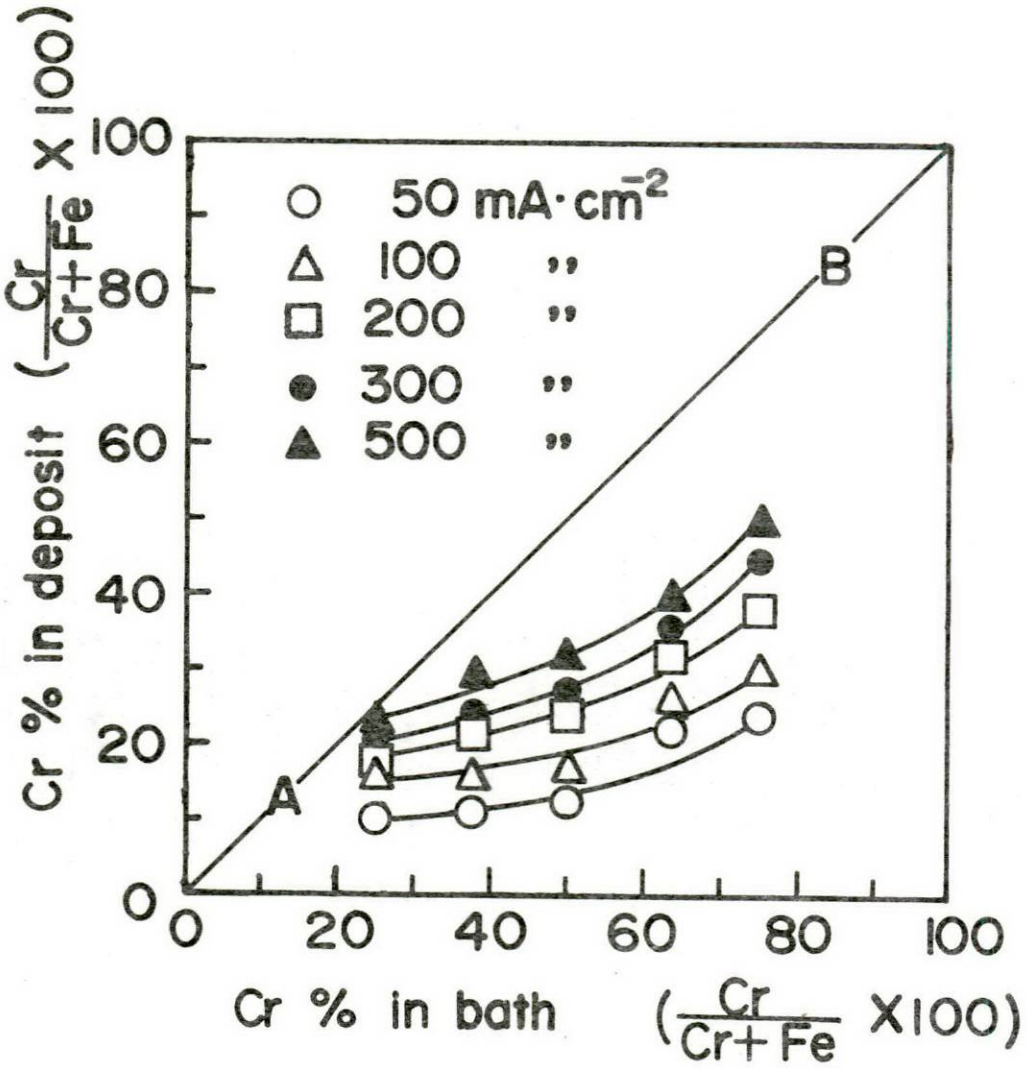


Fig. 2 Relation between Cr content in alloy deposits and i
in the electrodeposit

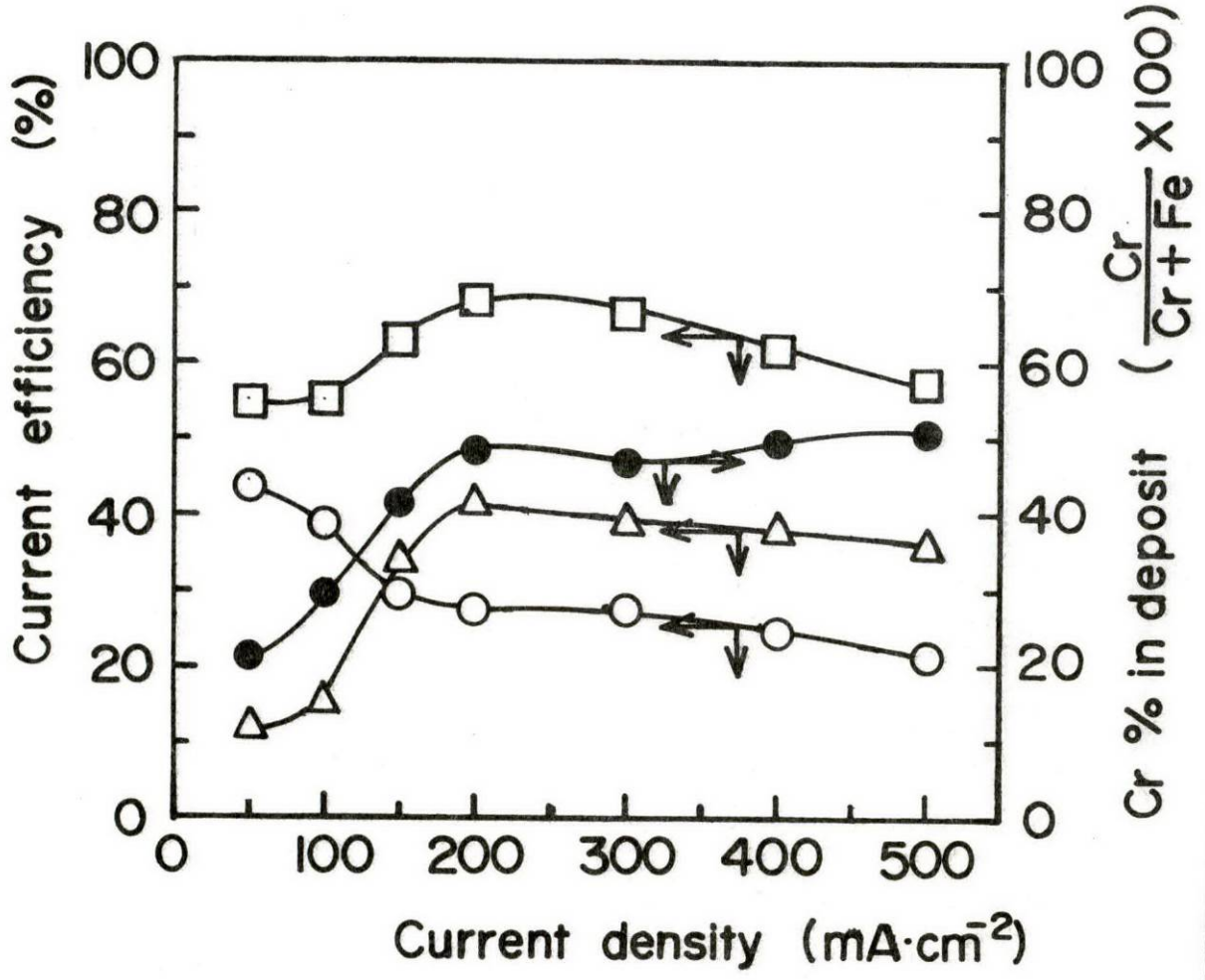


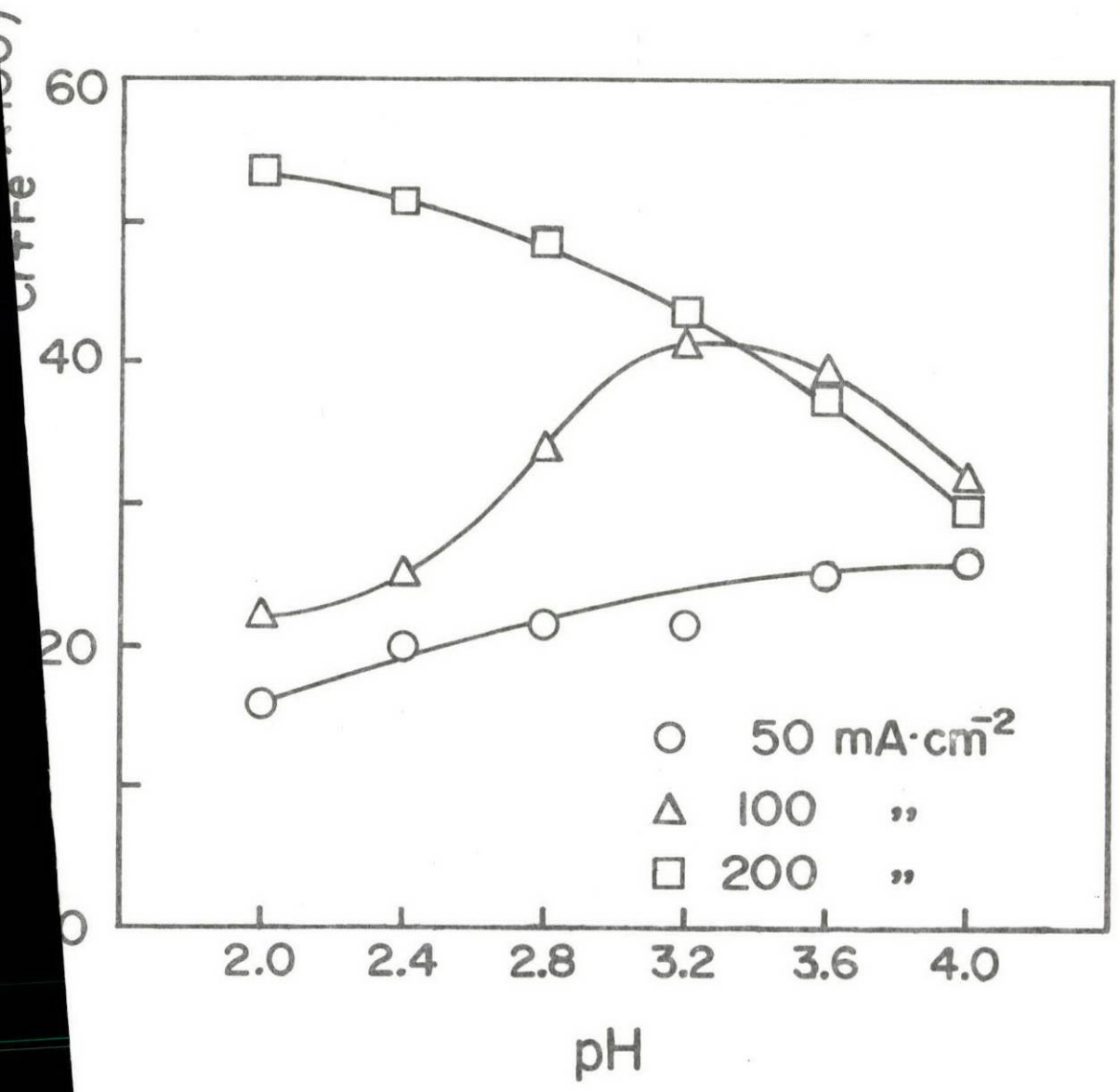
Fig. 3 Effect of current density on the cathode current efficie and Cr content in alloy deposits in the electrodeposition of Cr-Fe alloys in F-1 bath (pH 2.8, 30°C)

○ Cathode current efficiency of Fe

△ ,, Cr

□ ,, Alloy

● Cr content in alloy deposits



Effect of pH on Cr content in the alloy deposits as a unction of current density in F-1 bath (30°C)

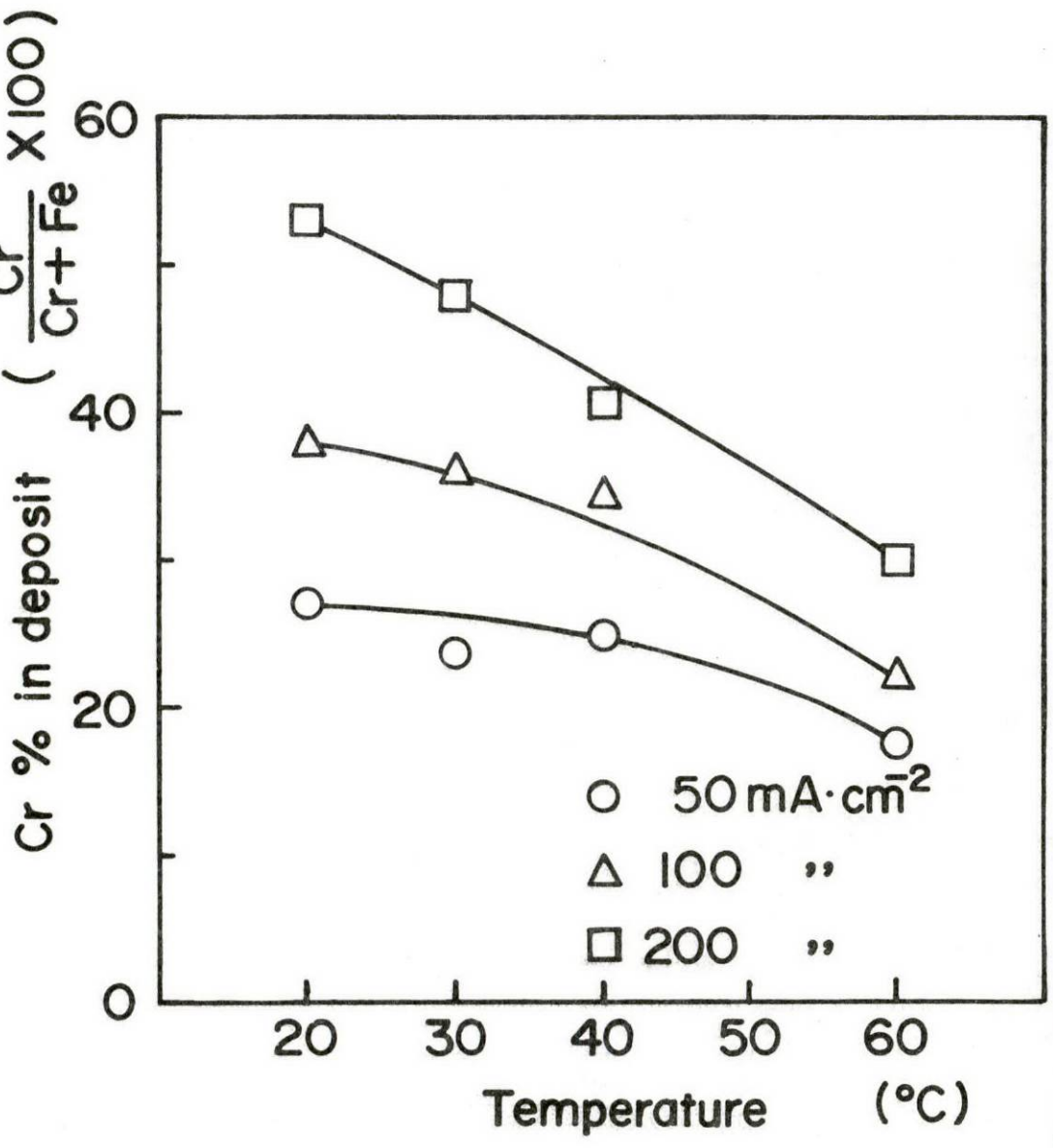


Fig. 5 Effect of temperature on Cr content in the alloy deposi
as a function of current density in F-1 bath (pH 2.8)

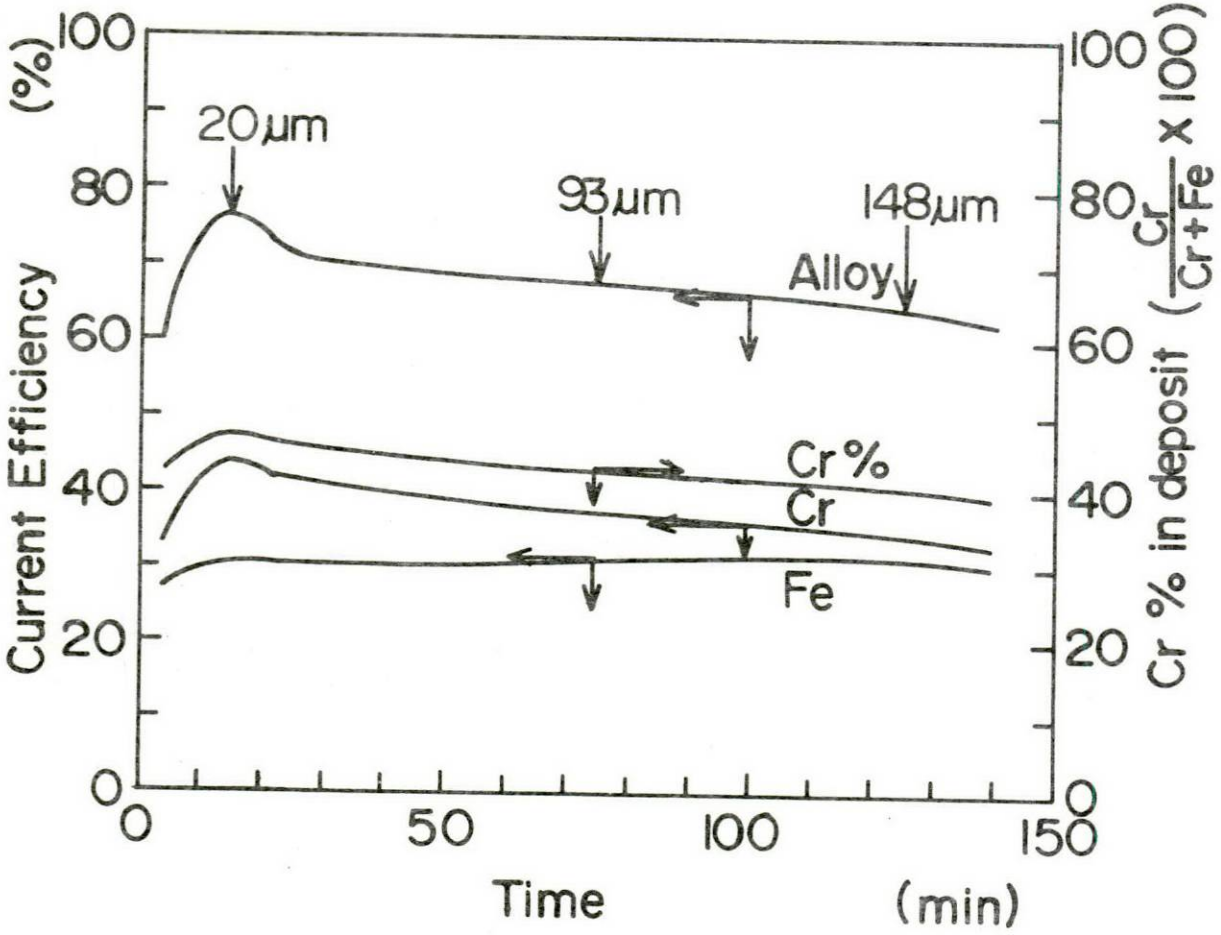


Fig. 5a Influence of prolonged electrolysis on the cathode current efficiency and Cr content in alloy deposits in the electrodeposition of Cr-Fe all
(pH 2.0

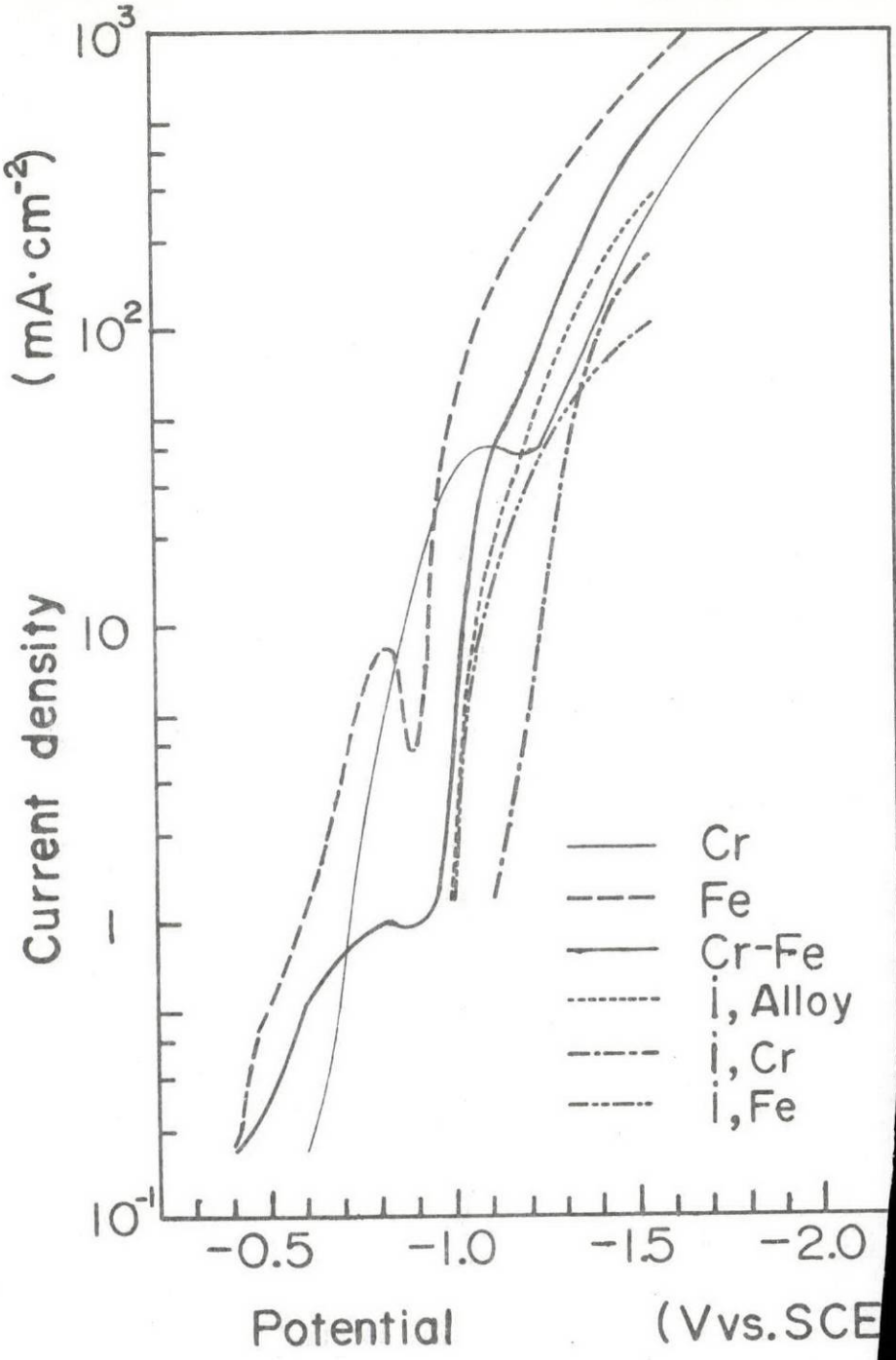


Fig. 6 Cathodic polarization curves obtained on Pt elect
in various electrolytes (pH 2.8, 30°C)

i,Alloy: Total alloy deposition
i,Cr: Partial curve for Cr
i,Fe: Partial curve for Fe] calculated
allo

Cr: Total current from F-7 bath
Fe: Total current from F-6 bath
Cr-Fe: Total current from F-1 bath

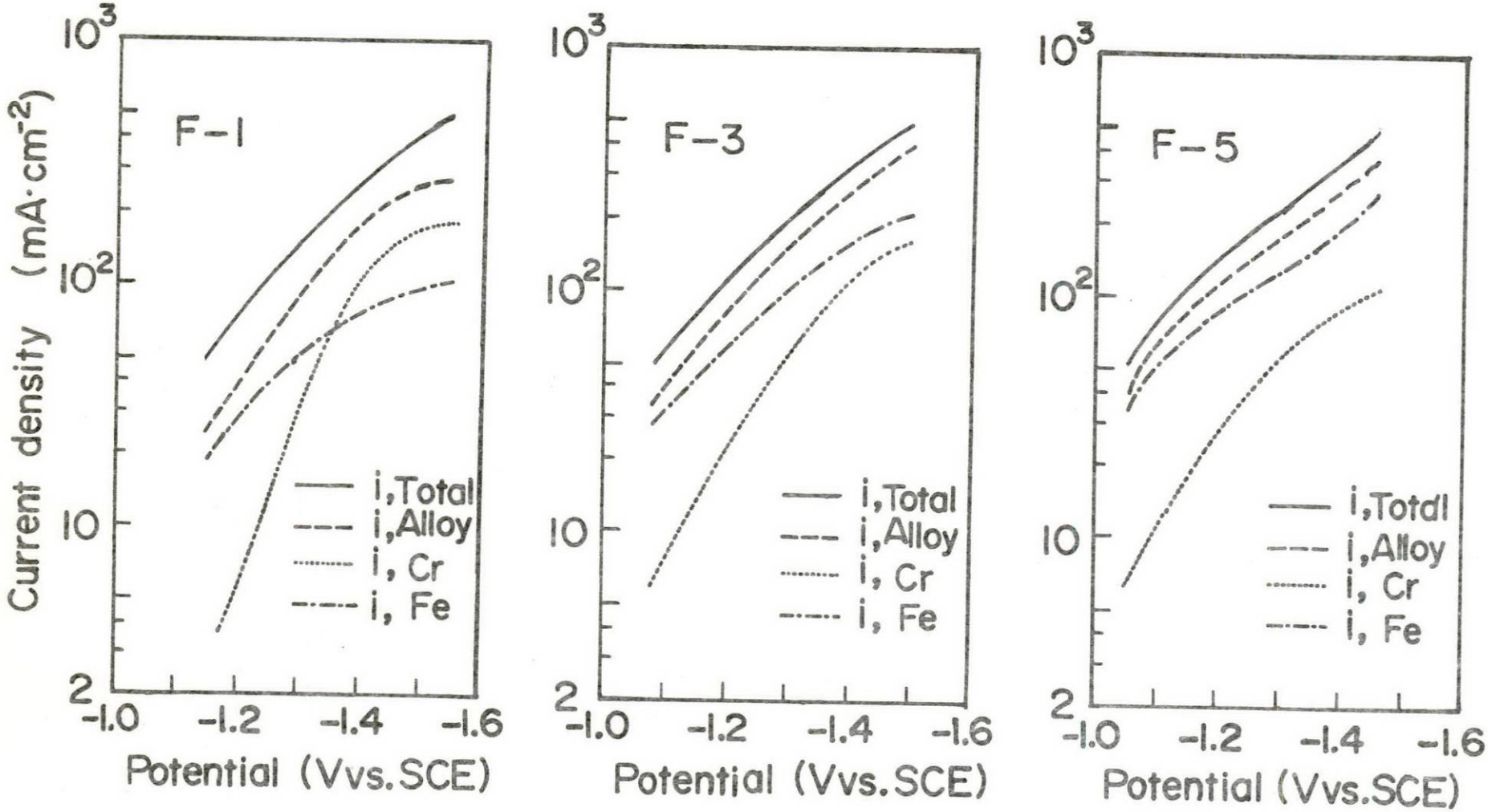


Fig. 7 Effect of bath composition on the current-potenti
curves for the electrod

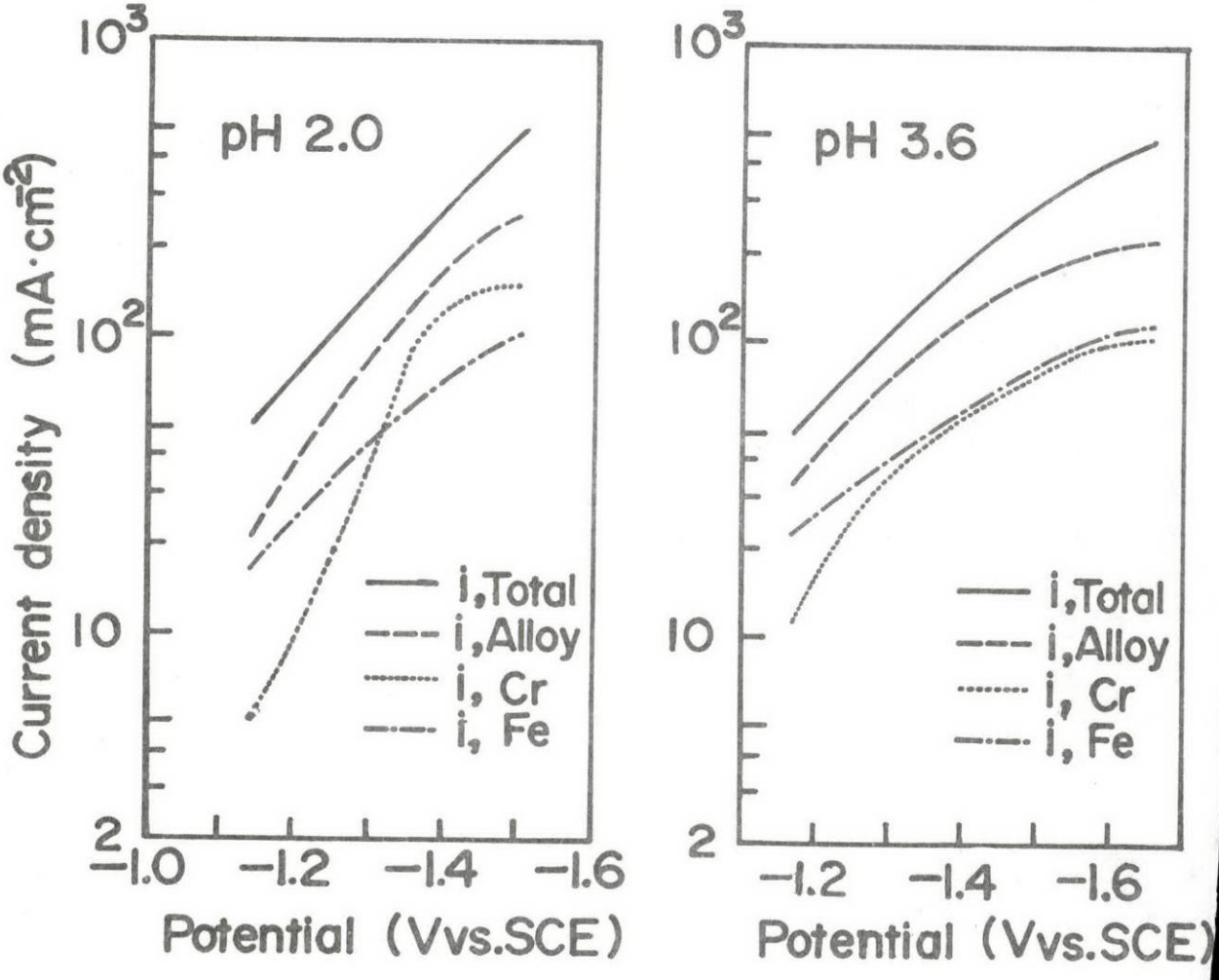


Fig. 8 Effect of pH on the current-potential curves for the electrodeposition of Cr-Fe alloys in F-1 bath (30°C)

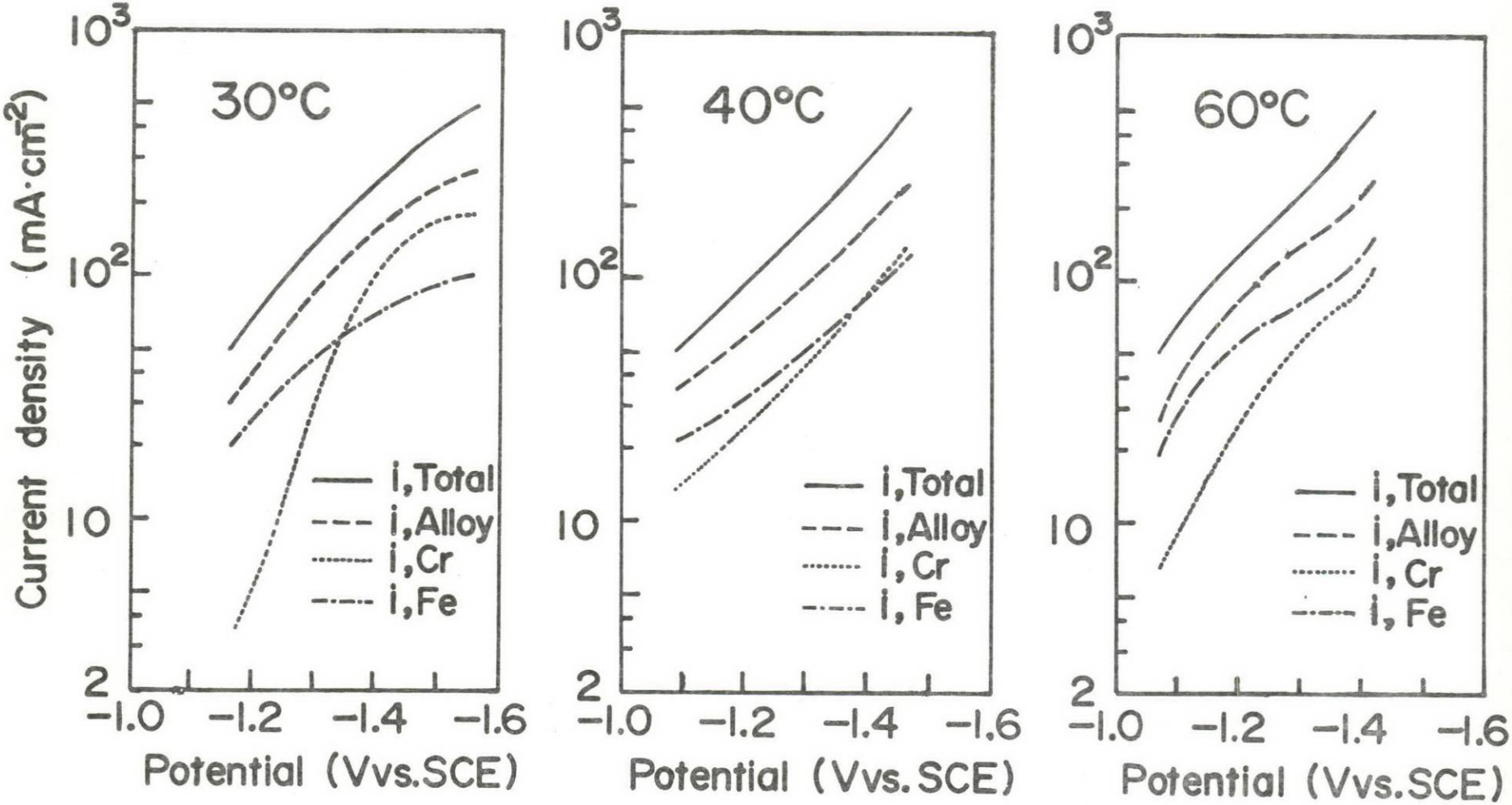


Fig. 9 Effect of temperature on the current

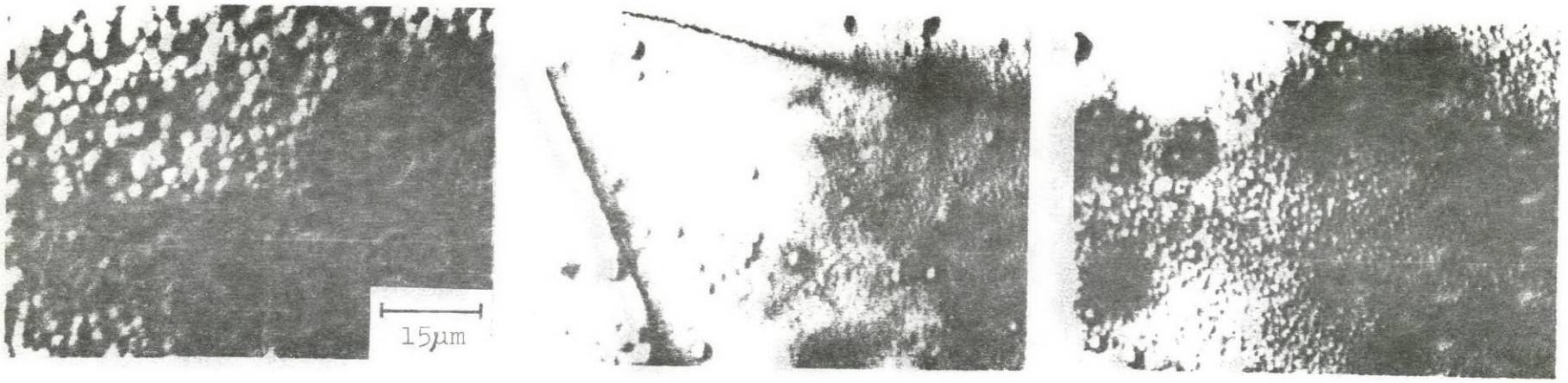
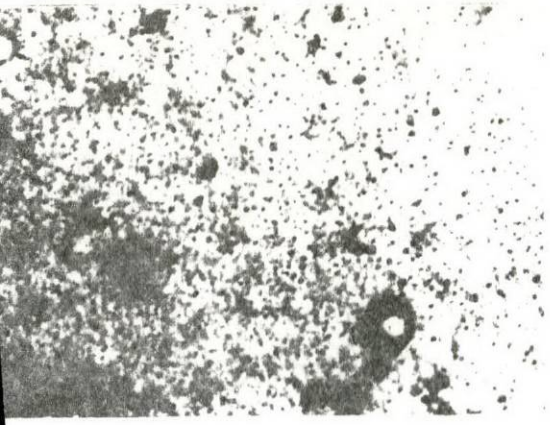
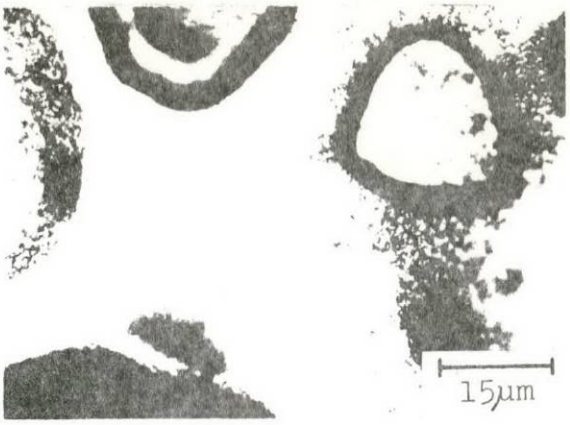


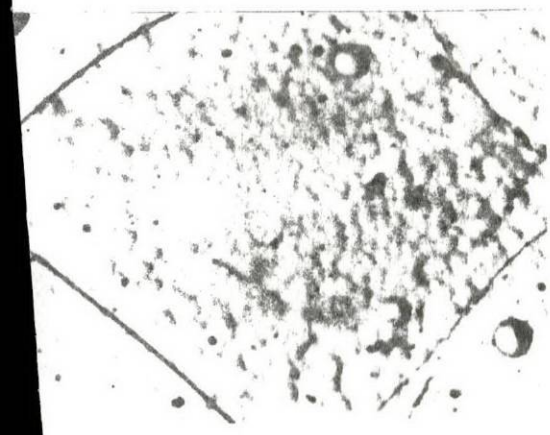
Fig. 10 Photomicrographs of Cr-Fe alloy electrodeposits obtained on copper substrate from F-1 bath (pH 2.8, 30°C)



F-3, 50mA·cm^{-2}



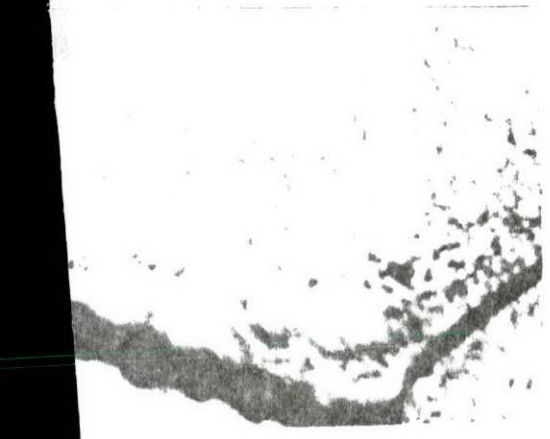
F-5, 50mA·cm^{-2}



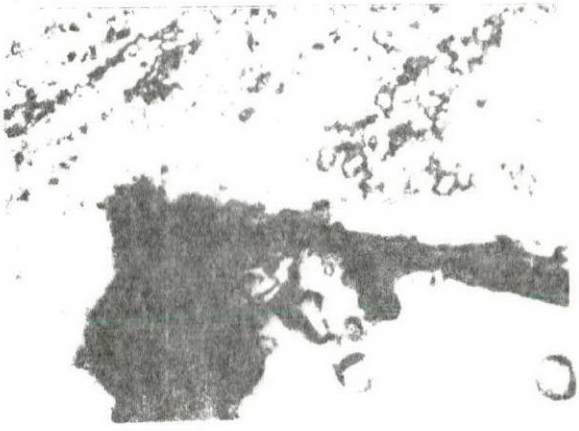
F-3, 150mA·cm^{-2}



F-5, 150mA·cm^{-2}

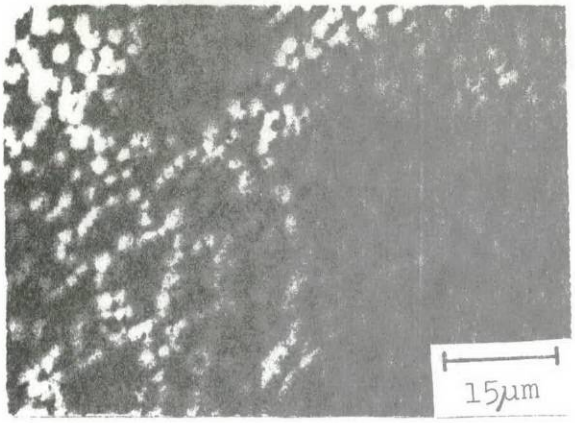


F-3, 300mA·cm^{-2}

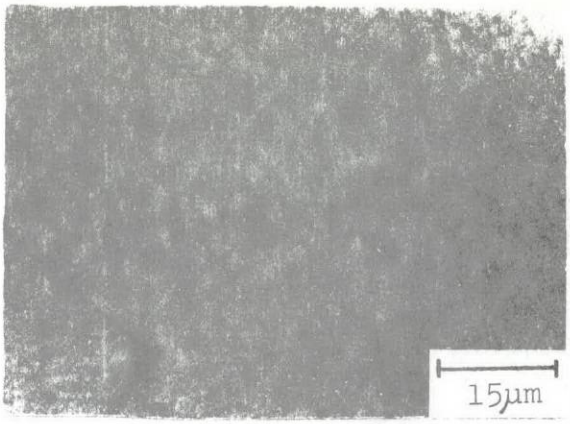


F-5, 300mA·cm^{-2}

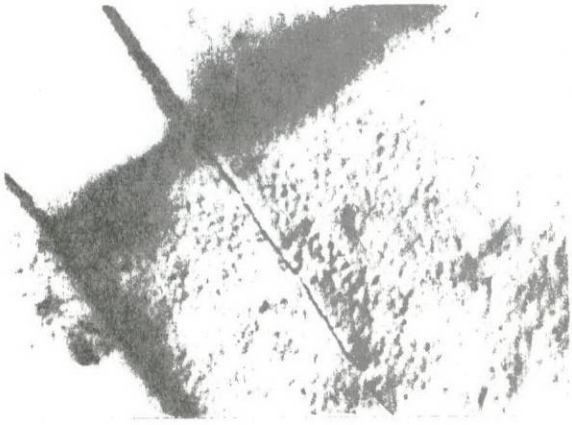
Photomicrographs of Cr-Fe alloy electrodeposits obtained rom F-3 and F-5 baths (pH 2.8, 30°C)



pH 2.0, 50mA·cm^{-2}



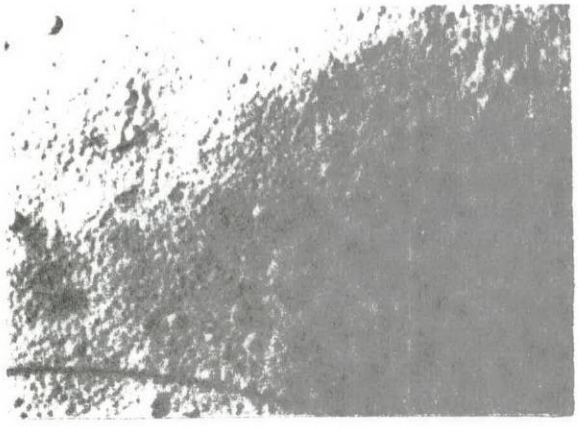
pH 4.0, 50mA·cm^{-2}



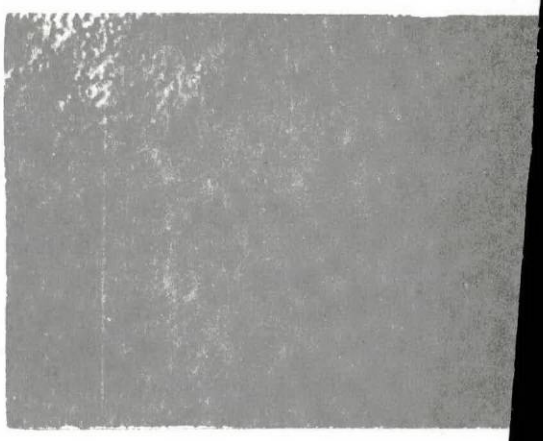
pH 2.0, 150mA·cm^{-2}



pH 4.0, 150mA·cm^{-2}



pH 2.0, 300mA·cm^{-2}



pH 4.0, 300mA·cm^{-2}

Fig. 12 Photomicrographs of Cr-Fe alloy electrodeposits obtai
from F-1 bath (30°C)

M-5

Chromium II
Session M

Chromium Plating of Steel Aircraft Components

S. Daniel
Sacramento Air Logistics Center
McClellan Air Force Base, CA

CHROMIUM PLATING OF STEEL AIRCRAFT COMPONENTS

By

Seymour Daniel

ABSTRACT

Some practical experiences with chromium plating on high strength steel aircraft components are outlined. Although several high strength steel parts are involved, the paper will deal primarily with hard chromium plating on D6AC steel, a specification MIL-S-8949 vacuum melted chromium-molybdenum-vanadium-nickel steel. An acceptance criterion for some of the parts was that the finished chromium deposit be free of mud-flat-cracking. Obtaining a deposit which was free of mud-flat-cracking was particularly difficult for one of the parts. The paper will include possible reasons why the chromium deposit on one part is free of mud-flat-cracking, while on another there will be excessive mud-flat-cracking.

CHROMIUM PLATING OF STEEL AIRCRAFT COMPONENTS

By

Seymour Daniel

The aircraft which are overhauled are equipped with a significant tity of chromium plated high strength steel components. During use he aircraft many of the components become unserviceable due to wear, osion or other surface defects. Affected parts are required to either crapped and replaced with new ones or salvaged by replating or another buildup process. Although a variety of steel parts are involved, are represented by 4130, 4340 and D6AC steels. A high strength steel iversally accepted as being a steel with a heat treat of 180,000 psi ksi) or above.

Salvaging of unserviceable parts by replating with a Specification 320, Class 2 chromium deposit was determined to be the most feasible of replacement for most of the parts. This paper will concentrate ily on experiences involving the chromium plating of D6AC steel com- s but will also include some details about plating parts which were ctured out of other high strength steels. All of the D6AC steel ents represent one aircraft, the F-111.

AC steel is a specification MIL-S-8949, Cr-Mo-V-nickel alloy which uced by the consummable electrode vacuum melting process. Vacuum reportedly improves the structure sensitive properties such as strength, ductility and impact strength. The ultimate tensil strength 000 to 240,000 psi (180 to 240 ksi). The chemical composition of D6AC mpared with 4130 and 4340 steels is as shown in Table I.

lating of used parts is usually a more challenging and difficult task ting newly manufactured ones. This is particularly true when replat- strength steel parts with a hard chromium. There are probably several which contribute to the difficulty. However, two factors are believed the results significantly. The first is contamination of the part, face and absorbed, which makes cleaning more difficult. Contaminants not sufficiently removed may prevent adherent subsequent electro- The second factor to consider is that a used part will usually ome reworking of the surface after the original deposit is removed. results in a reduction in the thickness of the basis metal which in a thicker electrodeposit necessary in order to restore the part to ed dimension. Obtaining a thicker deposit which complies with certain

specification requirements, such as a chromium deposit which is free of mud-flat-cracking, is likely to be considerably more difficult than a thinner deposit complying with the same requirements.

Specification QQ-C-320 provides two classifications for chromium electrodeposits, Class 1 and Class 2. Class 1 is described as a "corrosion protecting deposit with a thickness of 0.0001 to 0.0002 inch (0.0003 to 0.0 cm). Class 2 is described as an "engineering" or "hard" chromium which is used for wear resistance, abrasion resistance, and such corrosion protecti as the specified thickness may afford. The minimum thickness is 0.0002 in (.0005 cm). The Class 2 deposit is usually applied directly to the basis metal and is finished by grinding to the specified dimensions. Additional corrosion resistance can be obtained by use of an undercoat of electrodepo ed nickel in thickness of 0.0001 to 0.002 inch (0.0003 to 0.0005 cm) on ferrous parts, the minimum thickness to be determined by service condition Heavy deposits of the Class 2 plating may be used for buildup of worn or undersized parts, or for salvage purposes and to provide protection agains corrosive chemical environments.

Process solution formulations and operating variables, process seque and the results obtained from chromium plating of aircraft high strength components follows:

SOLUTION FORMULATIONS

The chromium plating bath is formulated and operated within th guidelines of MIL-STD-1501 (USAF) for obtaining a low embrittlement chromium deposit. Refer to Table II, Page 11.

The chromium strip solution for ferrous base parts is an aque solution of sodium hydroxide. Refer to Table III, Page 11.

ANODES

Anodes for chromium plating and stripping are made from a lea antimony alloy consisting of 93% by weight lead and 7% by weight antimony. Tank anodes are round and corrugated.

SEQUENCE OF PROCESSING PARTS

1. Degreased in a vapor degreaser. Tetrachloroethylene solvent is used in the vapor degreaser.

2. Preinspected to determine the extent of damage or wear, centricity and if an out-of-round condition exists.

3. The old chromium deposit is removed either by electroche anodic stripping or by machine grinding. Several factors are co ed in determining which method will be used. Other deposits, us cadmium or nickel are removed by chemical immersion.

4. Machine grinding is performed as necessary.

5. A specification MIL-C-16173 corrosion preventive or alternate may be applied between operations. If so, vapor degreasing is always performed prior to the next operation.

6. Stress relief baked for 3 hours at 375±25°F (191±14°C) after machine grinding.

7. Magnetic particle inspected in accordance with specification MIL-I-6868 for detecting imperfections at or near the surface.

8. Temper etch inspected in accordance with MIL-STD-867 (USAF).

9. Shot peened, when specified, in accordance with specification MIL-S-13165 to obtain compressive stresses on the peened surface to increase fatigue strength.

10. Vapor degreased.

11. Racked and masked. Electroplaters' yellow backed dhesive tape, lead backed adhesive tape, PVC gray non-adhesive ape and stop-off wax are used in the masking process. Three oats of wax are usually applied.

12. Maskant is selectively removed from the area to be ated.

13. The exposed area is solvent cleaned with a clean cloth tetrachloroethylene or freon TF solvent.

14. The area to be plated is usually dry blasted with 120 aluminum oxide at between 20 to 40 psi. Dry blasting with ss beads or garnet as alternates is sometimes done on some els but D6AC steel components are always abrasively cleaned aluminum oxide.

15. Rinsed thoroughly in clean cold tap water.

16. Immersed for 30 to 60 seconds in an aqueous rust inhibit- solution. This step is optional and may be omitted if plating be accomplished immediately.

7. Anodes are positioned and fixtures attached in a manner at all areas are plated as evenly as possible. Conforming and inside diameter anodes are utilized as appropriate.

. Part is immersed in the chromium plating tank with the t on as soon as possible after abrasive blasting. The current usted at between 2 and 4 amps per square inch (0.508 to 1.016 dm) for 1 to 3 minutes. There are advantages and disadvantages

for etching in a chromium solution which is used exclusively for reverse etching. There are also advantages and disadvantages to reverse etching in the plating tank. Due to the layout of the chromium plating line in our shop it is more advantageous to reverse etch within the plating tank than a separate tank.

19. The current is reversed and the part is made cathodic at 1.5 to 3 amperes per square foot (.16 to .32 amperes/sq dm) and plated until a chromium deposit of the required thickness has been obtained. Plating may be periodically interrupted to examine the quality of the chromium deposit and to determine the depth of the deposit.

20. The plated part is rinsed thoroughly and blown dry with clean shop air.

21. Part is dewaxed by hanging in the dewaxer cabinet which is equipped with infrared heating lamps.

22. Tape is removed.

23. Part is vapor degreased.

24. Racking and fixtures are removed.

25. Vapor honed to remove stains.

26. Baked for 23 hours at 375±25°F (191±14°C) if chromium plating is the only electrodeposit to be applied. Part is given an interim bake for 4 hours at 375±25°F (191±14°C) if subsequent electroplating or electroless plating is to be accomplished. Afte chromium plating some parts are required to be cadmium plated, som electroless nickel plated and some cadmium and electroless nickel plated.

CADMIUM PLATING OF CHROMIUM PLATED STEEL PARTS

After the interim 4 hour bake following chromium plating par are processed for cadmium plating as follows:

1. Vapor degreased.

2. Masked as necessary. Chromium plated areas are not mas as cadmium will not adhere to a chromium substrate.

3. Dry abrasively blasted with aluminum oxide grit, garne glass beads.

4. Rinsed thoroughly.

5. Plated immediately by immersing in cadmium plating tank with the current on. Cadmium plating is accomplished at 50 to 80 asf (5.38 to 8.61 asd) in a cyanide, low embrittling solution which contains no brightening additives. Refere to Table V. The alternate procedure for cadmium plating high strength steel parts is the stylus or selective plating process in which commercially formulated low-hydrogen-embrittling cadmium solution is applied in accordance with the manufacturer's recommendation.

6. Rinsed thoroughly.

7. If not to be subsequently electroless nickel plated all cadmium plated parts, tank and selectively plated, are baked for 23 hours. Parts which ar cadmium plated in the tank cyanide bath are intermittently baked for 4 hours at 375±25°F (191±14°C) prior to electroless nickel plating and then baked for 23 hours. Parts which are cadmium plated selectively with a low-hydrogen-embrittling solution are not baked prior to electroless nickel plating but baked for 23 hours at 375±25°F (191±14°C) afterwards.

8. Treated to obtain a type two supplementary chromate treatment, when specified.

ELECTROLESS NICKEL PLATING OF CHROMIUM PLATED STEEL PARTS

After the interim 4 hours bake following chromium or cadmium lating parts are processed for electroless nickel plating as follows:

1. Vapor degreased.

2. Racked and masked as necessary. A non-adhesive pvc strip sheeting and standard adhesive backed electroplaters' tape are ed for making areas not required to be plated.

3. The exposed area is solvent cleaned.

4. Dry blasted with aluminum oxide.abrasive or alternate.

5. Rinsed thoroughly.

6. Anodically cleaned in electrolytic alkaline cleaning solution.

7. Rinsed thoroughly.

8. Immersed in nickel strike solution (Table IV) with the nt off. Part is then made anodic at 5 to 7 amperes/sq. ft (0. o 0.753 asd) for 20 to 30 seconds. The current is reversed and art is made cathodic at 25 to 44 amperes/sq ft (2.69 to 4.73 es/sq dm) 6 to 7 minutes. The current is turned off prior to ing part from the nickel strike solution.

9. Rinsed thoroughly.

11. Plated in a commercially formulated electroless nickel bath to obtain a MIL-C-26074, Class 1 electroless nickel deposit. The bath is formulated and operated in accordance with the manufacturer's recommendations.

12. Rinsed thoroughly.

13. Masking and fixtures are removed.

14. Part is baked for 23 hours at 375±±5°F (191±14°C).

POST CHROMIUM PLATING PROCESSING

When all of the plating operations and the final baking step have been accomplished steel parts are processed as follows:

1. The chromium plated surface is ground to the required dimensions.

2. Stress relief baked for 4 hours at 375±25°F (191±14°C).

3. Inspected by flourescent penetrant in accordance with MIL-I-6866 for surface cracks or discontinuities. The presence of mud-flat-cracking in the chromium deposit is acceptable for some parts and unacceptable for others. Aircraft engineering personnel estab criteria for accepting or rejecting mud-flat-cracking. The functi of the part, amound of load, and the environment in which used, ar among important factors considered in the engineering determinatio

The depth of the finished chromium deposit on most of the pa processed as detailed above is between 0.005 and 0.010 inch (0.02 to 0.00127 cm). Consistently adherent deposits have been obtained though the area to be plated is not pumice scrubbed between maski and plating. The only problem encountered has been mud-flat-crac in the chromium deposit of one part, the F-111 wing pivot pin she lug, which is manufactured from D6AC steel. When inspection of t wing pivot shear lug removed from the aircraft during overhaul re crack indications in either the original chromium deposit or in surface of the basis metal, the lug must be reworked or replaced a new one. As there was no criterion for the chromium deposit t free of mud-flat-cracking on lugs which were first installed, no

was performed for the detecting presence of mud-flat-cracking. It is very likely that many of the first lugs installed had mud-flat-cracking, although inspection at overhaul has revealed that many did not. There is no evidence that the presence of cracks in the chromium deposit has had any detrimental effects upon shear lugs during more than 5 years use on the aircraft. The responsible engineering office has determined in the interim that because of the potential for propagation of cracking into the basis metal or the development of corrosion through cracks, mud-flat-cracking in the chromium deposit is now unacceptable both on new and reworked lugs.

Utilizing the low hydrogen embrittling bath per MIL-STD-1501 (Table II) and all of the techniques of fixturing, masking, cheating, conforming anodes and operating variables which have provided a crack free deposit on other parts have failed to produce such a deposit on shear lugs. There are two differences between shear lugs and other highstrength steel parts which are hard chromium plated. One is the thickness of the finished chromium deposit. The finished thickness of the chromium deposit on most parts plated is .005 to 0.0100 inch (0.0127 to 0.0254 cm). The reworked shear lugs require a finished chromium deposit with a thickness of 0.010 to .015 inch (0.0254 to 0.0381 cm) to restore dimension. Another difference is the configuration. Nearly all of the other parts are cylindrical. The configuration of the shear lug is very different and much more complicated.

There is not always cracking when the total thickness of the plated chromium deposited does not exceed 0.010 inch (0.0254 cm) but the results are not consistent. When the thickness exceeds 0.010 inch (0.0254 cm) mud-flat-cracking is nearly always present. There appears to be some relationship between chromium thickness and mud-flat-cracking. There is also apparently some relationship between part configuration and mud-flat-cracking. The more complicated the configuration the greater the tendency for cracking in the chromium deposit. A combination of the two, chromium thickness and complicated configuration, seems to increase the tendency for mud-flat-cracking chromium electrodeposits.

Because of futile attempts to consistently obtain a crack free chromium deposit on shear lugs plated in the shop, Aircraft Engineer- contracted out to a vendor for manufacturing a number of new r lugs with a specification QQ-C-320, Class 2, engineering chromium

deposit with no mud-flat-cracking. A partial delivery of fifty lugs were received and examined. The finished chromium ranged from 0.004 to 0.009 inch (0.0102 to 0.0319 cm) thick and each of the fifty lugs exhibited mud-flat-cracking in the chromium deposit on either one or both of the tang surfaces.

Comparing the results obtained on new shear lugs plated by the vendor with those resulting from replating used lugs in the base plating facility, there was a fleeting suspicion that the problem of mud-flat-cracking in the chromium deposit was caused by properties inherent in D6AC steel rather than by other factors. Certainly D6AC steel is subject to high internal stresses characteristic of high strength steels which are capable of inducing mud-flat-cracking in chromium deposits. Hoever, the thought of inherent properties being the sole cause for mud-flat-cracking has to be discounted because of the large quantity of landing gear pins and other D6AC steel parts that have been successfully chromium plated without mud-flat-cracking in the chromium deposit. It is quite feasible that inherent properties of D6AC steel in combination with other factors may contribute to the problems.

The difficulty of a private manufacturer to provide new shear lugs which were free of mud-flat-cracks in the chromium deposit and that of the base plating facility to rework used shear lugs without mud-flat-cracking in the chromium deposit presents the responsible engineering office with three alternatives for finishing shear lugs

1. Relax the present requirements and accept a Specification QQ-C-320, Class 2 deposit applied directly to the basis metal with the presence of mud-flat-cracking not being cause for rejection.

2. Accept a Specification QQ-C-320, Class 2 chromium deposit with a nickel undercoating with the presence of mud-flat-cracking not being cause for rejection.

3. To accept a sprayed metal coating as an alternate to chromium electroplating.

SUMMARY:

Hard chromium plating of high strength steel aircraft components salvage is a more difficult and challenging task than hard chromium pl newly manufactured parts. Two factors contribute to the difficulty, o is contamination of the part during use which makes cleaning difficult other is decreased basis metal thickness resulting from reworking to e surface defects. The former can affect adhesion if not sufficiently r

The latter results in a thicker electrodeposit being required to restore the dimensions. A thicker deposit meeting certain specification requirements is likely to be more difficult to obtain than a thinner deposit meeting the same requirements. For example, a chromium deposit of 0.010 inch (0.0254 cm) thick is more likely to develop mud-flat-cracking than a deposit 0.005 inch (0.0127 cm) thick.

A chromium deposit of a given thickness on a part with a complicated configuration is also more likely to develop mud-flat-cracking than a deposit of the same thickness on a part of simple design.

Inherent properties of a high strength steel in combination with a complicated design and a thicker deposit increases the tendency for mud-flat-cracking in chromium deposits on high strength steels.

In considering acceptance criteria for chromium plated reworked high strength steel components, the responsible engineering office should not arbitrarily impose the acceptance criteria for new parts. Serious effort and thought should be exerted to establish criteria for reworked parts that are reliable, practical and economically feasible even though those criteria differ significantly from those established for new parts.

TABLES

I. Composition of High Strength Steels

II. Chromium Plating Bath Formulation

III. Chromium Strip Solution Formulation

IV. Nickel Strike Solution Formulation

V. Cadmium Plating Solution Formulation

PHOTOGRAPHS

1. C-141 Aircraft Spoiler Actuator Cylinders
2. C-141 Aircraft Piston
3. C-141 Aircraft Piston
4. F-111 Aircraft Shear Pin, 4330 Va Steel
5. F-111 Aircraft Spike Actuator, D6AC Steel
6. F-111 Aircraft HSTA Barrel, D6AC Steel
7. F-111 Aircraft Cone Actuator Piston
8. F-111 Aircraft Primary Utility Piston D6AC Steel
9. F-111 Aircraft Utility Piston
10. F-111 Aircraft Wing Sweep Screw D6AC Steel, outside diameter
11. F-111 Wing Sweep Screw D6AC Steel, View of inside diameter
12. F-111 Wing Pivot Shear Lug D6AC Steel, Top View
13. F-111 Wing Pivot Shear Lug D6AC Steel, Side View
14. Chromium Plated Tang of Shear Lug After Grind
15. Chromium Plated Tang of Shear Lug After Baking
16. Chromium Plated Tang of Shear Lug After finish Grin
17. Chromium Plated Tang After Partial Grind
18. Chromium Plated Tang of Shear Lug After Partial Gri
19. Chromium Plated Tang of Shear Lug After Finish Grir
20. Chromium Plated Tang Surface of Shear Lug as Plated
21. Chromium Plated Tang Surface of Newly Manufactured Shear Lug
22. Chromium Plated Tang of Newly Manufactured Shear L
23. Chromium Plated Tang of Newly Manufactured Shear L
24. Chromium Plated Tang of Newly Manufactured Shear L

TABLE III

CHROMIUM STRIP SOLUTION

NOMENCLATURE	CONTROL RANGE
Sodium Hydroxide	10 to 15 oz/gal (284 to 425.2 g/l)
Temperature	70 to 90°F (21 to 32°C)
Current Density	60 to 75 ASF (6.5 to 8.1 amps/sq dm)

TABLE IV

NICKEL STRIKE SOLUTION

NOMENCLATURE	CONTROL RANGE
Nickel Chloride	14 to 18 oz/gal (396 to 501 g/l)
Hydrochloric Acid	7 to 9 oz/gal (198 to 255 g/l)
Temperature	75±10°F (18 - 29°C)
Cathodic Current Density	4 to 8 ASF (.03 to .06 amps/sq dm)
Anodic Current Density	25 to 44 ASF (.18 to .308 amps/sq dm) for 5 to 7 minutes

TABLE V

CADMIUM PLATING SOLUTION

NOMENCLATURE	CONTROL LIMITS
Cadmium Oxide	2.5 to 3.5 oz/gal (19 to 26 g/l)
Sodium Cyanide	12 to 16 oz/gal (90 to 120 g/l)
Sodium Hydroxide	1.0 to 3.0 oz/gal (7.5 to 22.5 g/l)
Sodium Carbonate	1.0 oz/gal (7.5 g/l) Make up only
Temperature	60 to 80°F (15 to 20°C)

TABLE I

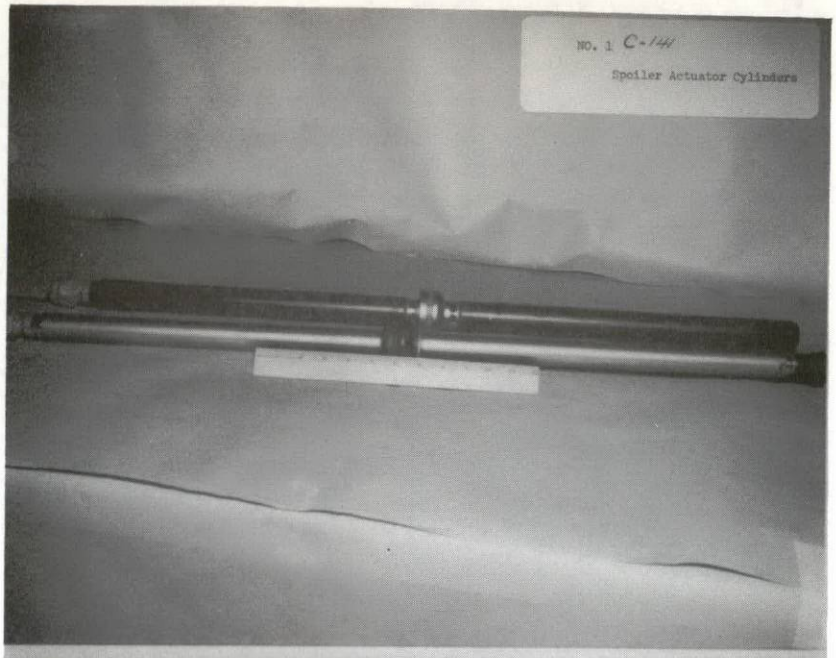
COMPOSITION OF HIGH STRENGTH STEELS

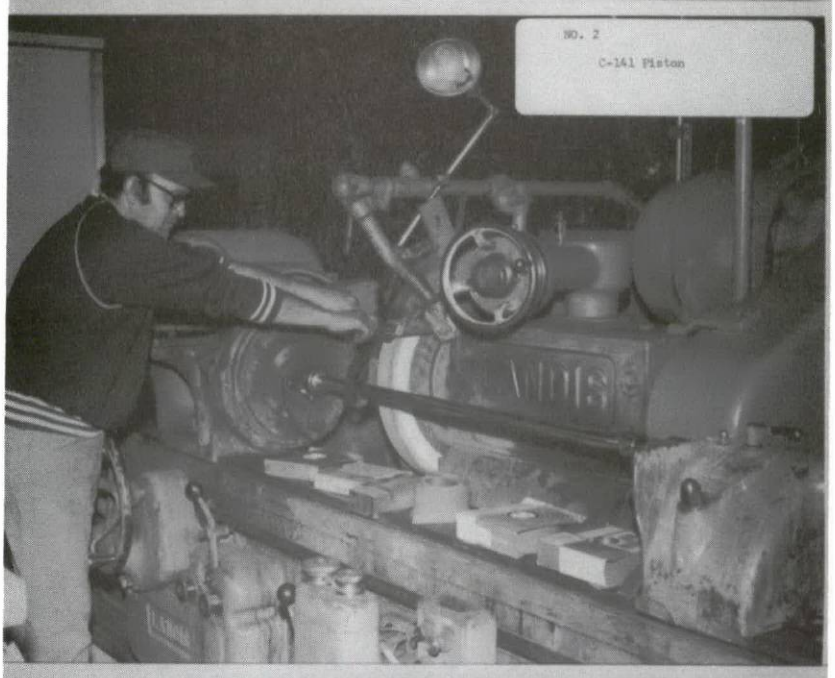
COMPOSITION	STEEL TYPE		
Element % by Wt.	D6AC	4130	4340
Carbon	.42 - .48	.28 - .33	.38 - .43
Manganese	.60 - .90	.40 - .60	.60 - .80
Silicon	.15 - .30	.20 - .35	.20 - .35
Phosphorous	.010 (max)	.040 (max)	.040 (max)
Sulphur	.010 (max)	.040 (max)	.040 (max)
Chromium	.90 - 1.20	.80 - 1.10	.70 - .90
Molybdenum	.90 - 1.10	.15 - .25	.20 - .30
Vanadium	.07 - .15	----	----
Nickel	.40 - .70	----	1.65 - 2.00

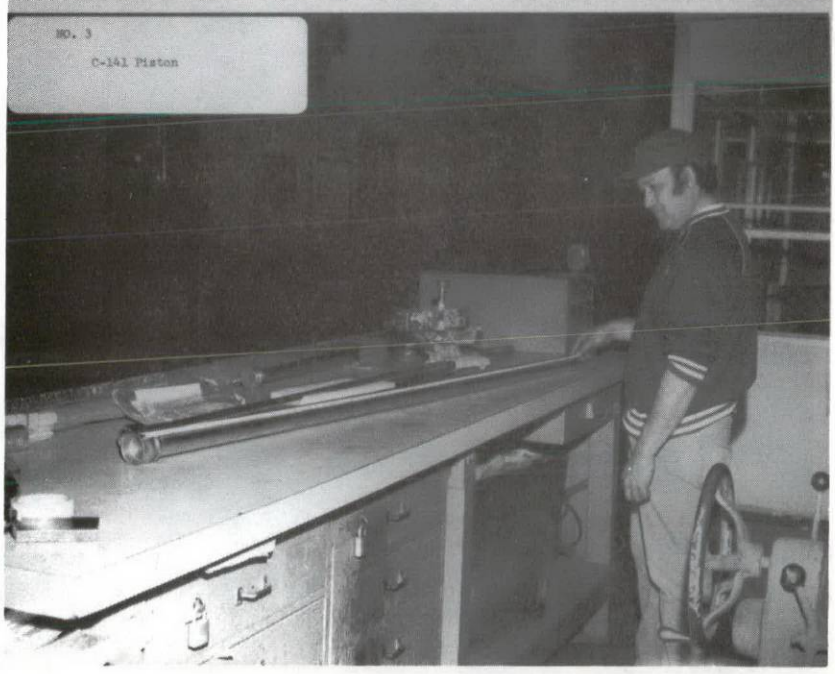
TABLE II

CHROMIUM PLATING SOLUTION

NOMENCLATURE	CONTROL RANGE
Chromic Acid	30 to 36 oz/gal (851 to 1021 g/l)
Sulfate Ion	0.30 to 0.36 oz/gal (85.1 to 102.1
Ratio of Chromic Acid to Sulfate Ion	90:1 to 100:1
Trivalent Chromium	0 to 4 oz/gal (0 to 113 g/l)
Temperature	130 to 140°F (54 to 60°C)
Current Density	1.5 to 3.1 ASF/in (23 to 48 amps/


NO. 1 C-141
Spoiler Actuator Cylinders


NO. 2
C-141 Piston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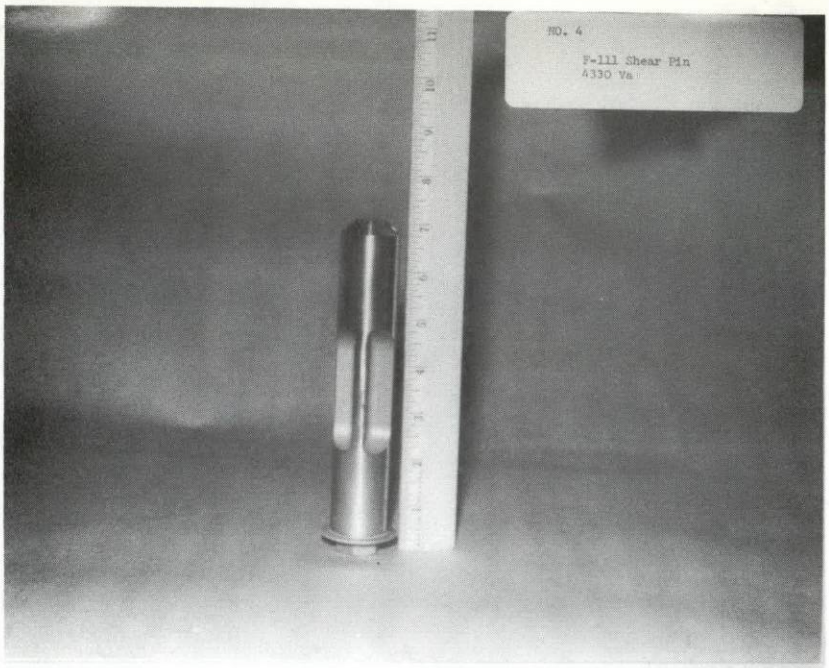
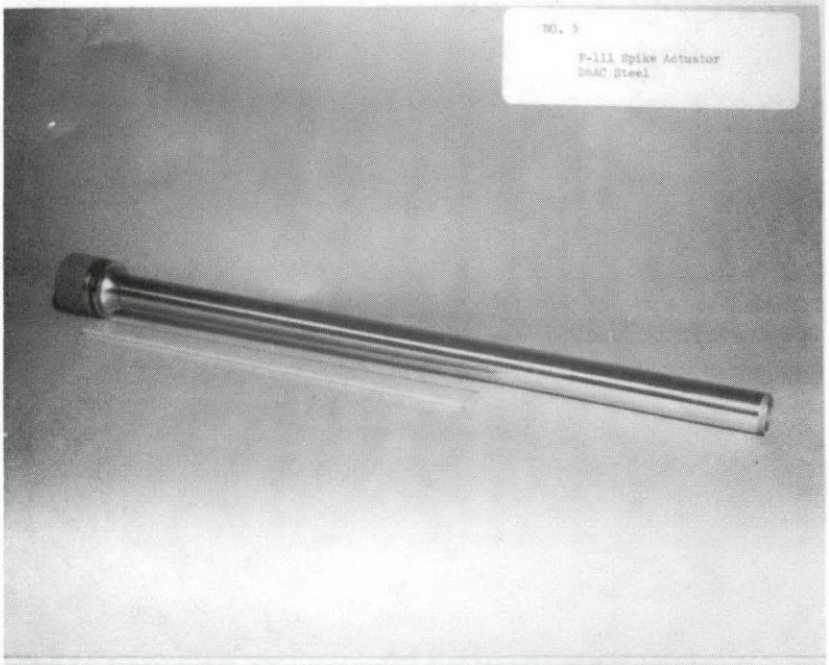
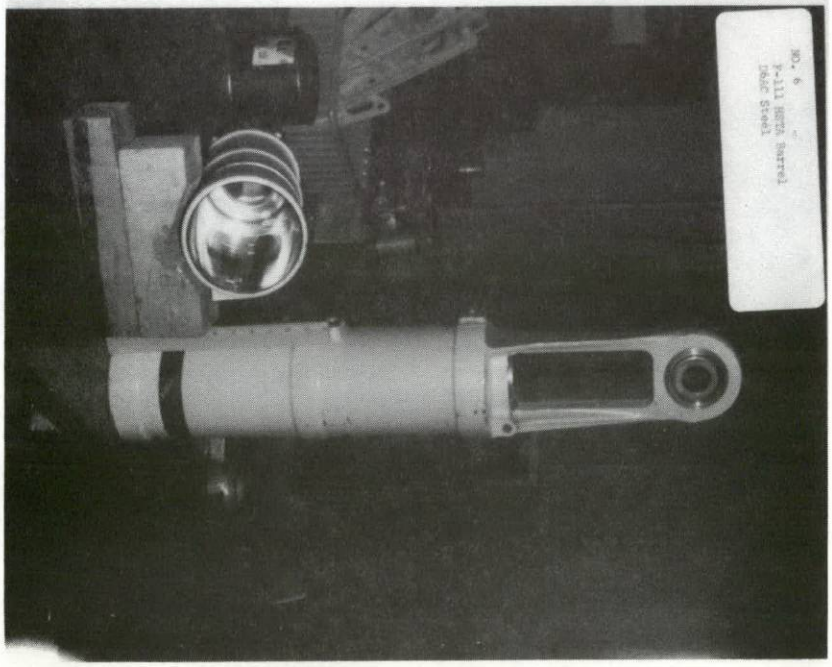
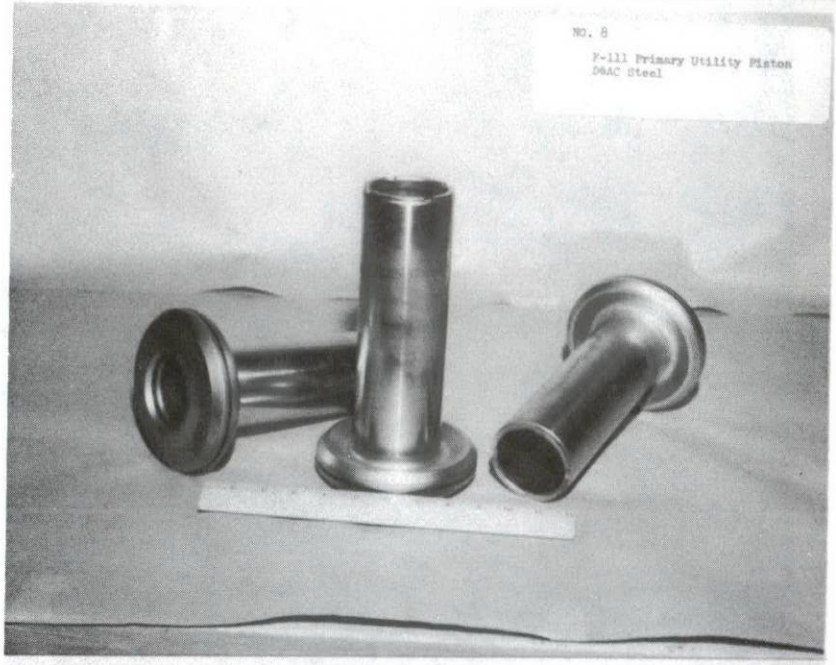
C-141 Piston


NO. 4
F-111 Shear Pin
4330 Va

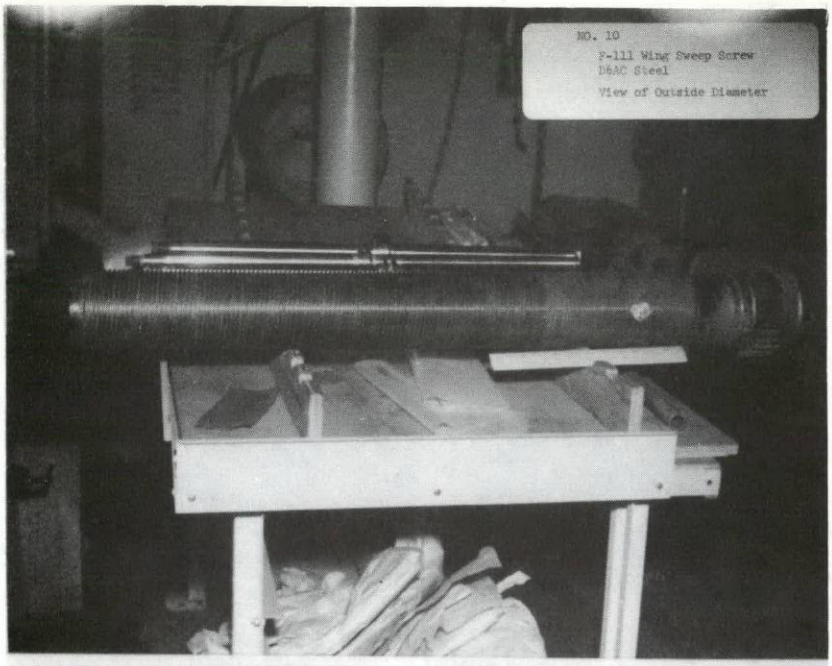

NO. 5
F-111 Spike Actuator
D6AC Steel

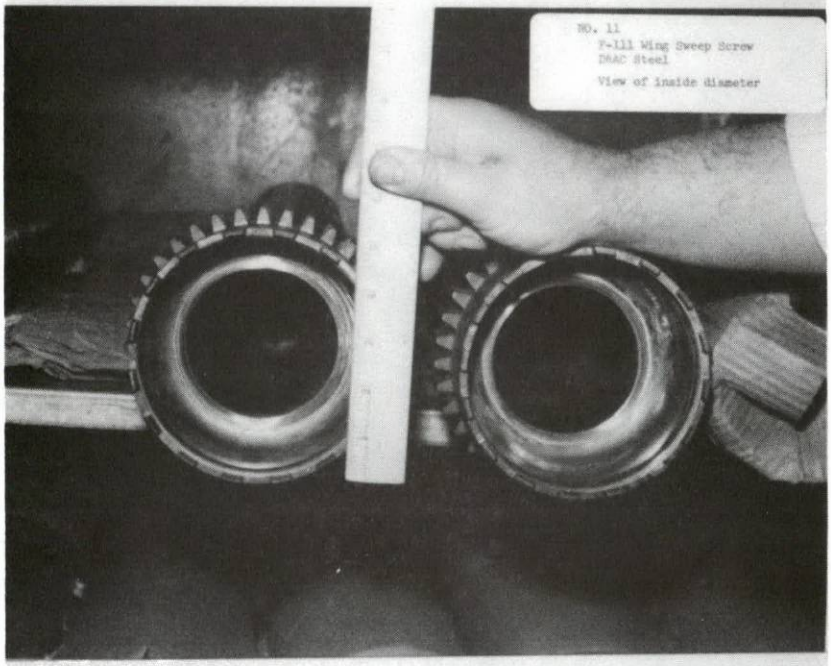

NO. 6
F-111 Nozzle Barrel
D6AC Steel

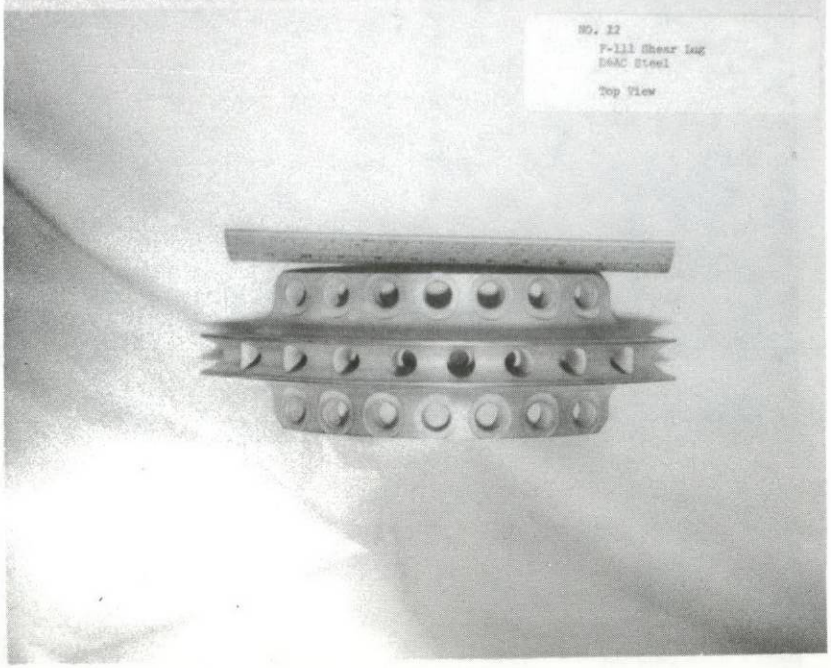

NO. 7
F-111 Cone Actuator
D6AC Steel

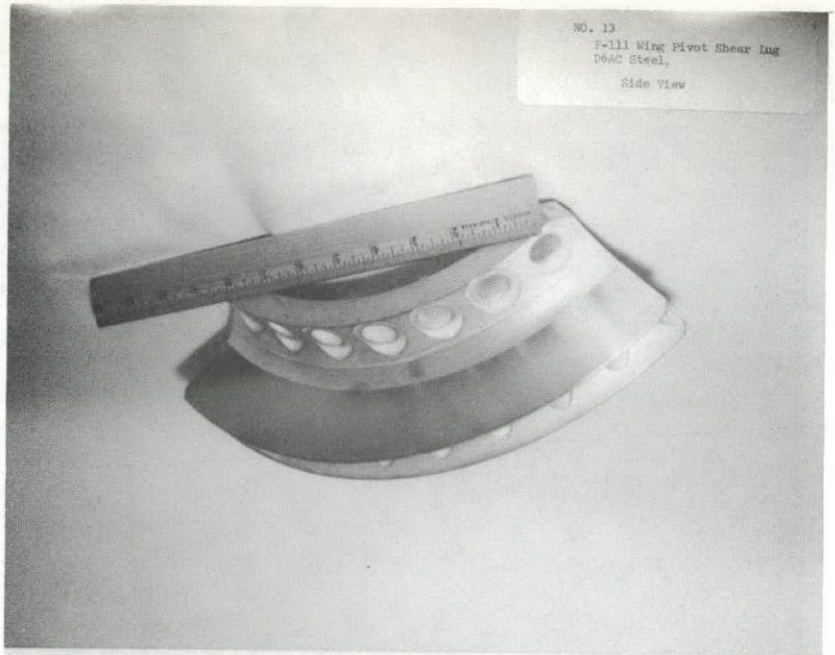

NO. 8
F-111 Primary Utility Piston
D6AC Steel


NO. 9
F-111 Utility Piston
D6AC Steel

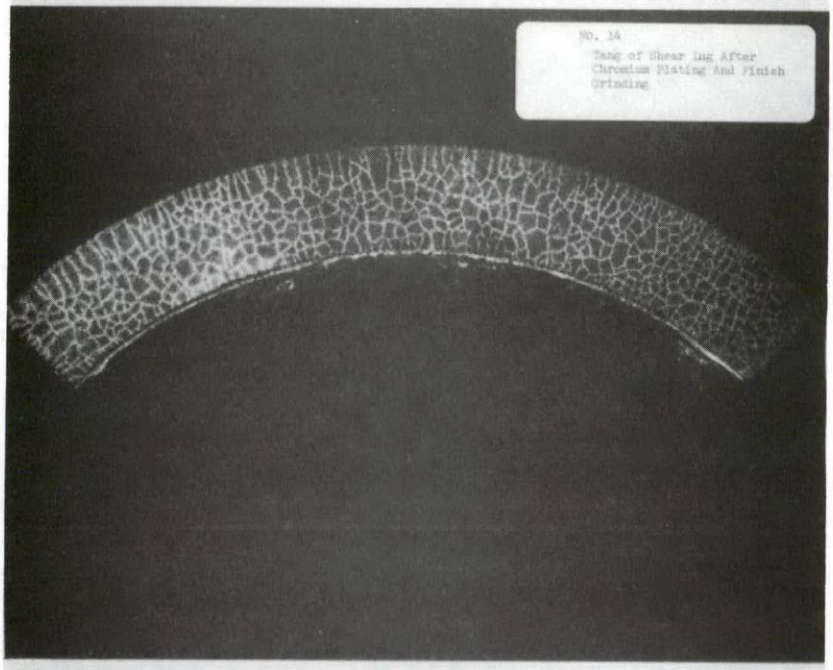

NO. 10
F-111 Wing Sweep Screw
D6AC Steel
View of Outside Diameter


NO. 11
F-111 Wing Sweep Screw
D6AC Steel
View of Inside diameter


NO. 12
F-111 Shear Lug
D6AC Steel
Top View



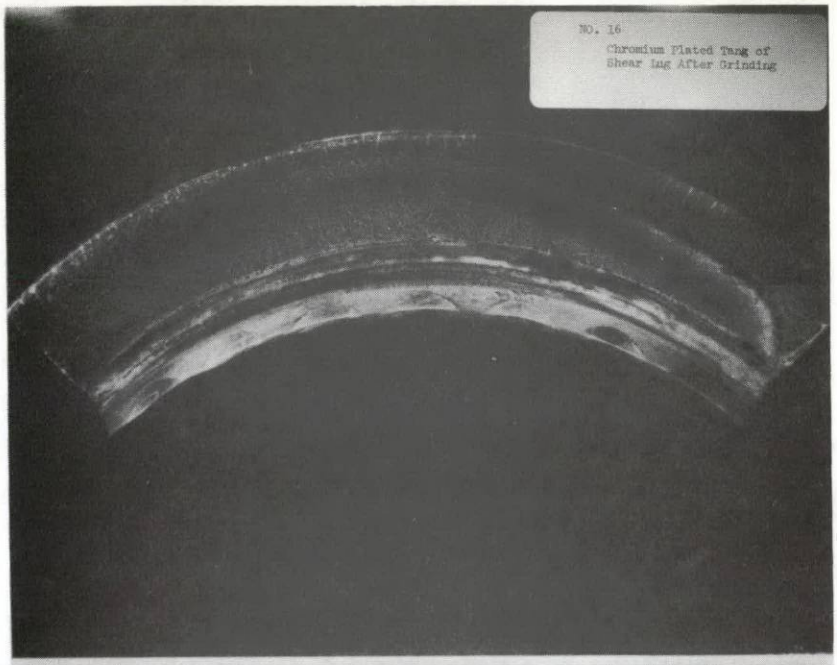
NO. 13
F-111 Wing Pivot Shear Lug
D6AC Steel,
Side View



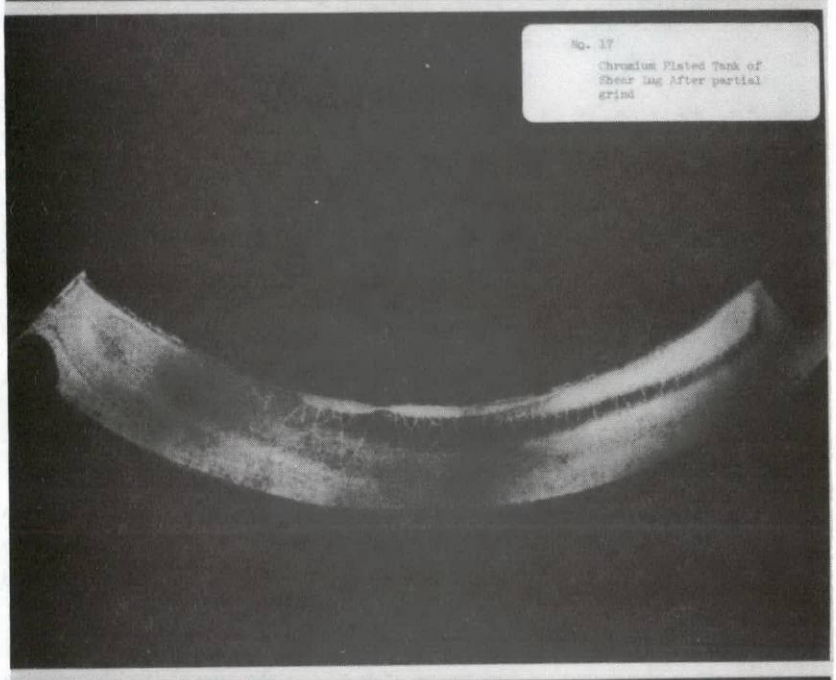
NO. 14
Tang of Shear Lug After
Chromium Plating And Finish
Grinding



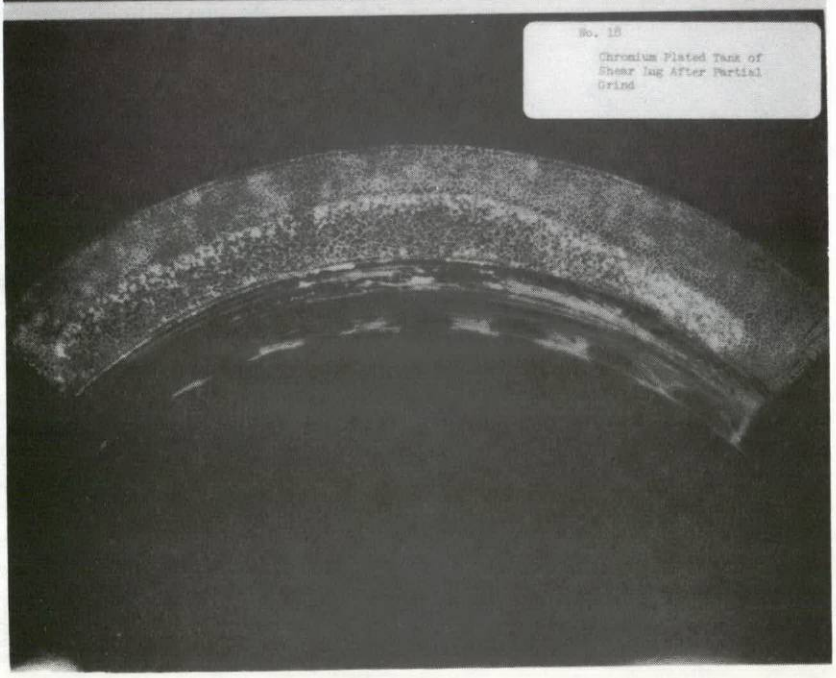
NO. 15
Chromium Plate Tang
of Shear Lug After Baking



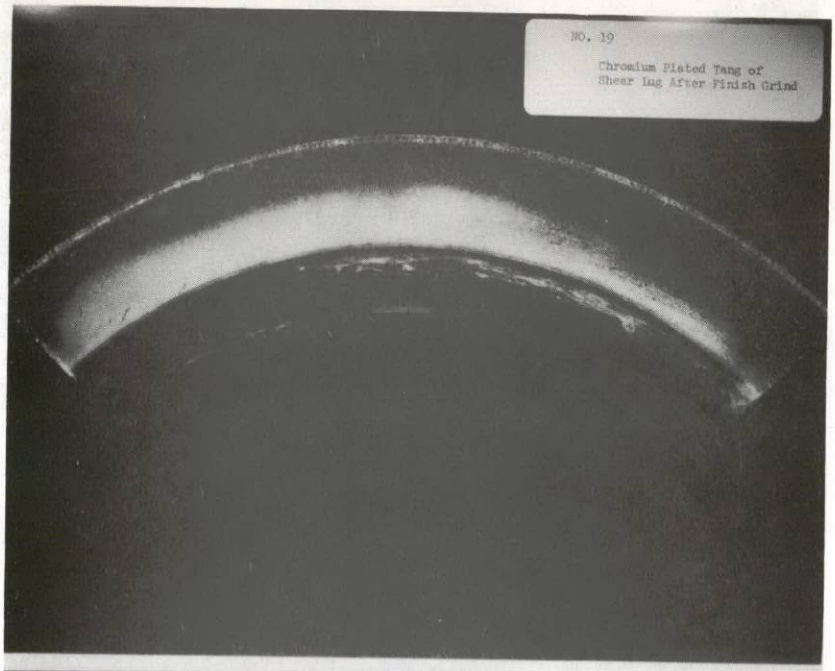
No. 16
Chromium Plated Tang of Shear Lug After Grinding



No. 17
Chromium Plated Tank of Shear Lug After partial grind

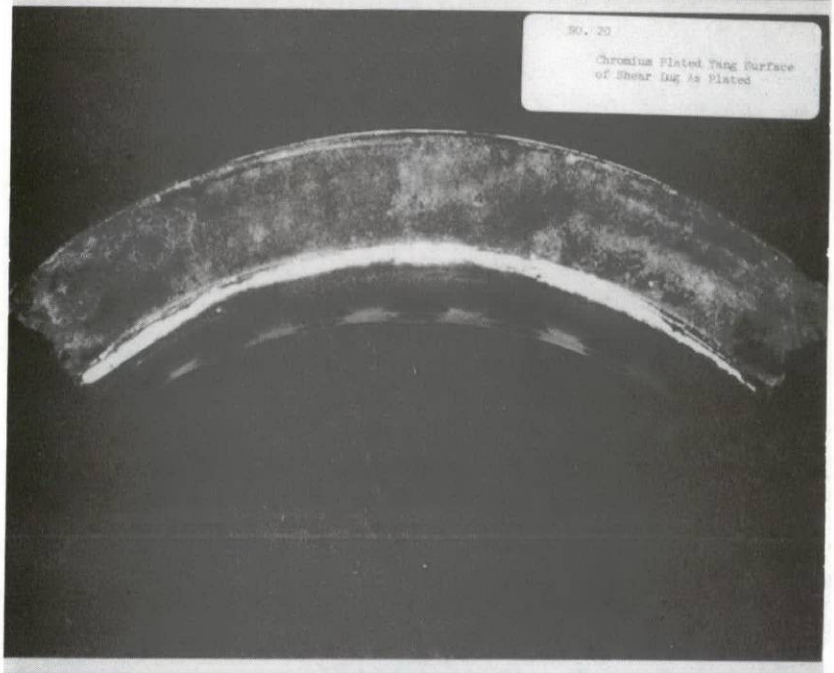


No. 18
Chromium Plated Tank of Shear Lug After Partial Grind



NO. 19

Chromium Plated Tang of
Shear Lug After Finish Grind



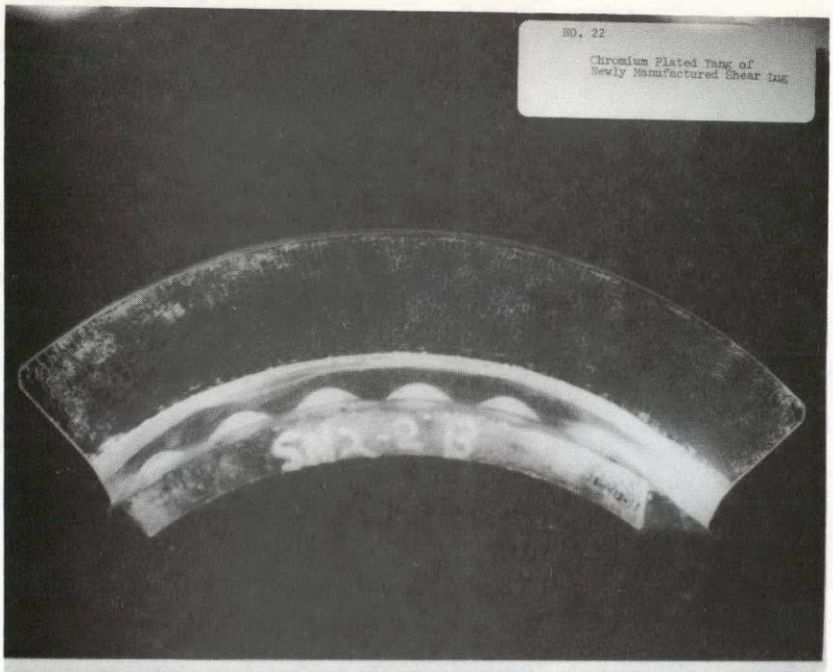
NO. 20

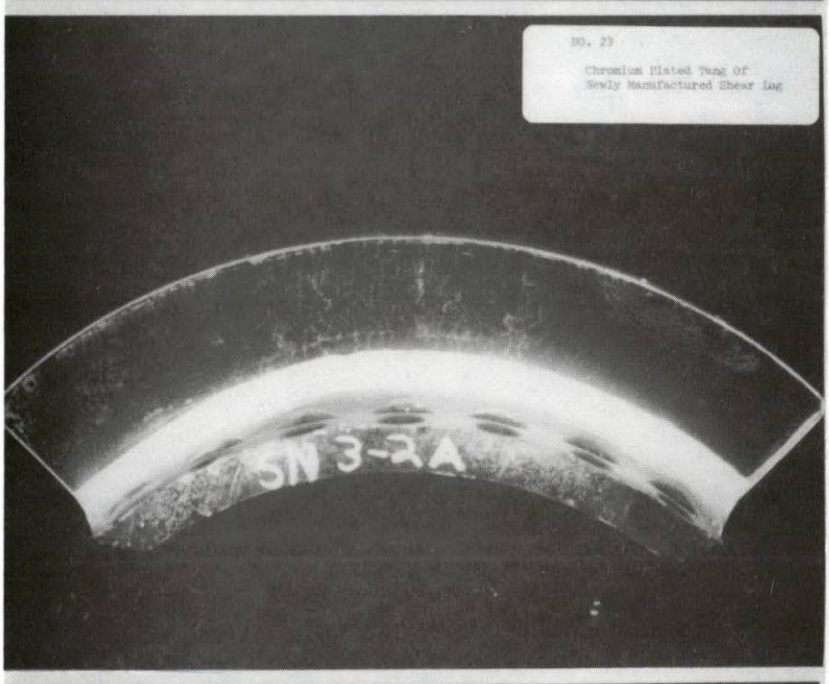
Chromium Plated Tang Surface
of Shear Lug As Plated



NO. 21

Chromium Plated Tang of Newly
Manufactured Shear Lug


NO. 22
Chromium Plated Tang of
Newly Manufactured Shear Lug


NO. 23
Chromium Plated Tang Of
Newly Manufactured Shear Lug
SN 3-2A


NO. 24
Chromium Plated Tang of
Newly Manufactured Shear Lug

N-1

Energy Conservation II
Session N

Case Study of Energy Conservation In a Captive Shop

R. E. Becht
Western Electric Co.
Columbus, Ohio

CASE STUDY

ENERGY CONSERVATION - COLUMBUS WORKS - WESTERN ELECTRIC COMPANY

The Columbus Plant of the Western Electric Company is dedicated to the manufacture of Telephone Switching Equipment. These manufacturing operations are housed in a single story building encompassing more than a 1,000,000 square feet. A three story office building totaling approximately 450,000 square feet adjoins the manufacturing area. Waste treatment facilities, a power plant and miscellaneous other facilities are housed in separate buildings.

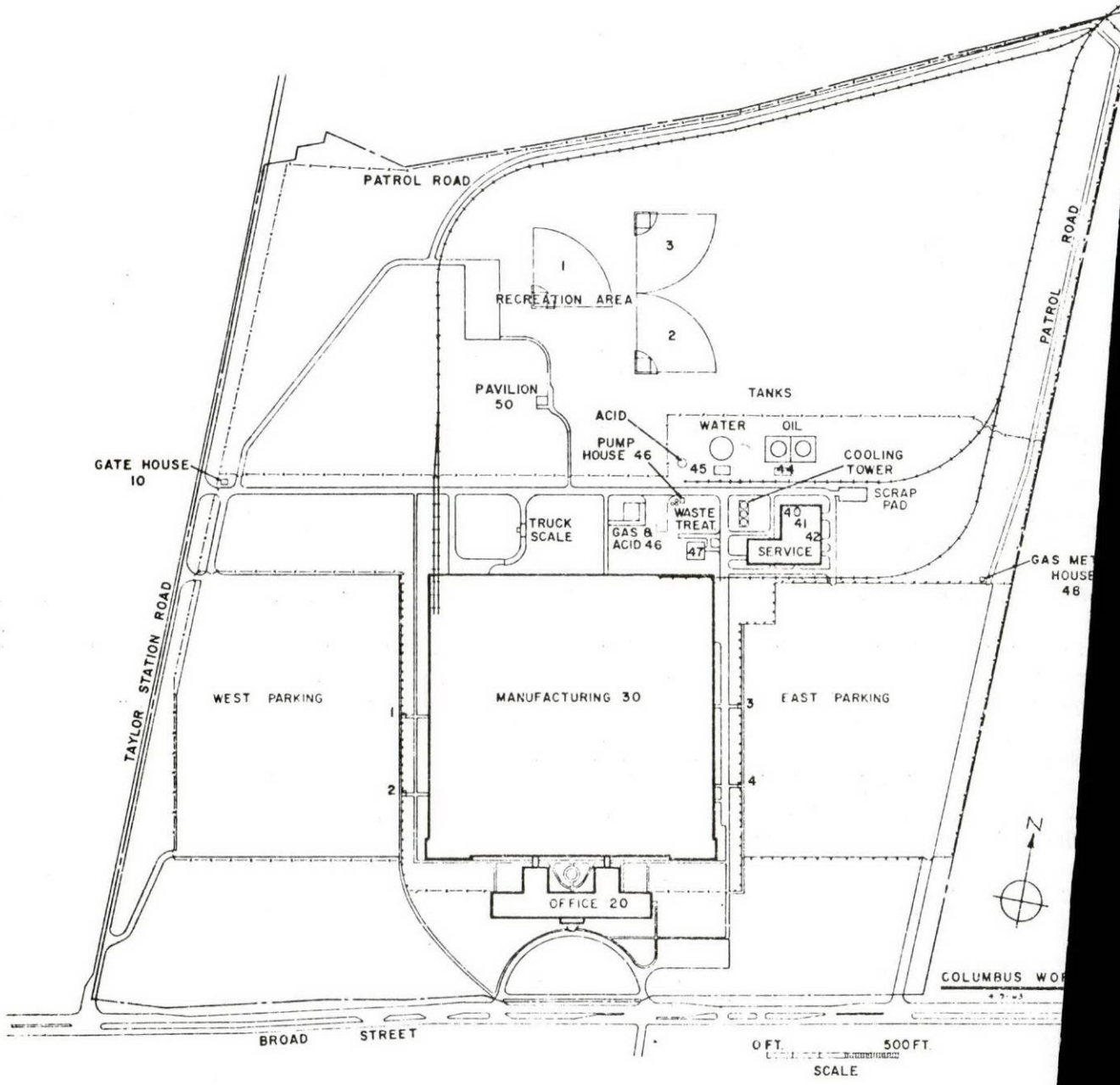
The manufacturing building is divided into three separate areas - A Low Bay Area, A High Bay Area, and a Peripheral Area. All of the low bay and most of the peripheral areas are air conditioned either for personnel comfort or because of product requirements. The high bay area and the plating facilities which are located in a portion of the peripheral space are not air conditioned.

Plating and etching operations occupy roughly 58,000 square feet or 6% of the manufacturing space. Exhaust systems in this area originally accounted for 40% of the total air exhausted from the plant or approximately (240,000 CFM). Of the total electric power consumed by the plant, 18% was used in finishing operations along with 6% of the total steam generated.

While the high exhaust volume in the plating and etching operations presented a possible lucrative energy conservation project, the magnitude of the use of electric power and steam did not. This conclusion has been typical of most of our manufacturing operations. This is not to say that more efficient energy use in production activity can not be achieved. It simply meants that for a given expenditure that a greater return can be obtained outside the manufactuirng area.

This case study, while not addressing conservation in finishing operations in particular, most of the principles can be applied universally. Optimization of the use of electric power, natural gas, fuel oil, etc., or the products of their use such as steam, hot water and compressed air is the objective of any conservation program.

Some of the projects were fairly straight forward and required a minimum expenditure of funds and time. Preliminary projects usually yielded high returns in monetary savings and energy reductions. As utility rates increased, more sophisticated approaches to conserving energy could be justified. None of these projects required more than a two (2) year payoff and most required much less than two (2) years. No attempt will be made to detail the amount of energy or money saved by individual projects since too many variables are involved. I will attempt a chronological listing as much as possible, realizing that at times a number of programs were being pursued simultaneously.


PATROL ROAD
PATROL ROAD
1
2
3
RECREATION AREA
PAVILION
50
TANKS
ACID
WATER
OIL
PUMP
HOUSE 46
45
44
COOLING
TOWER
GATE HOUSE
10
SCRAP
PAD
TRUCK
SCALE
GAS &
ACID 46
WASTE
TREAT.
47
40
41
42
SERVICE
GAS ME
HOUSE
48
TAYLOR STATION ROAD
WEST PARKING
MANUFACTURING 30
EAST PARKING
1
2
3
4
N
OFFICE 20
COLUMBUS WO
BROAD STREET
0FT.
500FT.
SCALE

PROJECT LIST

1. PLANT AND OFFICE TEMPERATURES
2. LIGHTING REDUCTIONS
3. COMPRESSED AIR LEAKS
4. STEAM TRAPS
5. EXHAUST SYSTEMS
6. SHUTDOWN OF HEATING AND COOLING EQUIPMENT
7. ELIMINATE PREHEAT COILS
8. MULTIZONE AIR HANDLING
9. TRANSFORMER HEAT RECOVERY
10. BOILER OPERATION
11. ECONOMIZER – PLANT BOILER
12. OXYGEN AND COMBUSTIBLES ANALYZER
13. FLASH STEAM RECOVERY
14. THERMOCYCLE COOLING
15. ENERGY MANAGEMENT COMPUTER

1. *PLANT AND OFFICE TEMPERATURES*

The first project was to lower thermostat set points during the heating season from 75° to 68° and to raise the thermostat set points from 73° to 78° during the cooling season. This required some control changes, since all heating and air conditioning systems were designed for automatic changeover. Outside air quantities were reduced to minimum levels. We have found that waste heat generated from lighting, machine operation and people is sufficient to maintain 68° during the heating season unless the outside temperature dips below 10°F.

2. *LIGHTING REDUCTIONS*

Physical removal of light bulbs and disabling of the balasts of fixtures located over aisles was the first step in reducing power for lighting (2400 fixtures). The second step involved reducing the lighting level over manufacturing and office areas. Our goal was to achieve a lighting level maintained at 70 foot candles in general office space, 50 foot candles in manufacturing space and 30 foot candles in storerooms and warehouse space.

Standard fluorescent tubes are being replaced with lower wattage tubes now marketed by most major manufacturers. Lumen output is not diminished in direct proportion to the wattage reduction.

3. *COMPRESSED AIR LEAKS*

During periods when no manufacturing was in progress, a 500 HP motor wa running at half load to produce 1300 CFM of compressed air. An intensiv maintenance effort reduced this load from 250 HP to 50 HP. Tank agitation b compressed air has been eliminated wherever possible.

4. *STEAM TRAPS*

Proper steam trap application was checked throughout the entire plant. portable infrared temperature sensor is now used by maintenance personnel on scheduled basis to assure proper operation of all steam traps.

EXHAUST SYSTEMS

At the onset of our conservation activities, a survey of exhaust system operation w made by checking exhaust operation versus manufacturing activity. It was found t 24,200 CFM was being wasted on the second shift, 38,800 CFM on the third shift 125,600 CFM on Sundays. These quantities were over and above the 240,000 CFM exhaust from the finishing and etching operations. An unexpected bonus also resul from these surveys. Thirty-three abandoned exhaust stacks were also found.

Naturally to compensate for these exhaust volumes, unnecessary quantities of outside air were being introduced to the manufacturing area. Selected individuals in each product shop were assigned the responsibility of shutting down exhaust systems and other equipment when not required. This procedure has worked very well and had the secondary benefit of involving shop employees in our conservation efforts.

In the finishing and etching operations, solution temperatures were lowered and tank covers were fabricated. This not only allowed us to reduce exhaust volumes but also saved steam and chemicals.

SHUTDOWN OF HEATING AND COOLING EQUIPMENT

Since approximately 40% of the steam generated and 30% of our electric power use are related to heating and cooling the building, it seemed reasonable to shut this heating and cooling equipment off when areas were not occupied. We did this manually at first and recorded inside and outside temperatures. After we satisfied ourselves that this concept was feasible, timers were installed to do the work automatically. These shutdowns reduced not only chilled water use and steam use, but also the electric power used to operate the blower motors.

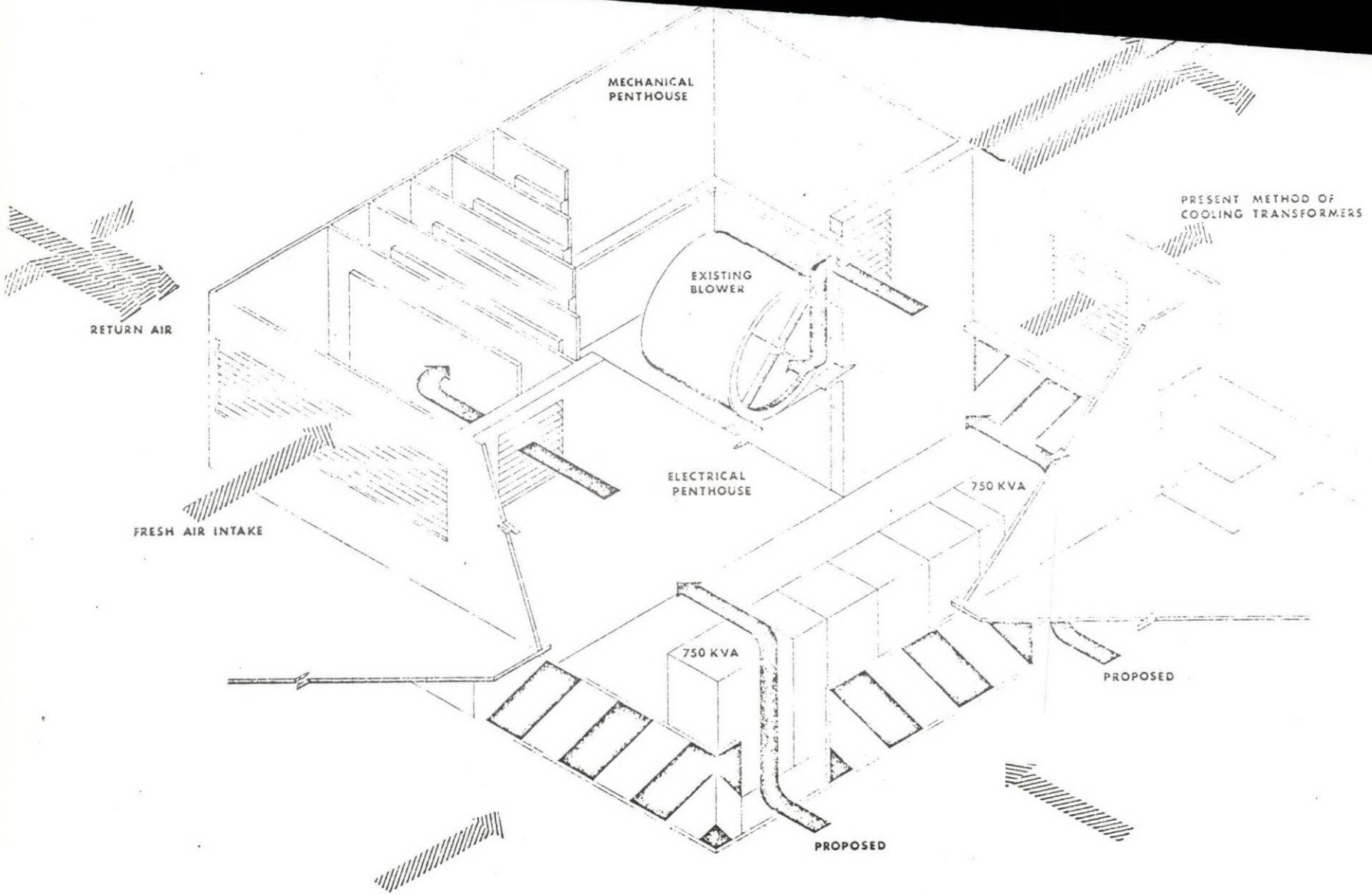
ELIMINATE PRE-HEAT COILS

Pre-heat coils in each of forty heating and air conditioning penthouses were being used to protect chilled water coils during the heating season. These coils were actuated by outside air thermostats and passed approximately 32,000 CFM each for a total of 1,280,000 CFM. The heat from these coils at times had to be offset by flowing chilled water through the cooling coil to prevent excessive heating of the space to be controlled.

As seen on the cross sectional view a baffle was designed to force an intimate mixture of the outside and return air. It was now possible to utilize the waste heat generated by equipment, lighting and people to control the temperature in the manufacturing area by modulating outside and return air dampers. The pre-heat coil control has been modified so that outside temperature no longer controls. Mixed air stays well above freezing assuring protection of the chilled water coils. Since the pre-heat coil operation no longer causes vertemperature conditions, chilled water use is unnecessary. The summer cooling operating is also more efficient due to this modification.

MULTI-ZONE AIR HANDLING UNITS

Various areas of the Columbus Plant are heated and cooled by the use of multi-zone air handling equipment. As you are probably aware, these units consist of a so called hot deck and a cold deck which are maintained at certain set temperatures. The cold air and hot air are then mixed to maintain a preset temperature in a zone. Since heating and cooling simultaneously are inefficient from an energy standpoint, we have converted these units to a variable volume configuration. A constant cold deck temperature is maintained in response to an outside thermostat. The hot deck is shut off. Thermostats modulate dampers on the cold deck to maintain space temperatures. This modification has proven quite effective in reducing steam usage.



HEAT RECOVERY ELECTRICAL PENTHOUSES

TRANSFORMER HEAT RECOVERY

Thirteen of our electrical power distribution penthouses are located immediately adjacent to heating and cooling penthouses in the manufacturing building. There is a mixture of 750 and 1000 KVA transformers in the electrical penthouses. A common wall separates the electrical and mechanical penthouses.

Ventilation of the electrical penthouses was by fixed louvers at either end of the penthouses and from openings to the manufacturing area at the floor of the penthouses.

Automatic dampers have been installed in the common wall between the electrical and mechanical penthouses and have also been used to replace the fixed louvers. During the heating season, the outside dampers are closed and the damper between the electrical and mechanical penthouses is open. Air sweepts over the transformers and assists in hesting the building. During the cooling season, the damper positions are reversed and normal cross ventilation removes transformer heat.

Plating rectifiers as well as all rectifiers are low efficiency devices and should present excellent opportunities for heat recovery. However, at the present time, our rectifier installations are too disperse to make this an attractive proposition.

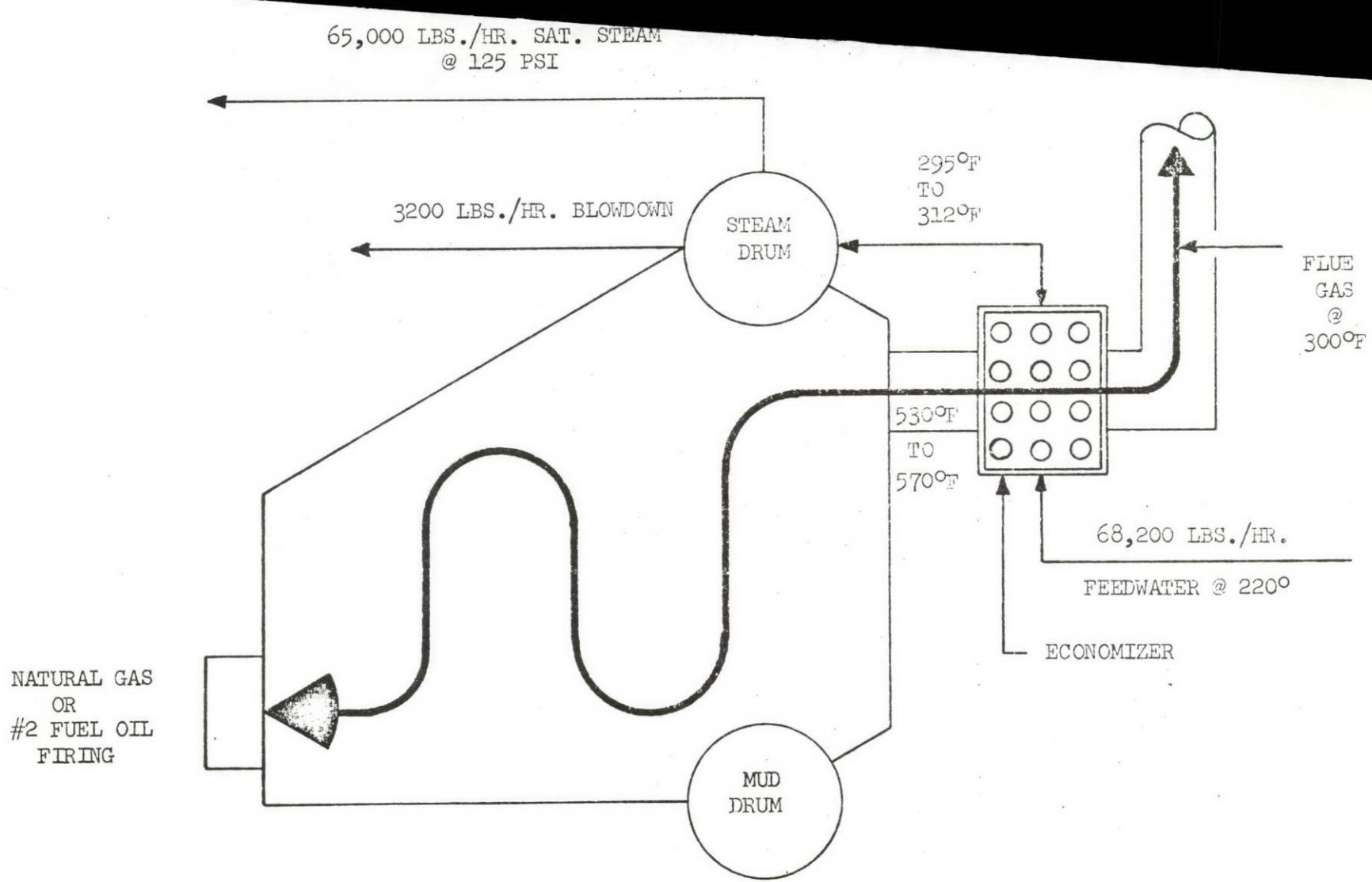
BOILER OPERATION

Procedures have been changed to eliminate standby boiler operation during extremely cold weather, steam is normally generated at 125 PSI. Peak loads are handled by allowing steam pressure to fall to a predetermined level while firing is manually controlled at a steady rate. When the pressure starts to rise, controls are restored to automatic mode and the pressure controller again controls the firing rate.

Boiler blowdown has been minimized by raising solids level permitted in the steam drum. Necessary boiler blowdown is flashed with the steam being used in the deaerating feed water heater and the condensate warming make-up water through a shell and tube heat exchanger.

ECONOMIZER - PLANT BOILER

An economizer has been installed on one of the plant boilers. This boiler is one of three 65,000 pound boilers originally installed for plant use, since our steam requirements, due to conservation, are adequately served by one boiler, only one boiler is being retrofitted. This economizer will reduce flue gas temperatures from 530°F at half load on gas and 570°F at full load on oil to 300°F. This reduction in flue gas temperatures will raise feed water temperatures between 75°F and 92°F respectively. Overall boiler efficiency will be increased between 5% and 6%.



BOILER ECONOMIZER

OXYGEN AND COMBUSTIBLES ANALYZER

An oxygen and combustibles analyzer was installed some 20 years ago when the Columbus Works was constructed. This device samples boiler flue gas and continuously records the oxygen and carbon monoxide levels. As an aid in operating the boilers, it is invaluable. Fuel-air ratio controllers were employed in the original boiler control system and did a good job in controlling combustion mixtures. However, we are presently in the process of improving our combustion efficiency by using the oxygen and combustibles analyzer as a combustion control. This device will then have an active rather than a passive function.

FLASH STEAM - RECOVERY

All low pressure condensate (5 to 10 PSI) is collected by a vacuum return system and pumped back to the boiler house. All high pressure condensate (10 PSI and above) was flashed to atmosphere. As long as a need for low pressure steam exists, the high pressure condensate is now flashed to 10 PSI steam for use in heating domestic hot water and for the hot water used in sidewall convectors.

THERMOCYCLE COOLING

During late fall, winter, and early spring, we have a need for chilled water for computer installations, and precise temperature and humidity controlled laboratories and manufacturing space. The refrigeration load during these periods averaged around 650 to 700 tons. This load was being carried by an 800 ton hermetic centrifugal water chiller.

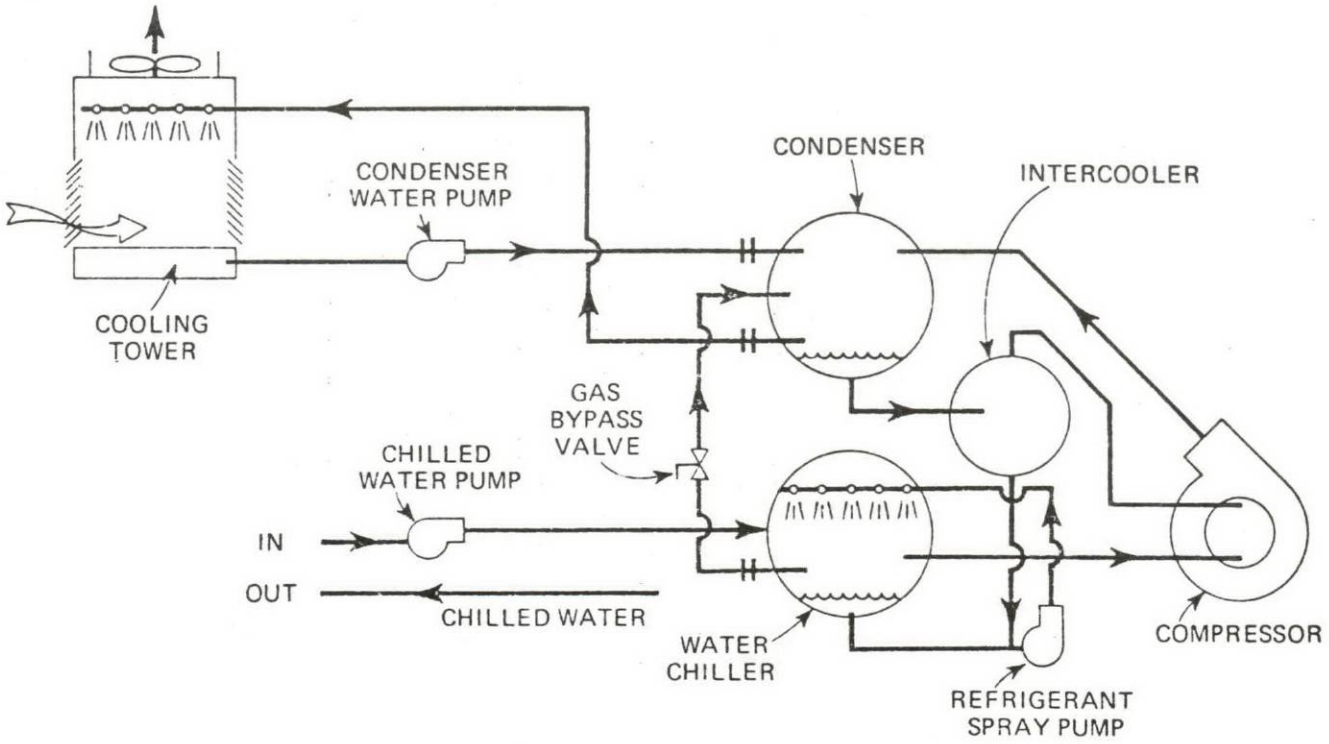
After some investigation, we found a system which could be retrofitted to one of our 2500 ton centrifugal water chillers and would produce up to 35% of the capacity of a 2500 ton machine without operating a compressor. This system could be used whenever the ambient wet bulb temperature was 42°F or below.

In the thermocycle mode of operation relatively cold cooling tower water is pumped into the condenser creating a low temperature, low pressure condition. Chilled water pumped through the evaporator creates a high temperature, high pressure situation. The refrigerant vapor naturally flows from the high temperature, high pressure area to the low temperature, low pressure area creating a refrigerating effect in the evaporator. An enlarged hot gas by-pass and a series of spray nozzles enhance the refrigerating effect.

This retrofit has allowed us to switch from operating an 800 HP compressor motor to the use of a 10 HP motor during approximately 6 months of the year.

ENERGY MANAGEMENT COMPUTER

At the present time, we have in operation a basic program on an IBM system 7 computer. This computer is performing some load shedding functions and also some monitoring functions. It has both digital and analogue capability. These are some of the functions we hope to have the computer perform:



THERMOCYCLE COOLING

LIGHTING

All lighting will be controlled by the computer with a timed manual override.

HEATING & AIR CONDITIONING

(1) All air handling units will be programmed off and on not only during unoccupied periods, but sequentially during occupied periods. (2) Thermostat set points will be adjusted during spring and fall when heating and/or cooling is required during the course of normal occupancy. (3) Enthalpy controls will trigger an economy cycle.

BOILER OPERATION

Fuel input and steam output will be monitored and gross efficiencies will be calculated. Excess air quantities will be recorded. Degree days will be calculated and fuel used per degree day determined. Monitoring of fuel oil consumed will also allow a continuous inventory of fuel oil supplies.

POWER DEMAND

Electric power peak use will be monitored and controlled as much as possible. If and when a new electric power demand is set, factors contributing to this new demand can be investigated expeditiously.

WATER CHILLER CONTROL

Design chilled water temperature is $40^{o}F$. The computer will raise the chilled water temperature inversely with outside temperature.

These are the preliminary operations we intend to have the computer perform. In the future, information compiled by the computer will be used for more on-line control. Exhaust systems may be added at some future date; however, we prefer the participation of plant employees at the present time.

summation, I hope that this presentation has been informative. It has not dealt with ating or etching operations at length, because in our overall program, we attempted institute conservation in areas which produced the greatest return. We have vested approximately $500,000 and five years of effort which has resulted in over 000,000 in savings. Our program is an ongoing operation. We have produced a video e illustrating most of subjects covered today.

N-2

Energy Conservation II
Session N

Steps Taken by an Average Size Electroplating Job Shop to Save Energy

D. P. Clemens
Wayne Metal Protection Co., Inc.
Ft. Wayne, Indiana

F O R W A R D

It was in the early 1960's that I first heard pronouncements such as - "The United States will have Energy problems within the next couple of decades." I paid little attention to this kind of statement because we were too busy installing another automatic plating machine and purchasing another more powerful truck. About this same time I had a conversation with my Uncle who worked for the Arabian-American Oil Co. (ARAMCO) in Saudi Arabia. In answer to my question "What in the world are you living in that God forsaken place?" he answered "Well, we are helping the Arabs pump oil out of the ground and trying to sell some of it to the Industrialized nations around the world. You see, oil is their only resource and their only export." He added "you wouldn't believe how much oil they have underground."

And so it is as we found out during the 1973-74 oil embargo.

While we are on the subject of prognosticating I should also mention that the feature article in the November 1978 National Geographic magazine concerned the tremendous amounts of untapped natural gas that is just waiting to be found 20,000 feet under the ground on our own continent. The article quoted Geology experts who said there was more gas available underground than has been used since the beginning of the industrial age. As a matter of fact they said there was enough gas available for 2500 years at our present usage rate. I certainly hope that these predictions are as true as those that we heard 20 years ago.

One prediction that you can safely bet on and be certain that will come true is that our Energy costs will continue to increase at an alarming rate.

I N T R O D U C T I O N

Before going into the various ways our company has attempted to cut Energy costs, I feel that certain information about our operation, our geographical loacation and our Energy supplies should be known.

Our company has 30 employees and our finishing operations are spread out over 20,000 Ft^2. The building itself consists of one rather old building that was added onto with a more modern steel building about 10 years ago. The older building is built into the side of a hill which is helpful in extreme weather. The present building is not as well insulated as one that we will be putting up later this year.

Though we are an average size job shop, I feel that we are not "average" in the services that we offer our customers. In addition to three automatic Zinc plating machines we do three type of anodizing, have a semi-automatic barrel plating line on which we plate tin, nickel and cadmium. We also have hand operations on which we do rack cadmium, copper, nickel, chrome, tin, silver, conversion coatings, hard chrome and polishing. At some later date I may report having fewer services available due to the loca POTW and EPA tightening their effluent requirements. I feel that we will not be able to afford waste treatment equipment to contr our variety of processes.

Our solutions are heated by steam from two gas or oil fired 125 H.P. boilers. We can normally operate on one boiler and the second boiler is in the event the first one fails for any reason I look on our boilers as our "heart" because all of our heating is done with lo-pressure steam with the exception of our Hard Chrome solution which is heated electrically.

Fort Wayne is located in the north east corner of Indiana; which is not exactly in the Sun-Belt. As a matter of fact the temperature averaged -17°C (0°F) the first two weeks in January 1979. 0°F is considered to be unseasonably warm when compared to the winters of 1977 and 1978. The low temperatures in 1978 were the most extreme in my memory. As you will see later in this paper, we used more Energy in 1978 than 1977 even though we began affecting Energy saving steps. Much of this was due to the fact that we had to run our boiler and electrically heat offices over many weekends and nights when our metal finishing operations were shut down.

We use three types of Energy in our operation; # 2 fuel oil, gas and electricity. At this time gas is far and away the least expensive fuel for us. This is true even though the cost has increased 200% in the last five years. Table I illustrates how our Energy costs have escalated in the last five years. It is interesting to note that our electricity costs .04¢/KWH while our friends in New York City pay .15¢/KWH. Our gas supplier has informed us that in the event we need more gas they will allow only an additional 10,000 cubic feet per day. Our neighbors in Ohio and Michigan have no such limits as this is being written.

T A B L E I

UTILITY COST INCREASE COMPARISONS

5 YEARS

FORT WAYNE, IND.

DATE	GAS COST	#2 OIL COST	KWH COST	WATER & SEW COST
Jan. 1974	.064/CCF	.22/gal.	.0197/KWH	.29/CCF
Jan. 1979	.22/CCF	.44/gal.	.04/KWH	.75/CCF
% INCREASE	244%	100%	103%	160%

E N E R G Y U S E R E D U C T I O N S

Since we did not have any one person responsible for Energy use reduction, I assumed the role of being the Energy Policeman. I have asked each employee to be on the alert for anyway they can cut Energy losses. I also asked the Supervisors to suggest how they felt we could save Energy and as a result we compiled a long list of ways we could cut down on Energy. What follows will list the steps that we have taken to cut costs but first I refer you to Table II which shows Energy cost comparisons between 1977 and 1978. You will note that we actually used more electricity and gas in 1978 than 1977. This was due to the fact that our sales volume and actual work volume increased about 10% in 1978. As mentioned earlier, we also had an extremely cold winter in 1978. It was the coldest winter in the last 25 years.

BUILDING

The older section of our building had several areas that allowed air to escape. At the loading docks we installed flexible boots around the perimeter of the openings. As a truck backs up to the dock it seals itself into the boot. On one of our docks, which is on side of the building, we actually enclosed the dock with plywood and another overhead door. We also found several windows that did not close tightly or had broken or loose fitting panes and of course these were repaired. Recently an employee told me that he could feel cold air creeping in around the windows, so we re-caulked them. All of the man-doors were checked for air leaks and where needed we added insulation strips.

The outdoor night security lights were originally installed by our Electric Utility Co. Five years ago the charges for these lights were nominal. Four of these large Mercury Vapor lights have increased in cost from $10/mo up to $75/mo. We asked the Utility to remove them and we replaced them with our own lights and expect to recover the cost in 3 years. In this instance we in fact added some kilo-watts to our electricity costs but we eliminated the extremely high "rental" costs of the light fixtures.

ENERGY USE COMPARISONS 1977 vs. 1978

YEAR	KWH	% KWH INCREASE	$ ELEC	% $ INCREASE	CCF GAS USED	BTU GAS USED	% BTU INCREASE	GAS $	% $ INCREASE
1977	6.4×10^5		20,331		6.7×10^6	6.7×10^9		13,976	
1978	7.4×10^5	15%	28,700	41%	8.7×10^6	8.5×10^9	27%	18,339	31%

B. ELECTRIC MOTORS

We have over 100 electric motors in our plant. As you know motors are designed to deliver enough power to take its' load from a dead stop up to operating RPM. After it reaches operating RPM it does not have to do as much work so part of the delivered wattage is wasted as heat. We are now installing "power factor controllers" on motors and the supplier tells us that we will save between 10-20% on electricity on the motors. Motors with built in PF controllers are now generally available as are controllers that can be added to motor starter boxes that lead to the motors.

BOILERS

Over a period of time, the insulation on the steam and return lines had somehow been removed from some areas of the piping and these are replaced as needed. Before the Energy crunch we didn't then insulate the return lines.

Our boilers can operate either on gas or #2 fuel oil. At present, we are only using the gas because it is cheaper than oil. years ago we has a gas shortage and had our gas shut off for week. We then switched over to oil. We were one of three Metal ishers in Indiana that was able to operate at full capacity. would be surprised at how many new friends we made in those days.

If we were to do our boiler installation over again, I would nitely make provisions to burn #6 fuel oil rather than #2. il is cheaper but requires a heater in the storage tank and fferent type burner. As this is written there is a glut of l and they are selling it for little more than what crude osts. It also has a higher BTU content than #2 oil. Since l has a higher Sulphur content than #2 oil, you must be in that the Sulphur will not damage the boiler.

We also regularly check the temperature and CO_2 content of the boiler exhaust. This allows us to see if we are getting proper combustion of the gas and to adjust our air/gas mixture if needed. The check is made using a kit which cost $130.00.

D. OVEN

We have a large continuous belt type gas fired oven that we use for Hydrogen-embrittlement relief. We have begun scheduling the plating of parts that require baking so that we have a large quantity to run thru the oven at any one time. This allows fewer oven start-ups and shut-downs that obviously waste heat.

E. POLISHING

In our polishing area we eliminated the large blower that carried polishing dust to an out-of-doors collector and replaced it with filtered dust collectors that expel the air back into the building.

F. CHILLERS

All of our solution chillers are the air-cooled type. In the winter we open louvers that allow the heated air to go back into the building and in the summer we send the air to the out-of-doors. The chillers are a type that was originally manufactu for the plastic molding industry.

G. PROCESS HEATING

Various studies over the last few years have shown that the majority (70-80%) of the Energy used by Metal Finishers is consumed in the actual overall plating or anodizing process. It was also determined that an electroplating process uses, overall, about 3 times more Energy than is used in the electrolysis portion of the process. The anodizing ratio is even greater at 5 times.

From this it is obvious that we began looking for Energy savings in the heated rinses, cleaners and dryers.

The first thing we did was to insulate any heated tank by cementing slabs of styrofoam plastic on the tank sides. The only problem with the styrofoam sheets is that pieces occassionally fall off and we then cement them back on to the tanks. Where possible we put plastic spheres on heated plating bathes and cleaners. One problem with plastic spheres is that they sometimes are carried out of the bath with the work or they may knock parts off of a rack. The next thing that we did was to try using "cold cleaners" where possible. I feel we should have tried cold cleaners long ago. Cold cleaners not only require less heat but they call for less ventilation. Recently one of our Supervisors told me that he operated one of our standard 170° cleaners at 100°F and found that it performed as well as the "cold cleaners" we was using elsewhere. Refer to Table III and IV to see how much money can be saved by operating certain solutionsat lower temperatures.

TABLE III

- 1,000 GALLON CLEANER TANK - SIZE 38" X 144" X 48" DEEP
- VENTILATED DURING OPERATION
- NO VENTILATION WHEN NOT IN PRODUCTION
- HEAT MAINTAINED 24 HOURS/DAY

TEMPERATURE	DAILY GAS* CONSUMPTION	DAILY GAS COST
100 F	572 cu ft	$ 1.43
120 F	977 cu ft	2.44
130 F	1,284 cu ft	3.21
140 F	1,624 cu ft	4.06
150 F	2,074 cu ft	5.19
160 F	2,596 cu ft	6.49
170 F	3,389 cu ft	8.47
180 F	4,389 cu ft	10.97
190 F	5,784 cu ft	14.46
200 F	7,845 cu ft	19.61

* Gas @ $2.00/MCG = .20¢/CCF

TABLE IV

SINGLE STATION BARREL CLEANER - 14" X 36" BARREL

250 GALLON CAPACITY

VENTILATION DURING OPERATION

NO VENTILATION WHEN NOT IN OPERATION

HEAT MAINTAINED 24 HOURS/DAY

TEMPERATURE	DAILY GAS * CONSUMPTION	DAILY GAS COST
100 F	215 cu ft	$ 0.54
120 F	372 cu ft	0.93
130 F	489 cu ft	1.22
140 F	619 cu ft	1.55
150 F	793 cu ft	1.98
160 F	995 cu ft	2.49
170 F	1,303 cu ft	3.26
180 F	1,692 cu ft	4.23
190 F	2,236 cu ft	5.59
200 F	3,038 cu ft	7.60

Gas @ $2.00/MCF

S U M M A R Y

The steps that have been covered thus far are for the most part the major ones.

I have found that we must constantly keep reminding people to be Energy conscious. It seems that they will be conscious of trying to save for a few weeks and then they will forget about it, and then they must be reminded again. One of our Supervisors is especially good at looking for ways to cut down. On his own, he tried the use of cold cleaners where I never would have thought to use them. Another fellow will always remind me of leaving my office lights on if I leave the building for lunch or for any length of time. If the majority of our employees think "save energy" I will be satisfi We are by no means finished looking for ways to cut Energy waste.

In the rush to find Energy leaks and eliminate them we have put not enough emphasis on measuring cost reductions. So our plans for the coming year are to continue looking for a more Energ efficient operation and at the same time to measure savings.

0-1

Research & General Interest II Session O

Grain Boundary Diffusion In Gold Electrodeposits AES Research Project #50

Dr. W. R. Bitler
Pennsylvania State University
University Park, Pennsylvania

This research is concerned with diffusion of substrate material through rodeposits with or without barrier layers at near ambient temperatures. ese temperatures diffusion is relatively rapid through grain boundaries r dislocations. Evidence has been accumulating that diffusion gh grain boundaries is enhanced if the boundaries move during the ion process. This study is directed at the kinetics of recrystalli- of electrodeposits and the interaction of the recrystallization reaction iffusion through the electrodeposit.

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Such data has been obtained and various anomalies have resulted. Analysis of diffusion through electrodeposits has often resulted in an apparent more rapid rate of interdiffusion than in other similar couples formed other than by electrodeposition. In the specific system gold

over copper it was found that diffusion at 100°C occured more rapidly than at 175°C contrary to the normal experience with thermally activated processes[3]. More recently it has been ascertained that grain boundary diffusion can take ~~phase~~ place more rapidly in a moving boundary as compared to a static boundary[4]. In order to understand and separate the various possible rate controlling steps one needs to know the relative rates of recrystallization and associated grain boundary motion as well as the apparent D_{gb} under different conditions of the grain boundary.

The current work explores these problems by first measuring the recrystallization kinetics of electrodeposits to be followed by measurem under the same conditions of the grain boundary diffusion kinetics.

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4) Smidoda, K., Gottschalk, W., and Gleiter, H., Diffusion in Migrat Intertaces Acta. Met. 26, 1833 (1978).

0-2

Research & General Interest II Session O

Cyanide Analysis
AES Research Project #52

Dr. V. Bodding
Manhattan College
Bronx, New York

Paper not available at time of printing of proceedings.

0-1

Research & General Interest II Session O

Grain Boundary Diffusion In Gold Electrodeposits AES Research Project #50

Dr. W. R. Bitler
Pennsylvania State University
University Park, Pennsylvania

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Electroless I
Session P

The Future of Electroless Nickel

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Nashville, Tennessee

THE FUTURE OF ELECTROLESS NICKEL

future of Electroless Nickel will be affected by many things. Not the least which will be the manufacturer's ability to convince this nation's engineers t they are finally able to produce a consistent product. Too many of the ineers who have tried Electroless Nickel in the past twenty-five years have e away from the experience feeling they have been "burned" by "overmarketing" process that had serious shortcomings.

e are, however, two major factors which will affect Electroless Nickel more anything else. Number one in consideration is the Chrome situation. In following dialogue we will consider:

Availability: How will the African situation affect us?

Cost: Chrome versus Electroless Nickel

Pollution Control

Facilities and Equipment

Capital Investment

ond factor will be supply of basic commodities. We will consider:

ypophosphite Suppliers

roduction Ability

mes Required to Handle New Growth

tential New Sources

nsistency of Supply

tential Nickel Problems

over these few points, the avenues that open for discussion are phenomenal.

There can be no doubt that chrome will have a direct affect on the growth of electroless nickel. Industry has used chrome in a variety of applications for which it is not suited. The reason is that nothing any better, or more consistent has ever come along. Now we have reached a point in "The State-of-One-A where there are at least five consistent proprietary suppliers of electroless nickel. We, therefore, must consider each application by itself. The guiding factors are generally corrosion, erosion and wear.

The first thing we can say is that chrome in itself is not corrosion resistant, especially where halogens are concerned. The second is that due to chrome's fractured and porous nature, it is not a good erosion resistant material. This leaves us with only the third item, "wear". This is where chrome started and still has its best place in the market. In certain striking wear applications (Ex: Catepillar Crank Shaft Journals) nothing can top hard chrome as a choice. In the hydraulic shaft, the choice is a coin flip. In many other applications, heat-treated electroless nickel is superior to hard chrome. What we are stating is that in the foreseeable future, electroless nickel can replace hard chrome in about 70% of all existing chrome applications with specific advantages. Whether or not you choose to switch may well depend on one or more of the following markets considerations.

Chrome's Availability - The largest single factor in the availability of chrome is the African situation. There are many different theories on how much of the U.S. Chrome comes from Rhodesia and South Africa. Whether the number is 50% or 90%, the end result is the same. If you remove over one-half of the available supply of any commodity from the world market, the value of the remain escalates. (Ex: Cobalt after Zaire attacks.) Our object here is not to theori on chrome's total availability to the U.S. Market, only to discuss what a shorta of any scale would do to the growth of electroless nickel. If we assume that many chrome applications can be replaced with electroless nickel, we must assume what will happen to electroless nickel's growth in usage should chrome become short or highly expensive.

The basic problem lies in the magnitude of chrome versus the relative infancy of electroless nickel. Even if all-out warfare does not take place, we must assume that the transitional governments which are planned after a peacefu takeover will lack in the ability to keep up production. "Murphy's Law" always prevails. The other line of thought is that even if chrome does continue to fl from South African ports, it will flow to governments other than ours. This, c course, means we will probably continue to get chrome, only at a drastically increased cost. We now must consider how much we will pay before we compare figures.

Cost: Chrome vs. Electroless Nickel - When we consider cost of electro nickel versus chrome, there are many things to compare. Chrome has a presentl cheaper metal cost, although electroless nickel is less "labor intensive". Wi inflation continuing as it is, this will cause the comparability gap to close This does not even consider inherent applicational advantages. When chrome i plated, we must consider the labor of fixturing, handling, and post-treatment Pollution Control will be covered later.

Electroless Nickel on the otherhand has higher chemical cost, however, less labor, especially on bulk or complex parts. The comparison must be boiled down to where a direct trade-off takes place regardless of application advantage. Assuming both products will satisfy customer needs, we must estimate a plater choice trade-off point. I feel that when the price of chrome gets to approximately ($1), there will be no cost advantage to chrome. At that point most of the advantages of electroless nickel should prevail.

Pollution Control - There can be no question that the E.P.A. has a gun to the head of every chrome plater. There are red lights that flash even at the mention of chrome, never mind actual presence in your effluent. No such lights presently flash at the mention of electroless nickel. What is the chrome plater to do when the lock goes on the door? (Fight or Switch!). The average chrome plater could not afford to buy the proper pollution control equipment even if someone would tell him what the limits next year were to be, and how to cope with them. Electroless Nickel on the otherhand has fairly well-defined control methods and limits. It also does not bear the stigma associated with a toxic metal. The phosphorus content in the effluent of an electroless nickel line would probably be compared to the average laundromat.

Less than one in ten electroless nickel platers even consider pollution control today, whereas every chrome plater has eminent disaster over his head in some form or another.

Most electroless nickel lines release below the 10,000 gallon per day of water which necessitate the consideration of even (Ni) control standards presently set by E.P.A.

Facilities and Equipment - Were a person to consider building a new facility for large scale chrome or electroless nickel, the choice would be obvious. The cost to install electroless nickel would probably be less than half before we even consider pollution control. The maintenance factor of electroless nickel is minor when compared to chrome. When one considers an electroless nickel facility, material requirements would only require a work space at less than 50' x 10' for the average plating line. Building requirements are easily satisfied as electroless nickel does not have the corrosive or toxic fumes associated with chrome. Less than 10% of the electroless nickel platers have exhaust systems. Though they are nice to have, they are not necessary.

Most good chrome platers have some sort of machine shop capability for pretreatment along with special anoding and racking facilities. None of this is required for electroless nickel.

Capital Investment - If we were to consider doing identical large parts in each bath, the electroless nickel installation would probably cost about one-half the cost for chrome. If we consider only the possibility of going into one process or the other, the differences become astronomical. For a person to consider starting a chrome shop, he should have a few hundred thousand dollars and a small amount of local political clout. To consider electroless nickel, one

should have approximately 2000 sq. ft. of acceptable space and $10,000. Approximately 80% to 90% of all electroless nickel work presently available will flow through a 150 gallon, (4' x 2' x 3') plating line. We therefore, must conclude that electroless nickel is neither an expensive addition or new venture. A standard rack, Zinc Line would probably be more expensive to install.

A prudent plater will usually have a lucrative electroless nickel job available to justify this installation. Electroless Nickel and precious metals are probably the only finishing areas where certain lucrative jobs still exist. Remember, electroless nickel is still a functional coating where many times nothing else will suffice. (Ex: Salvage work where coating cost, whatever it is has no effect on the end savings).

Hypo Suppliers - There are presently two domestic suppliers of this material. They are Stauffer and Hooker. Two other manufacturers who are basic in phosphates have shown interest in the potential growth of the electroless nickel market. These are F.M.C. and Monsanto.

The Foreign Supplier is Pierre Fite Auby. Other chemical producers, basic in phosphates, should look closely at this growing market (gold mine). Small suppliers of consistent material would probably have a field-day at existing price levels.

Production Ability - The total domestic production has risen in the last few years from four million pounds to about six to seven million pounds. Both suppliers speak in terms of a figure approaching double the production in the near future. Rumors have it that F.M.C. is considering a three million pound plant by 1981. Any small newcomer to this market, without large corporate load commitments, might provide market flexibility which large corporations are incapable of maintaining.

Time Required to Handle New Growth - Herein lies the major problem faci us. Should world or other conditions prevail in a rapid order, any large dema would immediately cause havoc in a market having no surplus. It takes approxi two years to bring a new source on stream or enlarge a present one. As Hypo i a very small component of two multibillion dollar corporations, they must see demand and profit to justify growth.

Most engineers associated with electroless nickel agree that the growth will be rapid and phenominal. The question is: When? We must only hope tha they will start feeding their work into the present mainstream with enough regularity to convince the suppliers that expansion of basic commodity supply justified.

Potential New Suppliers - It is imperative that new suppliers be lure this potentially enormous market. As more engineers realize the potential o electroless deposits, more work will be done on other metals to be reduced b Hypophosphite. The next extensive work will probably include Copper and Cob A huge market exists for both. Let us hope that at least the two aforementi

potentials see reason to become involved. This may at least decrease the volitility at the price situation present in the markets today.

Consistency of Supply - I believe that we may finally have reached a point where consistency is finally available from both the proprietary manufacturers of electroless nickel and the raw material suppliers. Even the foreign suppliers seem to be producing some decent material. There is still a question of amount of metal reduced per quantity of which Hypo used. Hopefully, those suppliers who switch sources with the whim of Purchasing Agents will make the required adjustments to maintain the consistency.

Potential Nickel Problems - I think that we can safely assume that the world nickel market is soft and that enough new world markets and sources will keep nickel at least in ready supply. As with any metal used in the finishing business, we may see rises and dips, however, we do not have the source problem of Hypo. I think we may also safely assume that the sources of new nickel are diversified to every known continent, therefore, we should not have the concern we have shown to chrome. Nickel should remain a Buyer's market for the foreseeable future.

Shortages will obviously remain a tool of the politicians and the money anagers of the world. However, it will remain available regardless of demand.

In summation, I believe that electroless nickel growth will be affected by e aforementioned conditions. However, the most drastic affect will be that of esent consumer interest and acceptance. Once we overcome the past twenty-five ars, we must convince the end user of its presently available form. The consumer st start immediately to utilize the product if we are to develop a raw material urce. Hopefully, the demand will not come all at once such as in the case of ome shortage. We then, should have time to grow into this new market.

If we look at some things such as an Aluminum Bumper Program which rumor has would need 10 million pounds of Hypo, and millions of feet of oil well pipe. is not hard to envision why we should try to induce the manufacturers, both ic and otherwise to actively pursue electroless deposition by Hypophosphite uction as a thing of the future, not to be stymied by neglect.

P-2

Electroless I
Session P

Electroless Nickel—Many and Varied

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AUTOCATALYTIC (ELECTROLESS) NICKEL——MANY AND VARIED

by

Donald W. Baudrand

ABSTRACT

Since there are now numerous types of electroless nickel plating solutions available, the problem of selecting an appropriate solution to produce the results desired is becoming more complicated. This paper attempts to characterize various types of electroless nickel plating solutions by the deposit characteristics, performance criteria, operating parameters and typical uses.

Nickel-phosphorus baths are discussed, pointing out that variations in solution composition can result in higher or lower phosphorus content in the deposit, and variations in corrosion resistance, electrical and magnetic properties, ductility, hardness and wear resistance. Nickel-boron alloy producing solutions are discussed in terms of how solution composition and operating conditions affect the deposit characteristics. Alloys of nickel and boron, molybdenum, tungsten, tin and copper can be produced with electroless solutions, each with interesting deposit characteristics.

About the Author

Don Baudrand is Vice-President of Allied-Kelite Division of Richardson Chemical Company in charge of Research and Product Development, located at 29111 Milford Road, New Hudson, Michigan. Baudrand graduated from Whittier College with a BA in chemistry and mathematics. Graduate studies at U. C. Berkeley consisted of nuclear physics and chemical engineering. He has served Allied-Kelite since 1966 after their acquisition of Electrochemical Laboratories in Los Angeles, a firm he founded and served as president for 14 years. Baudrand is a member of the Detroit Branch of A.E.S.

AUTOCATALYTIC (ELECTROLESS) NICKEL--MANY AND VARIED

By
Donald W. Baudrand

The technology of autocatalytic (electroless*) nickel plating is advancing at a rapid pace. Today there are many types of autocatalytic nickel alloy processes, each with deposit characteristics that make it suitable for specific applications. The purpose of this paper is to describe some of the more prominent types of autocatalytic nickel alloy plating systems, their deposit properties and their use applications. Table I at the end of this paper lists the autocatalytic system(s) most suitable for obtaining specific deposit characteristics.

NICKEL-PHOSPHORUS SYSTEMS

Since the discovery by Brenner and Riddell[1] of an autocatalytic nickel-phosphorus plating system, researchers have developed a variety of chemical methods of altering deposit characteristics to meet specific applications. The solutions are more stable and much easier to use than ever before.

Acid Solutions

Generally, nickel-phosphorus alloys deposited from acid solutions have similar characteristics. Typically, the nickel content ranges from 88% to 93% and the phosphorus from 7% to 12%. It is difficult to obtain deposits that vary outside this range. The most common alloy is about 91% nickel and 9% phosphorus. Within the range of 7% to 12% phosphorus we find little difference in most deposit characteristics. For example, hardness of the as-plated deposit is around 450-513 DPH and after heat treatment (400°C, 1 hr) it is 695-1000 DPH. However, other deposit characteristics, such as porosity and resistance to chemical attack, can be altered over a wide range by changing the complexing system (combination of organic complexing agents) and the type and amount of stabilizers.

For plating on aluminum, autocatalytic nickel solutions are available that have a high tolerance to zinc and other metallic contaminants likely to be introduced from an aluminum preparation line. Enhanced corrosion resistance is another important consideration for autocatalytic nickel plating on aluminum. The deposit can still have all the desirable physical characteristics such as high hardness, natural lubricity, and wear resistance.

For plating on steel and stainless steel alloys, a different stabilizer and complexing system than that used for plating on aluminum can produce a high deposition rate, economical plating, and good corrosion resistance.

Careful selection of combinations of complexing agents can result in a deposit with altered crystal structures. Thus, characteristics such as solderability, chemical resistance, surface microsmoothness, and magnetic properties can be controlled. A common misconception regarding magnetic properties is that the higher the phosphorus content of the alloy, the lower the ferromagnetic retention. This is often true because the alteration of a

* ISO and ASTM have recommended that the term "autocatalytic" be used in place of the term "electroless" as being more definitive.

complexing system which leads to low magnetic, or so-called non-magnetic, deposits also leads to high phosphorus content. However, it has been shown by Mallory[2] that low phosphorus deposits can have low ferromagnetic characteristics (non-magnetic). Low magnetic electroless nickel deposits are used as a base coating for magnetic memory devices, usually made from aluminum. Bright and bright-leveled deposits also are possible from specially formulated baths. Properly done, there is no sacrifice in hardness or other desirable properties.

Alkaline Solutions

Plated deposits from alkaline solutions are typically low in phosphorus content, varying from a few tenths of a percent to 5%, but usually 3% to 5%. These solutions are usually less stable than acid solutions. They plate somewhat slower, and are often more difficult to control. Low phosphorus alloys find application primarily in the electronics industry when enhanced solderability is required. Some deposits can be easily brazed. Low phosphorus producing solutions can be operated at low temperature, often room temperature, thus finding application for plating on plastics and on other materials which tend to distort or melt with heat.

NICKEL-BORON SYSTEMS[3]

Investigation of alternate reducing agents to sodium hypophosphite led to the use of borohydrides and amine boranes. Some of the earlier patents issued cover sodium borohydride or dimethylamine borane as reductants.[4-7] Boron content of deposits from these solutions may vary from 0.1% to 10% depending on the chemical makeup of the plating solution. The amount of boron co-deposited can be controlled within narrow limits. When sodium borohydride is the reductant, a solution pH greater than 12 must be maintained to prevent rapid hydrolysis and decomposition of the solution. The complexing system used for nickel must, because of the high pH, be much tighter than for acid or mildly alkaline solutions. Borohydride reductants result in a higher boron content in the deposit, usually from 3% to 6% boron. The higher boron content results in high as-plated hardness values. Values up to 800 DPH have been reported[3]. Typical values are 750 DPH for commercial solutions. On heat treating, the hardness increases to 1000-1200 DPH (Vickers), about the same as nickel-phosphorus.

Amine boranes can be used over a wide pH range from acid pH 4.0 to alkaline pH 10.5. It is possible to produce essentially pure nickel deposits (99.9%) by careful selection of the complexing agents and operating conditions. High electrical conductivity, good solderability, good diode bonding (ultrasonic method) and excellent wetting of brazing alloy are characteristic of deposits in the 1% or less boron content range. It is possible to increase the boron content of a deposit from amine borane-reduced systems up to 3% to 5% by the addition of certain exaltants[8], depending on operating conditions. The advantage of this technique is that the solution is easier to operate and control. It is more stable than the high pH borohydride solutions, and it will produce high as-plated hardness. The ha

deposits can eliminate the need for heat treatment. This becomes a great advantage when the basis metal is aluminum or other metal whose properties might change due to the heat treatment step.

POLYALLOYS[7-8]

It is possible to include a number of different alloy constituents into autocatalytic nickel plating solutions, thus producing a wide variety of alloy deposits with a wide variety of deposit characteristics. Many of these alloys show superior corrosion resistance, superior hardness, high temperature resistance and interesting and unusual electrical characteristics including non-magnetic as well as magnetic behavior. There are many commercial polyalloy solutions available.

Prior to 1963, alloys deposited by autocatalytic means were limited to nickel-phosphorus and group VIII metals (Fe, Co, Ni). In 1963 Pearlstein, Weightman and Wick[8] reported autocatalytic nickel-tungsten-phosphorus alloys. Others[9] reported nickel-rhenium-phosphorus and nickel-copper-phosphorus.[10] Mallory[7] introduced ternary and quaternary alloys of nickel with boron, phosphorus, molybdenum, tungsten, tin, copper, iron and cobalt in many combinations.

Nickel-molybdenum-boron and nickel-tungsten-boron exhibit properties which make them suitable for diode-bonding (ultrasonic method). Both alloy deposits are solderable, and the Ni-W-B system shows unique ductility as well as superior corrosion resistance. Nickel-tin-boron and nickel-tin-tungsten-boron alloys show outstanding chemical resistance while having favorable soldering characteristics. One of the nickel-molybdenum-boron solutions will plate directly on copper without any previous activation steps or contacts with dissimilar metals. In other words, copper appears to be catalytic to this solution. It finds application for plating isolated circuit patterns rendering protection, good electrical conductivity and a solderable surface.

Another alloy combination solution produces a non-magnetic coating whose magnetic properties do not change on heat treating or aging, thus providing a superior base coating for magnetic memory devices.

Table 1. Autocatalytic Nickel System(s) Most Suitable For Obtaining Specific Deposit Characteristics

Characteristics Desired	Autocatalytic System Most Suitable
Wear resistance	1. Nickel-phosphorus, acid solution
Corrosion resistance	1. Nickel-phosphorus, acid solution formulated for maximum corrosion resistance on the basis metal selected 2*. A polyalloy of nickel-tin-phosphorus, nickel-tin-boron, nickel-tungsten-phosphorus, nickel-tungsten-boron, nickel-tungsten-tin-phosphorus, nickel-tungsten-tin-boron, or nickel-copper-phosphorus. *Selection depends on severity of requirements and on economics. Boron-reduced systems are about 5 times more costly in terms of $/mil-sq. ft. However, lower thicknesses may be used.
Hardness	1. Nickel-phosphorus, acid solution—heat treated 2. If heat treatment is not practical use nickel-boron of 3% or more boron
Lubricity	1. Nickel-phosphorus, acid solution—highest phosphorus content
Chemical resistance	1. Nickel-phosphorus, acid solution 2. Polyalloy system
Solderability	1. Nickel-boron—low boron content, less than 1% 2. Polyalloys—exhibit excellent shelf-life solderability
Diode-bonding	1. Polyalloys 2. Nickel-boron, less than 1% boron
Non-magnetic	1. Polyalloys
Magnetic (for memory)	1. Nickel-cobalt-phosphorus 2. Nickel-cobalt-boron 3. Cobalt-phosphorus 4. Nickel-cobalt-iron-phosphorus
Electrical conductivity	1. Nickel-boron with boron less than 0.3% (resistivity is about 5.8-6.0 μohms/cm/cm^2)
Electrical resistance	1. Some polyalloys 2. Nickel-phosphorus—high phosphorus conten
Rhodium replacement	1. Nickel-boron, 1-3% boron
Gold replacement	1. Nickel-boron—low boron for soldering, 0.1 0.3%B; higher boron for contacts, 0.5-1% 2. Polyalloys of phosphorus or boron if belo 0.5% P or B

REFERENCES

1. A. Brenner and G. Riddell, Proc. Am. Electroplaters' Soc., 32, 23 (1946).
2. Private communication between G. O. Mallory and D. W. Baudrand (1976).
3. G. O. Mallory, Plating, 58 (4), 319-327 (1971).
4. R. M. Hoke, U.S. Patent 2,990,296 (1961).
5. T. Berzins, U.S. Patent 3,045,334 (1962).
6. H. G. McLeod, U.S. Patent 3,062,666 (1962).
7. G. O. Mallory, U.S. Patent 4,019,910 (1977).
8. F. Pearlstein, R. F. Weightman and R. Wick, Met. Fin., 61, 77 (1963).
9. K. M. Gorbunova, A. A. Nikiforova and G. A. Sadakov, "Modern Problems of Metal Deposition by Reduction with Hypophosphite", Electrochemistry, 1966, ed M. M. Mel'nilova, p 41 (references 118).
10. A. M. Lunyatskas, Chemical Deposition of Nickel-Copper-Phosphorus Platings, Zashchita Metallov, 1968, 4, No. 3, 315, May-June.

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Electroless I
Session P

Care and Feeding of Electroless Nickel

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Paper not available at time of printing of proceedings.

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Electroless I
Session P

Electroless Nickel Baths as a Factor In Producing Blisters on Aluminum

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Electroless Nickel Baths as a Factor in Producing Blisters on Aluminum

E. F. Yarkosky, M. Aleksinas, A. Marczak

Introduction

Plating nickel electrolessly on aluminum is a process that will ontinue to remain attractive and receive more attention in the metal nishing industry. The problems of plating on aluminum, however, are ell recognized by electroplaters. Because of the natural protective oxide ating and the variety of aluminum alloys, special pre-plating operations e required to condition the aluminum surface. In general, after deoxidizing ery thin immersion layer of zinc is applied as a barrier coating against xidation. An inferior or inadequate pre-plating process will result in r adhesion and frequently in blistered deposits.

It is well known that electroless nickel baths have a shorter functional for plating on aluminum than on steel. This characteristic of the bath fests itself in the form of blistered, non-adherent deposits. The accumu- of zinc in the nickel bath through the dissolution of the zinc immersion it traditionally has been considered the cause of this premature failure. ture on this topic is sparse, hence the purpose of this work is to:

1) evaluate the electroless nickel bath as a source of blistered deposits on aluminum

2) determine and interpret the cause of any bath malfunction

3) discuss the results with the aim of extending the bath life for aluminum.

Experimental & Discussion:

Two functional and yet diverse baths were selected and prepared from suggested classical formulations[1]. They are described as Baths A and B.

A		B	
Ni^{++} $(SO_4^{=})$	0.10M	Ni^{++} $(SO_4^{=})$	0.10M
Gylcolate (Na^{+})	0.28M	Lactate (Na^{+})	0.12M
Citrate (Na^{+})	0.02M	Malate (H^{+})	0.09M
Acetate (Na^{+})	0.13M	Acetate (Na)	0.08M
Hypophosphite (Na^{+})	0.27M	Hypophosphite (Na^{+})	0.2M
Pb^{++} $(NO_3^{\bullet})$	1 mg/l	Pb^{++} (NO_3)	1 mg/l
pH	4.4 - 5.2	pH	4.4

These formulation choices were selected for:

1. o-phosphite tolerance
2. pH maintenance with NH_3 or alkali addition
3. plating rate, .35 $\leftrightarrow$ .50 mil/hr.
4. diversity in chelating system

The following outline summarizes the experimental conditions and limitations to be employed for the subsequent tests:

Plating Conditions:

Aluminum Alloy	1100, 3003
Bath volume	800 ml
Work area	258 cm^2 (40 $in.^2$)
Work load	323 cm^2/l (1.3 ft^2/gal.)
Plating time	30 min.
Temperature	88°C. (190°F.)

Pre-Treatment Cycle:

Degrease	
Alkaline Clean	1 min. @ 66° C. (150°F.) CWR
Alkaline Etch	1 min. @ 66° C. (150°F.) CWR
$HF-HNO_3-H_2SO_4$	20 sec. @ R.T. CWR
Zincate	20 sec. @ R.T. CWR

eriment #1 - Effect of Zinc Concentration

Steel panels were processed in Baths A and B and the baths nished appropriately. Zinc was added to the baths, as below, and num panels processed.

Table 1

mg Zn^{++}/l	Bath A	Bath B
50	no blisters	no blisters
100	"	"
150	"	"
300	"	"

The blister-free deposits obtained from these baths suggest other factors are responsible for eventually causing blistered nickel deposits on aluminum.

Experiment #2 - Effect of pH

Since pH is an integral part of the electroless nickel plating proce its affect on aluminum was studied. Table 2 lists the results of the platin tests in terms of metal turnovers vs. initial bath pH_i values.

pH was adjusted to the initial pH_i value with ammonia at the end each plating cycle; bath replenishment was also made at this time.

Table 2

pH_i	Turnovers (T) Bath A		Turnovers, Bath B
4.4	3.1	1 T = 5.8 g/l Ni	4.3
		" " = 0.04 M glycolate	
4.9	4.8	" " = 0.04 M lactate	5.6
		" " = 0.25 M NH_3	
5.2	5.9	" " = 0.36 M $H_2PO_3^-$	7.5

Baths with lower pH_i values produced blistered deposits soon baths with higher pH_i values had significantly longer bath lives. Howe

the conclusion that the pH is solely responsible for blistered deposits is inaccurate. If this were true, blistered deposits should have been produced immediately, i.e. after less than one metal turnover. The accumulated bath constituents and reaction products, such as carboxylic acids and o-phosphite must be considered with pH. These carboxylic acids, as well as o-phosphite, are weak acids and as such are not 100% ionized. Hence pH is not a true measure of the acidity of the bath.

Experiment #3 - Effect of Chelator Concentration

The notable difference in bath life between Baths A and B should not be surprising since the formulations are different. However, these differences suggest that the chelation systems do affect the quality of deposit on aluminum. To substantiate this, Baths A and A´ were prepared and plating tests performed. Note in Table 3 that Bath A´ has an increase in chelator concentration.

Table 3

	Bath A Concentration		Bath A´ Concentration
ckel	0.10 M		0.10 M
rcolate	0.28 M		0.43 M
rate	0.02 M	1 T = 5.8 gm/l Ni	0.03 M
tate	0.13 M	" = 0.04 M Glycolate	0.20 M
ophosphite	0.27 M	" " = 0.25 M NH_3	0.27 M
d	1 mg/l	" " = 0.36 M $H_2PO_3^-$	1 mg/l
4.4	3.1 Turnovers (blisters)		2.6 Turnovers, (blisters)
4.9	4.8 " "		4.3 " "
5.2	5.9 " "		4.7 " "

The decrease in bath life with an increased chelation concentration is evident. Further evidence of this is seen later in Bath B as well.

Figure 1[2] shows the corrosive effects of certain carboxylic acids on aluminum at elevated temperatures. Although glycolic acid is not shown, it is reported to be aggressive toward aluminum also[3].

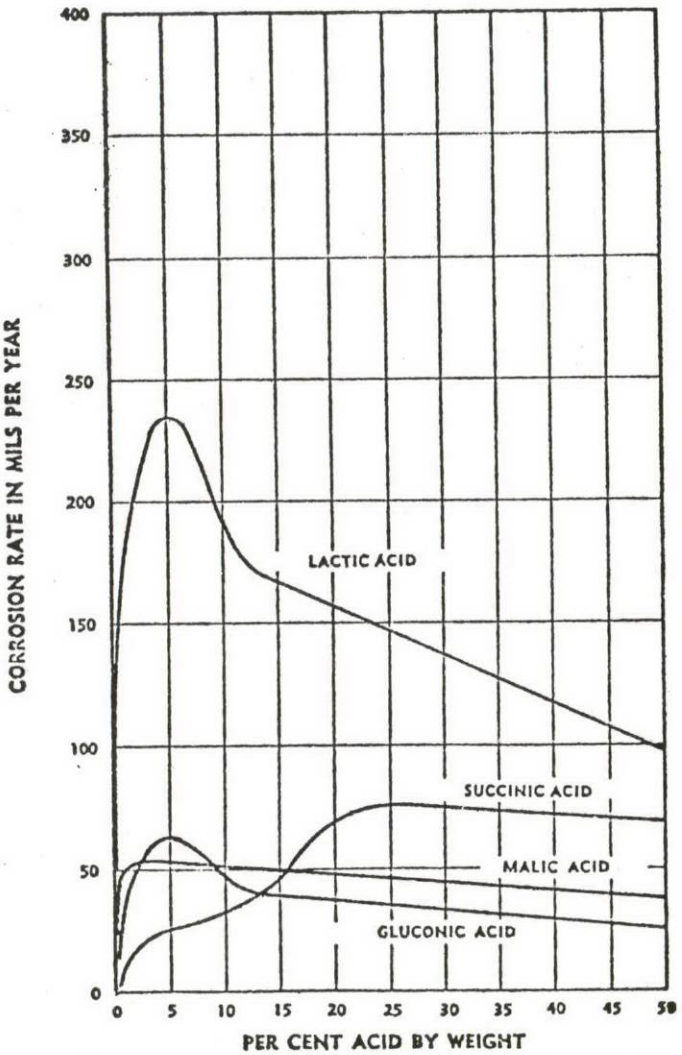

Figure 1—Comparison of the effects of lactic, succinic, malic, and gluconic acids on alloy 1100 at 100°C.

The relationship of pH to the carboxylic acid and primary o-phosphite concentration is shown as follows:

a) $pH = \log \left[\frac{L^-}{(K)(HL)} \right]$ where K = dissociation constant

b) $pH = \log \left[\frac{HPO_3^=}{(K)(H_2PO_3^-)} \right]$ HL = carboxylic acid concentration
L^- = anionic ligand concentration

The significance of a) and b) is that, despite maintaining a constant pH value of an electroless nickel bath, the total acidity of the bath will change due to primary o-phosphite buildup and chelator replenishment.

It should be noted here that bath failure, characterized by blistered deposits, is accompanied by a noticeable difference in the quality of gas bubbles formed during the plating operation. The gassing is more vigorous and suggestive of an etching process.

Experiment #4 - Effect of Ammonia

Another main constituent of most baths is the ammonium ion, the result of bath pH adjustment with ammonia. Ammonium ion also influences total acidity and behaves as a weak acid similar in strength to boric acid.

$$NH_4^+ \rightleftharpoons H^+ + NH_3 \qquad K_a = 5.7 \times 10^{-10}$$

Its effect on aluminum was studied by operating Baths A and B ammonia-free. pH adjustments were made with an alkali solution. Table 4 compares the results of an ammonia-free system to those systems previously described.

Table 4

	Turnover Bath A		Turnover Bath B	
pH_i	NH_3	K_2CO_3	NH_3	K_2CO_3
4.4	3.1	3.6	4.3	5.3
4.8	4.8	7.1	5.6	8.0
5.2	5.9	-	7.5	-

A substantial increase in bath life occurs when ammonia is eliminated from the electroless nickel bath. A further confirmation of the deleterious effects of NH_4^+ on aluminum was demonstrated as follows

1. pH of malfunctioning NH_3 Baths A and B were adjusted to pH 12 with NaOH.
2. solutions agitated and allowed to mix overnight to expel NH_3.
3. pH readjusted to 4.4 with H_2SO_4 and filtered.
4. baths readjusted to nickel and hypophosphite levels.
5. aluminum panels processed as before.

Blister-free deposits were obtained from both baths.

Experiment #5 - Effect of Nickel Concentration

A higher concentration of nickel will reduce the total acidity of bath in a given system by consuming some of the free chelator constitu The effect of nickel on the system is demonstrated by adding nickel to A' at their points of failure. Table 5 shows the improved results.

Table 5

Bath A'

pH_i	Ni, 5.8 g/l	Ni, 7/5 g/l
4.4	2.6 T (blisters)	3.9 T (no blisters)
4.9	4.3 T "	5.6 T " "
5.2	4.7 T "	6.7 T " "

The above baths were replenished only with nickel and hypophosphite after blistered deposits occured.

Experiment #6 - Effect of Fluoride

Fluorides are added to electroless nickel baths to act as an exaltant[4][5]. The effect of fluoride in promoting or retarding blisters was evaluated in Bath B. pH adjustments were made with ammonia and alkali. Table 6 summarizes the results.

Table 6

Bath B

Turnovers, NH_3		$[F_f^-]_M$		pH_i	Turnovers, K_2CO_3		$[F_f^-]_M$
1.9	(4.3)	.011		4.4	3.9	(5.3)	.019
2.8	(5.6)	.015		4.8	5.6	(8.0)	.026
5.0	(7.5)	.024		5.2	-	-	-

These results show the deleterious effects of fluorides on the deposi and also re-confirm the previous findings, i. e. the negative effects of ammo and lower pH values. The figures in parenthesis reflect the Turnovers achieved without fluoride additions.

Summary:

One of the causes for blistered nickel deposits on aluminum can be electroless nickel bath. The total acidity of the bath appears responsible fo this failure and may be expressed as follows:

$$\text{Total Acidity Concentration} \cong \left[H^+ + H_2PO_3^- + NH_4^+ + HL\right]$$

The following guidelines will minimize the development of blister and thereby extend the functional bath life.

1. Select and evaluate baths for maximum longevity.
2. Employ a separate bath for plating on aluminum.
3. Operate and maintain the pH at maximum pH levels.
4. Minimize the use of ammonia.
5. Eliminate any source of contamination by drag-in.
6. Maintain the nickel at optimum recommended concentration.
7. Increase the operating pH values gradually as the bath ages.

The formulation of the bath and the combinations of the ingredi have a strong influence on the quality of the nickel deposit on aluminum. In general an effective bath will:

a) operate at pH's 5.0 - 5.5.

b) be well buffered in this range.

c) require a minimum amount of ammonia for pH adjustment.

d) function with a minimum amount of chelator.

For the conditions described, zinc in solution does not have an observable effect in causing blistered deposits.

Bibliography

[1] G. Gutzeit, P. Talmey, W. Lee, U.S. Patent 2,935,425 (1960)

[2] Aluminum Association, "Aluminum with Food and Chemicals", p 43 (1967)

[3] Ibid, p44 (1967)

[4] R. Reschan, A. Krieg, U.S. Patent 2,694,017 (1954)

[5] G. Gutzeit, U. S. Patent 2,694,019 (1954)

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Electroless I
Session P

Renewal of Spent Nickel Plating Baths

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RENEWAL OF SPENT ELECTROLESS NICKEL PLATING BATHS

by Konrad Parker

ABSTRACT

During the electroless (autocatalytic) plating of nickel the hypophosphite reducing agent is continuously oxidized to phosphite. Thus, for each mil-square foot of nickel-phosphorus alloy deposited about 100 g of sodium phosphite are formed. After six nickel turnovers the phosphite content of the bath exceeds 20%; plating rate and deposit quality deteriorate and the bath has to be discarded.

The partial removal of the accumulated phosphite by either precipitation or ion exchange treatment was investigated. Precipitation of phosphite by the addition of inorganic salts is feasible, however, this introduces undesirable cations into the plating bath. - Weak base anionic resins can exchange their hydroxy for phosphite ions thereby reducing the phosphite concentration. By repeated passes through a resin column, a spent bath can be reclaimed to plate normally on both steel and aluminum substrates.

RENEWAL OF SPENT ELECTROLESS NICKEL BATHS

by Konrad Parker

I INTRODUCTION

In most electroless nickel plating baths the nickel ions are catalytically reduced by sodium hypophosphite which is oxidized to phosphite in the redox reaction. As shown by the equation, three moles of hypophosphite are required to reduce one mole of nickel.

$$Ni^{2+} + 3H_2PO_2^- \xrightarrow{Cat.} Ni + 2H_2PO_3^- + P + H + H^-$$

Thus: for each mil-square foot (19-20 g) of nickel-phosphorus alloy plated about 100 g of sodium orthophosphite are generated in the plating bath. If air is used to agitate the bath an additional 5 to 10% of hypophosphite is oxidized.

During the plating process the nickel and hypophosphite are continuously depleted and must be replenished in order to maintain the chemical balance of the bath. Addition of either ammonia or sodium hydroxide is also necessary to keep the pH in the preferred range of 4.5 - 4.7. In a typical plating solution containing 7.5 g/L (1 oz./gal.) nickel and 36 g/L sodium hypophosphite the sodium phosphite concentration increases by about 35 g/L for each nickel turnover. After six turnovers the phosphite level reaches 20% (2M) and the plating solution may turn cloudy when hot. This is due to nickel phosphite precipitation since its solubility decreases to less than 3 g/L at 98°C & pH 4.6. At that point the plating rate has decreased to less than 0.4 mil/hr and the plater may decide to discard the bath. Another reason for making up a fresh plating solution is blistering of deposits on alumi

substrates which frequently occurs after six turnovers. Of course, plating baths operating with high dragout will have considerably higher number of turnovers.

Due to more stringent effluent regulations the dumping of spent nickel solutions is no longer permitted. The EPA limits the nickel concentration discharged to streams and sewers to less than 1 ppm and in some localities the phosphorus content is also regulated.

At today's prices the make-up cost of a plating bath from proprietary concentrates averages $2.25 gal. The most expensive component is the sodium hypophosphite (about $1.40/lb.).

There are therefore two reasons to prolong the life of an electroless nickel bath:

1. Savings in expensive make-up chemicals; and
2. Decrease in frequency of bath disposal.

A "spent" electroless nickel bath contains the following chemicals:

Nickel sulfate	20-30 g/L
Sodium hypophosphite	20-40 g/L
Sodium phosphite	200+ g/L
Sodium sulfate	80+ g/L
Chelating acids, buffers	40+ g/L
Total Solids	350+ g/L

Some ammonium salts and small amounts of stabilizers are also present, as well as accumulated iron, aluminum, copper, calcium and zinc salts plus chloride, nitrate, phosphate from drag-in contamination.

Several methods for treating spent electroless nickel baths have been reported. Precipitation of phosphite with ferric chloride as $Na_2Fe(H)(HPO_3)_2$ 20 H_2O was tried in Russia.[1] A reduction in phosphite from 29.9 to 29.6 g/L in a glycine and from 51 to 28 g/L in a glycolate bath was achieved. In the U.S. GATX[2] patented the addition of ferric sulfate

and also a calcium phosphite precipitation process by the addition of lime and gypsum. To obtain satisfactory plating a second precipitation to remove the residual calcium with sodium fluoride was necessary. The fine calcium fluoride precipitate was very difficult to filter but could be separated in a centrifuge.

In 1955 Spaulding[3] patented the treatment of a used bath with an anion exchange resin which had first been treated with a hypophosphite solution. In one example the phosphite content was reduced from 70.6 to 37.8 g/L, in another from 110.8 to 50.4 g/L. Grobunova[1] also reports the partial removal of phosphite by means of resin treatment in Russia, however, to date this process has not been used in industry.

The experiments reported here investigated the efficiency of phosphite removal by precipitation and ion exchange methods. A drum of a spe proprietary bath was obtained from a plating company. It was found by an lysis to contain 3.4 moles phosphite indicating nine to ten turnovers. T bath was still plating satisfactorily on steel, but not on aluminum work pieces.

Samples of this bath were used in most of the experiments as des cribed in the following sections:

Precipitation experiments.

Ion exchange experiments.

II ANALYTICAL METHODS

All solutions were analyzed for nickel content by EDTA titration. Phosphite and hypophosphite concentrations were determined by oxidation with excess hypochlorite followed by KI addition and back titration with sodium thiosulfate. Plating rates were determined by weight gain of 20 cm^2 coupons plated in 1 L of plating solution.

III PRECIPITATION EXPERIMENTS (Table I)

A. Procedure

The precipitation of phosphite was carried out in beakers by slow addition of respective salt solutions to 1 L of hot spent bath. Stirring was continued for about 30 minutes during which the bath was allowed to cool. After settling the solution was filtered on a Buchner funnel using coarse Whatman No. 3 paper with an aspirator hose on the suction flask.

Table I shows the amount of the various salts added in grams and on a molar basis. In most experiments 0.36 moles were added which theoretically should precipitate 0.72 moles of a divalent phosphite compound equal to the amount of phosphite generated in two nickel turnovers. The amount of dry precipitate is also shown. The filtrate was analyzed for nickel, hypophosphite and phosphite. It was then replenished to the specified nickel (7.5 g/L) and hypophosphite (36 g/L) content before evaluation for plating rate and deposit quality.

The salts were selected on the basis of phosphite solubility data, availability and cost. Only the partial (20%) removal of phosphite was attempted, since the complete removal would require the addition of five times the amount of salt making filtration, very difficult or impossible.

B. Results and Discussion

1. Iron Salts

Ferrous and ferrous ammonium sulfates were equally effective in reducing the phosphite concentration by 0.8 mole/L; however, all of the hypophosphite and about half the nickel in the solution were also removed. Filtration was easy and the amount of cake was relatively small. Although the filtrates contained 1,700 ppm. ferrous ions by AA analysis, they plated satisfactorily after replenishment.

On an equal molar basis the ferric chloride precipitated about 20% more phosphite. Thus, the addition of 98 g $FeCl_3$ reduced the phosphite concentration by 1 mole/L. None of the nickel, but over half the hypophosphite were also removed. With ferric sulfate the highest reduction in phosphite, 1.6 mole/L, was achieved with little loss of nickel, but total loss of hypophosphite. Since the ferric salts reduce the pH of the bath to 3, large additions of caustic are necessary to raise it back to 4.6. The ferric filtrates contained 30 to 800 ppm iron and produced dull, streaky and/or discolored deposits.

2. Calcium Salts

The addition of 0.36 mole/L lime and 0.36 mole/L calcium sulf as slurries was tried separately and in combination. The latter was effective and precipitated 0.6 mole phosphite at pH5. No decrease in nickel and hypophosphite content was found, since calcium hypophosphi is quite soluble. To remove residual calcium ions in the filtrate o mole/L of sodium fluoride was added. The calcium fluoride precipita was very slow filtering. Although the filtrate produced good deposi it plated out on the walls of a glass beaker due to fluoride etchin Calcium salts have the advantage of low molecular weight requiring

addition of relatively small quantities for phosphite precipitation. It should be mentioned that the presence of appreciable amounts of calcium interferes with the usual EDTA titration for nickel.

Other calcium salts such as the acetate, sulfamate and hypophosphite can be used to precipitate calcium phosphate. However, they also introduce a certain amount of "free" calcium ions into the bath. By close control of pH and temperature during the calcium phosphite precipitation the "free" calcium can be held to about 200 ppm. This amount may reduce the brightness of the deposit and also the adhesion especially on aluminum.

3. Barium, Strontium, Magnesium Salts

The addition of barium chloride was ineffective, while barium oxide decomposed the bath. Strontium chloride addition did not precipitate any appreciable phosphite. Magnesium hydroxide reduced the phosphite by 0.9 mole/L; however, filtration was quite slow. The filtrate was cloudy and plated dull deposits. Neither magnesium chloride or sulfate were effective; however, in combination with magnesium hydroxide the phosphite concentration was reduced by 0.5 mole/L. The filtrates plated either dull deposits or had slow plating rate. The nickel concentrations could not be determined by EDTA titration.

4. Increase in pH

Since the solubility of nickel phosphite decreases with increase n pH and temperature, the pH of the hot bath was raised to 5.7 and 6.8 y the addition of 10% sodium hydroxide solution. Only a small amount f gelatinous precipiate was obtained which was very difficult to filter. ltration was facilitated by subsequently decreasing the pH to 4.6 with etic acid. The filtrate showed no appreciable decrease in phosphite.

It had a plating rate of only 0.3 mil/lin and produced blistered deposits on aluminum. Due to large amounts of chelating agent, the "free" nickel ion concentration in the bath is quite low and insufficient for the precipitation of nickel phosphite.

5. Decrease in temperature

Sodium sulfate readily crystallizes in the bath when it is cooled. After 24 hours storage in a refrigerator at 38°F(3°C) 70 g of large crystals were produced in one liter, while in the freezer compartment at 5°F (-15°C) 50 g of small crystals separated. The phosphite concentration remained unchanged.

SUMMARY

The addition of iron salts removes not only phosphite but also most of the expensive hypophosphite which makes their use uneconomical. The addition of calcium salts is most effective in precipitating only the phosphite without simultaneous reduction in nickel and hypophosphite concentrations. However, calcium ions left in the nickel plating bath may produce dull and rough deposits, as well as loss of adhesion. The calcium can be precipitated as the fluoride but calcium fluoride is very difficult to filter. These results confirm those obtained earlier by GATX. Further work with calcium salts to minimize the excess calcium ions left in solution is warranted. Combinations of magnesium compounds partially precipitate phosphite; however, "excess" magnesium ions are detrimental to appearance and/or plating rate.

Any precipitation process requires a large plate and frame filter press capable of holding at least one pound of wet cake per gallon of spent bath. To obtain the desired clear filtrate precoating may be necessary. There is considerable labor involved in emptying and cleaning the press. Proper disposal of the filter cake could be costly.

IV ION EXCHANGE EXPERIMENTS

A. Procedure

Preliminary screening of 12 ion exchange resins of various types from two manufacturers showed the weak base anion type to be the most effective in adsorbing phosphite as follows:

$$ROH + H_2PO_3^- \longrightarrow RH_2PO_3 + OH^-$$

The strong base anionic resins precipitated nickel hydroxide on the resin surface.

A total of 10 weak base anionic resins from four companies were selected for laboratory evaluation of phosphite removal efficiency.

Three sizes of resin beds were used: 80 mL, 160-180 mL, and 260-320 mL. The corresponding spent bath volumes used were: 250 mL, 500-750 mL, and 1,000 mL. A ratio of 3 to 4 solution volumes to 1 of resin bed volume was maintained. The elution rate was controlled in four fractions. Each sample was analyzed for phosphite, hypophosphite and nickel. The results shown are averages of the analyse for all fractions to make up the original bath volume put through the re spective resin bed. By this method, break-through of phosphite due to resin saturation was determined.

After each bath treatment the resin bed was washed, regenerated with one bed volume of 4% sodium hydroxide solution and washed again thoroughly with D.I. water to remove excess caustic from the resin. Another sample of bath was then treated. Most resins were tested twic With the IRA-93 resin 8 runs were made. It was also used for the tr ment of a spent bath from another plater.

B. Results and Discussion (Table II & III)

The results obtained with the various weak anionic resins were quite similar when compared at equivalent volume ratio of solution treated to resin bed. The maximum effective ratio was found to be 3 volumes of bath to 1 volume of resin. Thus, 1,000 mL of solution shows a reduction in phosphite of 0.4 - 0.5 mole/L after passing through a 320 mL bed of resin, or on a larger scale, each pass of 25 gallons of spent bath through one cubic foot of resin removes 0.4 moles of phosphite. About one-half of the hypophosphite is also adsorbed on the resin and the pH of the bath is increased to 5.7.

Prior treatment of the resin with hypophosphite (run #6) to effect a hypophosphite for phosphite exchange decreased the phosphite reduction to 0.2 mole/L and it is therefore not worthwhile.

Of all the resins evaluated the Rohm & Haas IRA-93 was judged to be the best in regard to uniformity of bead size and column formation which, in turn, produced more uniform flow rate and reproducible adsorption. The resin was easy to wash and regenerate. Its operating life is almost indefinite except for small losses due to mechanical attrition of resin particles.

The IRA-93 has a macroreticular (rigid, sponge-like) structure with polystyrene amine functionality. Its exchange capacity is rated as 1.2 meq. $CaCO_3$/mL wet resin. (It presently sells for about $130 per cubic foot.)

C. ION EXCHANGE PILOT PLANT EXPERIMENTS (Table IV)

Two runs were made using one cubic foot of IRA-93 resin in a cylindrical fiberglass tank with top and bottom flow control valves designed for ion exchange. After trying a number of pumps, a plastic

drum pump was found to be the most convenient pump to use since it requires no priming and provides the desired pumping rate of about 1GPM.

A spent bath treatment cycle was as follows:

Thirty gallons (113L) of the spent bath was slowly pumped into the top inlet of the tank. The first five gallons of water white effluent were discarded. The green effluent was then collected. After all the spent bath had been pumped into the tank, 5-10 gallons of D.I. water were used to flush the bath through the bed. The effluent was collected until it changed to light green. The resin was washed with 20 gallons water and then regenerated with 10 gallons of 4% sodium hydroxide pumped at 1 GPM. The bed was then back washed with 20 gallons of water and finally with 5 gallons of D.I. water. The resin was now ready for another bath treatment.

Four successive treatments of spent bath reduced the phosphite from 3.4 mole/L to 1.4 mole/L; however, about 20% of that was due to dilution. Therefore, the actual reduction due to ion exchange only was 1.6 mole/L. Primarily because of unavoidable dilution the original nick concentration was reduced 30%. Most of the reduction in hypophosphite from .19 mole/L to 0.1 mole/L was due to resin adsorption.

After regeneration with nickel and hypophosphite as determined by analysis, the pH is reduced to 4.7 with sulfuric and acetic acids. The treated and regenerated bath produced excellent deposits on both steel and aluminum. In another run only 24 gallons of spent bath were treated and the phosphite was reduced by 1.0 mole/L (corrected for 20% dilution). As expected, the decrease in ratio of solution vo ne to resin bed volume from 4 to 2.5 doubled the amount of phosphite remove

A larger run was made with 50 gallons (190L) of another spent

bath using 2.75 cubic feet of fresh IRA-93 resin. This bath had experienced about 12 nickel turnovers and contained not only 4.6 mole/L of phosphite, but it was also supersaturated with sodium sulfate which had crystallized on the bottom of the drum. The phosphite was reduced to 4.2 mole/L in the first pass through the bed and to 3.6 mole/L in the second treatment. As before, the nickel content was reduced 20% by dilution. All of the hypophosphite was adsorbed after two passes. An actual reduction of 0.4 mole/L of phosphite per pass was achieved. However, the ion exchange treatment was unsuccessful with this bath, since it did not plate satisfactorily. After 12 turnovers it apparently contained too many contaminants for renewal. Much difficulty in pumping this supersaturated solution through the resin was encountered. Therefore, it is better to treat a bath after 6 to 8 turnovers before it is too high in solids for renewal. In the winter it might be practical to cool the spent bath by outside storage and treat the supernatant solution after the sodium sulfate has crystallized out.

D. SUMMARY

Weak base anionic resins offer a simple method for phosphite reduction. Although the initial cost for the resin is quite high, it can be regenerated any number of times, thereby reducing the cost per treatment. For the treatment of 100 gallons of spent bath, a 4 cubic foot resin bed is required to reduce the phosphite concentration by 0.4 mole/L per pass, 30 lbs. of phosphite equal to about one turnover are removed. Unavoidably, the resin also adsorbs 0.1 mole/L of hypophosphite.

With an initial investment of about $2,000 in resin and equipment a small plater could rejuvenate a 250 gallon electroless nickel bath at an amortized cost of $20 per treatment. Other expenses would be 30 lbs. caustic soda, 3 gals. acetic acid, nickel and hypophosphite regenerating solutions plus two hours labor and one hour analytical work. The total cost of chemicals for bath renewal is estimated at $1.00 per gallon. The pay-out would be even better for 1,000 gallon bath although this will require an initial investment of $5,000 for resin alone. In a larger installation the ion exchange treatment can be automated.

The number of renewal treatments for each bath is limited, since other chemicals and contaminants build up and are not removed by the ion exchange treatment. If necessary, an activated carbon treatment is most effective in removing organic and some heavy metal contamination. With repeated ion exchange treatment the effective life of an electroless nickel bath can be doubled and extended to at least 12 turnovers. If sodium sulfate is crystallized by chilling, 20 turnovers of the bath appear possible. For best plating, it is recommended that the phosphite concentration in the plating bath be maintained between 1 to 2 mole/L.

CONCLUSIONS

Spent electroless nickel plating baths can be renewed by removal of the accumulated phosphite. By either precipitation or ion exchange treatment the phosphite can be not completely but partially removed. Precipitation requires the addition of undesirable cations, such as calcium, which are difficult to eliminate. More work is needed to perfect the precipitation process.

For the ion exchange treatment a resin bed of four cubic feet per 100 gallons of spent bath is needed. Each pass through the resin bed removes 30 lbs. of phosphite (0.4 mole/L). The resin can be regenerated with a weak caustic solution and reused many times. Both nickel and hypophosphite are depleted and must be replenished before plating. The total cost of the ion exchange treatment is about half that of a proprietary bath make-up.

A closed loop operation for electroless nickel plating is only feasible if the phosphite generated during plating can be reduced to hypophosphite. Electrodialysis, electrolysis, or a reducing ion exchange resin of the quinoid type should be investigated as potential reduction methods after the phosphite has been separated from the spent bath by ion exchange,

At the present state of the art it may be more practical to prolong the life of the bath by deliberate drag-out of plating solution and increasing replenishment.

ACKNOWLEDGMENT

The author thanks Joe Jenista of Enthone's Bridgeview Laboratory for most of the analytical work.

REFERENCES

1. K. M. Grobunova et al. Physicochemical Principles of Nickel Plating. Acad. Sci. USSR (1960) p. 49-52.

2. U.S.P. 2,872,354; 2,886,451; 3,325,279.(GATX).

3. U.S.P. 2,762,968; 2,762,969.(GM).

TABLE I - PRECIPITATION EXPERIMENTS

COMPOUND ADDED	ADDITION g/L	ADDITION Moles	PRECIPITATE Grams-dry	FILTRATE pH	FILTRATE PHOSPHITE mole/L Decrease		FILTRATE HYPO-PHOSPHITE moles/L	FILTRATE NICKEL grams/L	FILTRATE PLATING RATE mils/hr	DEPOSIT
SPENT BATH	-		-	4.7	3.4	-	.20	7.2	0.4	OK on steel NG on alum.
$FeSO_4 \cdot 7H_2O$	100	0.36	63	5.0	2.6	0.8	0	3.9	0.4	OK
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	142	0.36	60	5.1	2.6	0.8	.01	3.2	0.39	OK
$Fe_2(SO_4)_3 \cdot n\ H_2O$	244	0.4	280	2.5	1.8	1.6	.01	6.4	0.2	Streaky
$FeCl_3 \cdot 6H_2O$ pH5	98	0.36	120	4.6	2.4	1.0	.11	7.1	0.16	Dull
" cold	98	0.36	150	3.0	2.4	1.0	.07	6.9	0.47	Dull
" warm	150	0.55	365	2.0	1.8	1.6	.01	6.4	0.14	Streaky
" cold-hot	50	0.18	60	2.0	2.7	0.7	.06	7.4	0.1	Dark
$Ca(OH)_2$	27	0.36	-	5.7	3.1	0.3	.20	-	-	-
$CaSO_4 \cdot 2H_2O$	62	0.36	-	4.4	3.0	0.4	-	-	-	-
$Ca(OH)_2 + CaSO_4 \cdot 2H_2O$	25+62	0.7	120	4.9	2.8	0.6	.17	-	0.4	Dull
" " " +NaF	+42	1.0	-	5.1	2.4	1.0	.20	6.2	0.57	OK
$Al_2(SO_4)_3 H_2O$	167	0.36	500	3.1	2.2	1.2	.10	6.6	0.3	Black Streaks
$Ba\ Cl_2$	167	0.8	$Ba\ SO_4$	4.2	-	-	-	-	-	-
Ba O	171	1.0	decomp.	-	-	-	-	-	-	-
$SrCl_2 \cdot 2H_2O$	80	0.33	-	4.3	3.3	0.1	-	-	-	-
$MgCl_2 \cdot 6H_2O$	100	0.5	none	4.2	-	0	-	-	-	-
" + $Mg(OH)_2$	+25	0.9	150	6.0	2.5	0.9	.18	?	0.5	Dull
$Mg(OH)_2$	30	0.5	GEL	6.0	2.9	0.5	.13	-	-	-
$MgSO_4$	60	0.5	None	4.5	-	0	-	-	-	-
" + $Mg(OH)_2$	+25	0.4	200	5.5	2.9	0.5	.1	?	0.3	Bright

TABLE II

ION EXCHANGE EXPERIMENTS

RESIN	pH	PHOSPHITE M	HYPOPHOSPHITE M	NICKEL grams/L	AV.FLOW RATE ml/min.
SPENT BATH	4.7	3.4	.20	6.4	-
IRA-93	5.7	2.9	.09	6.5	14
IRA-94	5.5	3.1	.14	6.2	8
WGR	5.4	3.0	.06	6.8	8
MWA	5.7	3.0	.10	6.6	10
A-328	5.4	3.1	.09	6.9	8
A-329	5.5	3.0	.10	6.4	10
A-365	6.0	3.0	.07	6.8	7
ES-368	5.9	3.0	.09	6.9	4
ES-374	5.8	3.0	.15	6.6	9
ES-377	5.8	3.1	.16	6.6	10

VOLUME RATIO BATH TO RESIN = 3.3

TABLE III

IRA - 93 RESIN EXPERIMENTS

	pH	PHOSPHITE M	PHOSPHITE CHANGE	HYPOPHOSPHITE M	NICKEL g/L	VOLUME RATIO BATH / RESIN	FLOW RATE mL/min. Average	DEPOSIT on ALUMINUM	PLATING RATE mils/hr
Spent Bath "T" Feed	4.7	3.4	-	.19	6.4	-	-	Blisters	0.4
Lab. Run 1	5.7	2.9	- .5	.08	6.5	3.1	15	OK	0.5
" 2	5.6	2.9	- .5	.09	6.5	3.1	15	OK	0.5
" 3*	5.7	2.8	- .6	.09	6.3	3.1	12		
" Hot 4A	5.6	3.0	- .4	.08	7.1	2.9	16		
" 4B	5.6	2.8	- .2	.07	6.8	4.4	14		
" Hot 5A	5.6	3.0	- .4	.08	7.1	4.4	14		
" " 5B	5.7	2.8	- .2	.01	7.4	4.4	12		
" 6**	5.6	3.2	- .2	.16	7.2	4.4	15		
Spent Bath "C" Feed	4.4	1.5	-	.04	3.1	-	-	-	-
Run 1	6.5	1.0	- .5	.02	3.2	2.9	15	OK	0.6
" 2	6.0	1.0	- .5		2.9	2.9	15		

*After sodium sulfate removel by crystallization
**After hypophosphite treatment of resin.

TABLE IV

IRA - 93 RESIN PILOT RUNS

	pH	PHOSPHITE M	PHOSPHITE CHANGE	HYPOPHOSPHITE M	NICKEL g/L	VOLUME RATIO BATH / RESIN	FLOW RATE GPM	DEPOSIT on ALUMINUM	PLATING RATE mils/hr
Pilot Run (1 cu.ft.) IA	6.0	2.9	- .5	.10	6.5	4	1.0	OK	0.2
" IB	6.5	2.3	- .6	.08	5.6	4	0.5	OK	0.44
" IC	6.9	1.8	- .5	.08	4.8	4	0.5		
" ID	7.9	1.4	- .4	.06	3.9	4	0.5	OK	0.43
" II	5.6	2.2	-1.2	.07	5.1	3	0.5	OK	0.5
Spent Bath "A" Feed	4.5	4.6	-	.24	7.7	-	-	Blisters	0.1
Pilot Run (2.7 cu.ft) A	6.3	4.2	-0.4	.20	7.1	2.5	1.0	Blisters	0.2
B	6.3	3.4	-0.8	.13	6.5	2.5	0.5	"	0.2

*After sodium sulfate removal by crystallization

**After hypophosphite treatment of resin.

Q-1

Environmental I
Session Q

Recovery of Nitric Acid Metal Surface Treatment Baths

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1. INTRODUCTION

Nitric acid, sometimes in conjunction with minor amounts of hydrofluoric acid is used in a variety of metal etching, stripping, and pickling baths (see Table I). In most of these baths, attack of the acid on the outer metal oxide layer and/or elemental metal substrate results in buildup of dissolved metallic ion impurities in the bath. These impurities inhibit the effectiveness of the process. As the concentration of impurities increases bath performance deteriorates, often to the point where it must be discarded, usuallywhileit still contains appreciable levels of free acid.

Table II shows the composition of a typical spent nitric acid bath used to strip copper and nickel from plating rack tips and rejected plated plastic parts. In this case, although 62.5% of the nitrate ion is still in the free acid form, the rate of metallic dissolution is so slow as to make operation of the bath impractical on a production basis.

2. STANDARD DISPOSAL PRACTICE

s recovery of spent nitric acid baths had previously not been attempted on wide commercial scale, there were only two disposal options open;) neutralization with an alkali, or b) hire a waste disposal service to aul to spent acid away. As the laws regarding trucking and disposal of azardous wastes such as nitric acid becomes more stringent, more and ore plating and metal surface finishing firms are finding neutralization the ly route open to them.

fortunately, neutralization of spent nitric acid baths has a number of wbacks, including the following:

high cost of neutralization chemicals,

high replacement cost of nitric acid,

due to the high concentration involved, periodic dumping of a spent bath can frequently overload a "flow-through" type waste treatment system,

batch neutralization of a full strength bath is somewhat hazardous because of the large amount of heat evolved, and

although the acidity and metal ions can be removed, the objectionable itrate ion passes through the waste treatment system.

As shown in Table II the cost of neutralization (with caustic) of a gallon of the bath shown in Table I is calculated as $1.01. This excludes labour and the cost of solids separation and sludge disposal. The cost of 70% nitric acid is about $0.10/lb or $0.14/lb on a 100% basis so that the replacement cost of a gallon spent bath would be about 8.38 x $0.14 = $1.17. The total cost of neutralizing and replacing this solution would then be $2.18 per gallon.

3. THE ACID PURIFICATION UNIT

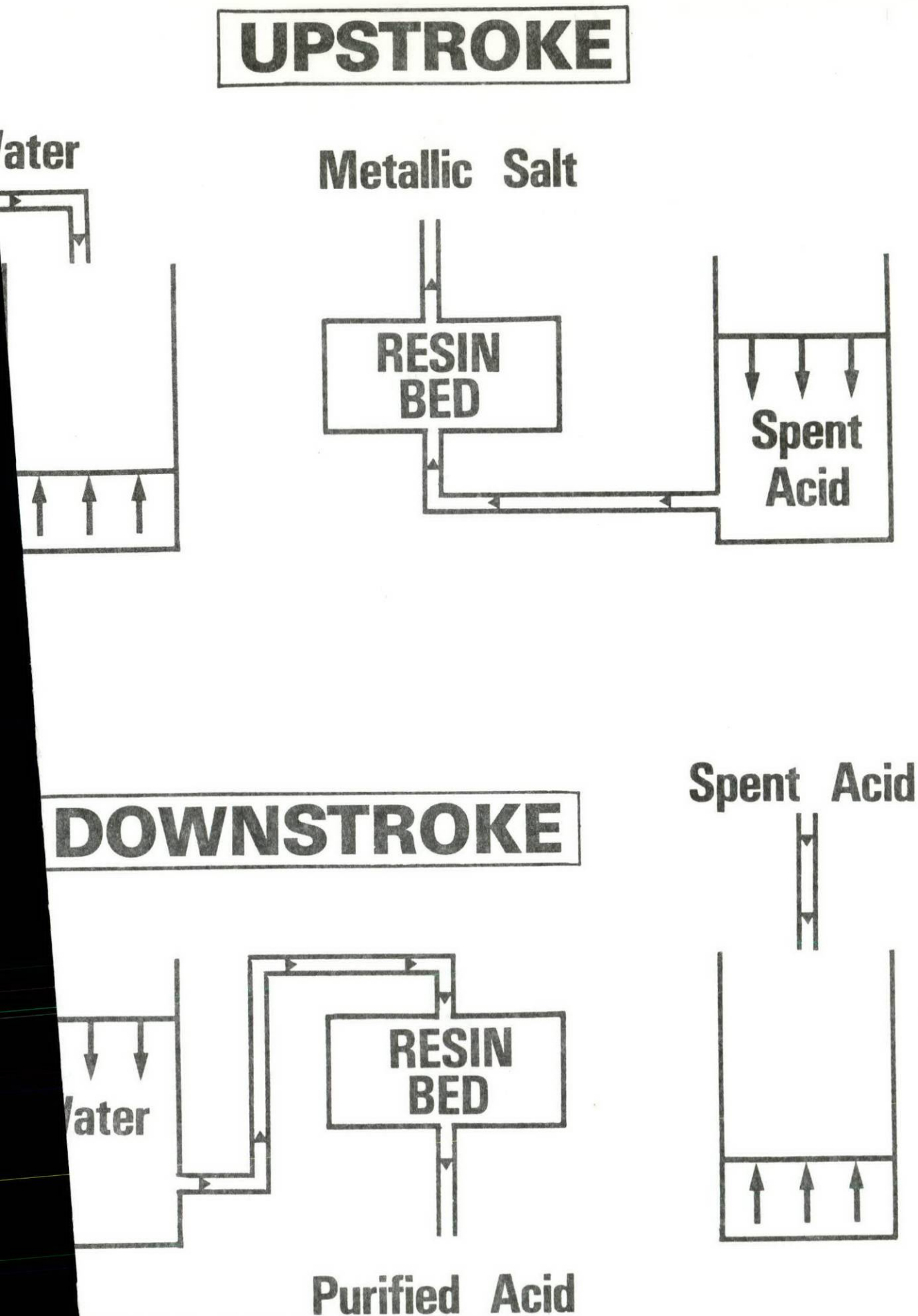
A new system for the purification of spent mineral acids based upon a phenomenon known as "acid retardation[1]" has recently been commercialize The system uses a resin capable of absorbing strong mineral acids and exc metallic salts of these acids. The resin is incorporated into a patented process [3,4] that is based upon the techniques of a novel ion exchange process called Reciprocating Flow Ion Exchange. A means of contacting the spent acid solution with a fixed bed of the resin in an extremely effici manner is thus achieved.

The process is factory assembled into a compact, skid mounted, totally automated unit called an "Acid Purification Unit" (APU). The APU basica consists of the resin bed, two hydropneumatic metering tanks, an electri control panel, plastic piping and several pneumatically operated plastic control valves. (See Figure One). A typical unit occupies from six to tw four square feet of floor area and is less than six feet tall.

There are two basic steps in the process - the "upstroke" and the "down (See Figure Two). During the "upstroke" spent acid is forced by air pre from the acid tank up through the bed. Acid is absorbed into the resin p and the remaining de-acidified metallic salt byproduct or waste solution collected from the top of the bed. Next, during the "downstroke", wate by air pressure from the water tank into the top of the bed, displacing t acid from the resin so that a purified acid product is collected from the of the bed.

4. APPLICATION OF THE APU TO NITRIC ACID RECOVERY

An experimental program was begun in the summer of 1976 to determine applicability of the APU to nitric acid recovery. The first commercial ation was started up in 1977 on a nitric copper/nickel application. B of plant interruption, this unit saw only intermediate use until early 1 which time it began to see continuous use. A number of other units h installed for similar applications. Full scale pilot programs for nitri



IGURE TWO - BASIC OPERATION OF THE APU

hydrofluoric stainless steel, pickling acid recovery and laboratory tests for nitric/hydrofluoric titanium and zirconium pickling acid recovery, are now being conducted.

5. RESIN STABILITY

Polymeric substances, such as the resins employed in this process, are know to be susceptible to attack by strong oxidizing agents such as nitric acid. Consequently, the question of resin stability and the possible safety implica of a violent attack on the resin immediately came to the fore.

As an initial test, a sample of the resin was placed in a 50% by volume solution of nitric acid, at room temperature, and withdrawn weekly for evaluation over a period of three months. No obvious degradation or advers effects on process performance were observed over the duration of the test.

Two unique features of the APU process tend to inhibit the initiation and propogation of resin degradation a) short resin/acid contact times (typicall 1.5 minutes) and b) short bed heights (typically 30cm (12 inches). Field experiences on commercial units operating over periods in excess of one ye have confirmed that resin degradation is not a problem.

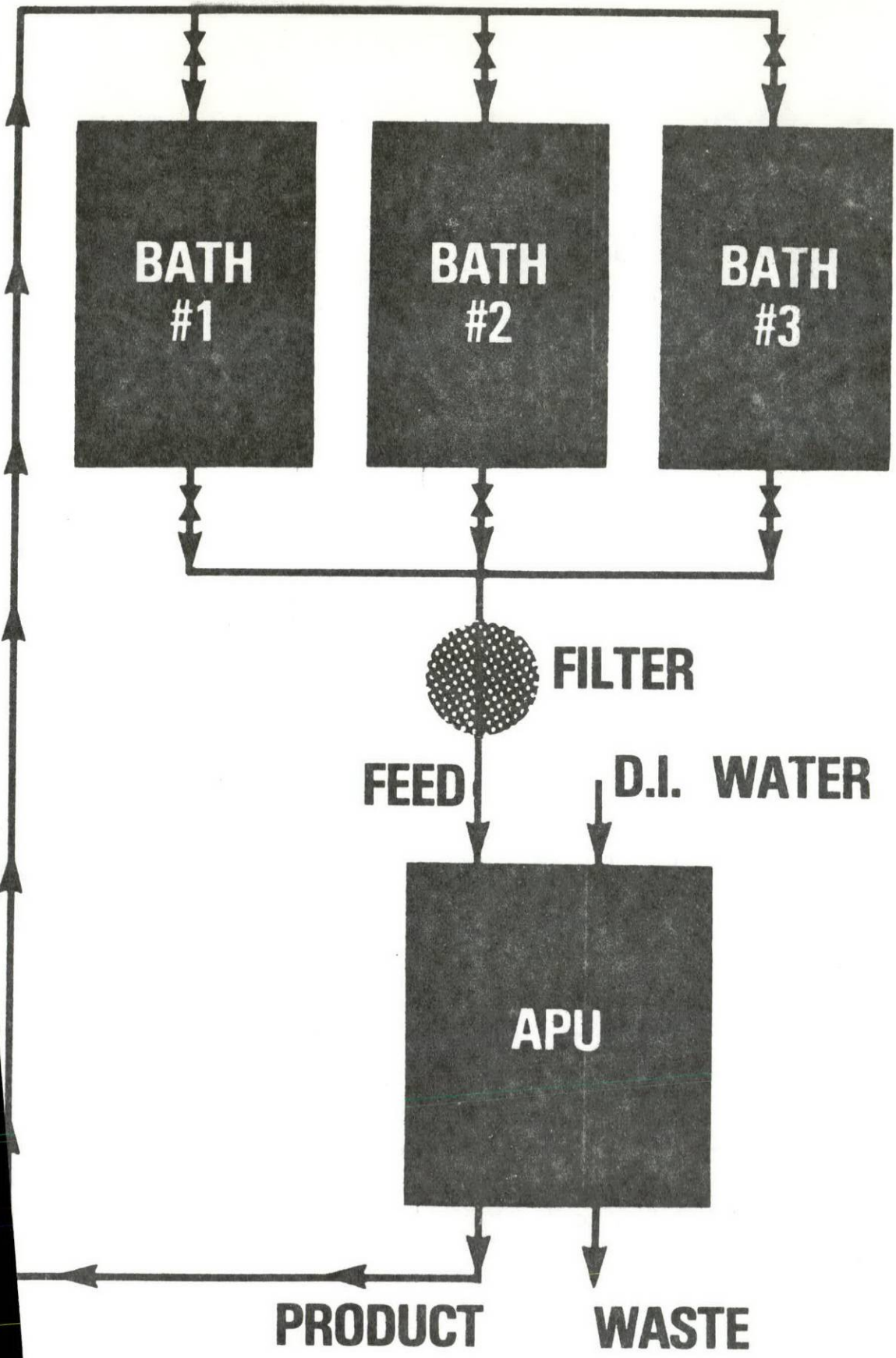
6. FIELD EXPERIENCE

A schematic representation of a typical APU installation is shown in figure Valves are installed on the feed and product lines at each bath so that the APU can be run on any of the three baths as required.

Basic operation of the system is as follows:

Bath solution flows by gravity or low pressure pump to the APU. A supply tap water elutes acid product from the resin, the purified acid product be recycled directly back to the bath. The metallic salt byproduct produced the unit normally flows to the plant waste treatment system or a small ba neutralization tank. A supply of compressed air and electricity are also required for the operation of the unit.

Due to the extreme simplicity of the process and its control circuit, reli of APU's in the field has been very good. The prime problem initially w adequate pre-filtration of the bath solution prior to treatment by the APU the case of baths used to strip copper and nitric from rack tips, large amounts of fine chromium particles which break off during the stripping process but are not dissolved by the acid, passed through the nominal micron cartridge filter initially installed and lodged in the resin bed. cartridges were subsequently installed and the problem has been allevi



URE THREE - TYPICAL APU PLANT LAYOUT

7. RESULTS

Table IV shows typical data collected from an APU operating on a nitric acid copper/nickel rack stripping operation. This data indicates that essentially all of the free nitric acid is recovered for re-use in the stripping operation. Makeup of fresh concentrated nitric acid to the bath is required, to replace nitric acid neutralized through metal dissolution, in order to maintain bath strength and effectiveness.

8. ECONOMICS

Table V summarizes the economics of recovery nitric acid baths used for stripping copper and nickel. Three hypothetical plating installation are examined each annually discarding approximately 30,000 litres (7500 gallo 120,000 litres (30,000 gallons) and 200,000 litres (50,000 gallons) of bath solution. It is assumed that prior to installation of the APU, the bath was discarded upon reaching the composition shown in Table II. Based upon th composition, it is estimated that operation of an APU would result in a 60% reduction in acid purchases for bath makeup and caustic purchases for neu tralization.

As shown in Table V, payback periods of less than one year are achievabl for all three installation examined, making nitric acid recovery an extrem attractive proposal for this application.

9. ADDITIONAL BENEFITS

In addition to the obvious economics benefits discussed above, the APU system offers the following additional advantages:

1. more uniform rate of etch because of uniform bath composition,
2. reduced level of nitrate discharge,
3. elimination of shock loading of plant waste treatment system, and
4. elimination of labour required to pump out old bath and make up a new bath.

10. METAL RECOVERY

Many of the metals contained in these baths, notably copper and nick considerable potential value. A number of chemical, electrolytic and exchange techniques are currently being investigated for conversion o

nitrate salts to more valuable forms. This can further improve the economic justification for installation of a system of this type.

11. CONCLUSION

A unique system for the purification of nitric acid metal surface treatment baths has been developed and field proven. This system utilizes a simple, low cost, low maintenance process to remove dissolved metallic impurities from the process bath. As a result, pollution is abated and bath performance is improved.

An economic evaluation which takes into account the cost of alternate waste treatment by conventional means, (ie. neutralization) shows that appreciable savings can result through operation of the system, in some cases enough to quickly pay off the original capital investment.

TABLE I TYPICAL NITRIC ACID METAL SURFACE TREATMENT PROCESSES

1. pickling and etching copper and brass
2. de-smutting aluminum
3. pickling stainless steel (with HF)
4. pickling exotic metals (eg. titanium, zirconium (with HF)
5. copper and nickel plating rework and rack stripping.

TABLE II TYPICAL SPENT COPPER/NICKEL STRIP BATH

$(Ni^{++}) + (Cu^{++})$ = 180 g/l (1.5 lb/gal)

(free) (HNO_3) = 630 g/l (5.25 lb/gal)

total nitrate (as HNO_3) = 1008 g/l (8.38 lb/gal)

$$\text{portion recoverable acid} = \frac{630}{1008} \times 100\%$$

$$= 62.5\%$$

TABLE III COST OF NEUTRALIZATION OF COPPER/NICKEL STRIP BATH

$$\text{amount of NaOH req'd} = 180\ \frac{(40)}{(30)} + 630\ \frac{(40)}{(63)}$$

= 640 g/l (5.33 lb/gal)

cost of liquid caustic = \$0.19/lb NaOH

cost of neutralization = (5.33) (\$0.19)

= \$1.01/gal

(average equivalent weight of metals assumed to be 30)

TABLE IV TYPICAL APU RESULTS - NITRIC ACID RECOVERY

	Feed (Bath)	Product (Recycle)	Byproduct (waste)	Water
HNO_3(g/l)	353	378	7.6	-----
Cu + Ni(g/l)	89.1	42	70.5	-----
approximate relative flow rate	1	0.902	0.744	0.646

TABLE V ECONOMIC EVALUATION - NITRIC STRIP RECOVERY

	30,000 litres/yr (7500 gal/yr)	120,000 litres/yr (30,000 gal/yr)	200,000 lites/yr (50,000 gal/yr)
approx. APU cost	$ 9,400	$11,300	$ 18,400
previous neutralization cost	$ 7,575	$30,300	$ 50,500
revious acid ost	$ 8,775	$35,100	$ 58,500
tal previous st	$ 16,350	$65,400	$109,000
nual savings	$ 9,810	$39,240	$ 65,400
yback period	11.5 mon.	3.5 mon.	3.4 mon.

is

sizing based upon 4000 hr/yr operation, bath held at 50% of spent bath; contamination level shown in Table II.

neutralization costs include cost of caustic only, excluding solids separation disposal costs and labour;

costs for neutralization and replacement of acid lost due to dragout are excluded since this occurs in any case;

overall recovery efficiency of acid by APU is 60%.

REFERENCES

1. M.J. Hatch and J.A. Dillon, Industrial and Engineering Chemistry Process Design and Development Vol. 2, No. 4, 253 (1963)

2. C.J. Brown, D. Davy, P.J. Simmons, Plating and Surface Finishing, Vol. 66, No. 1, 54 (1979)

3. R.F. Hunter, U.S. Patent 3, 385,788 (1968)

4. R.F. Hunter, U.S. Patent 3, 386, 914 (1968)

Q-2

Environmental I
Session Q

Recovery of Potassium Zinc Chloride Plating Solution

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RECOVERY OF POTASSIUM ZINC CHLORIDE PLATING SOLUTION

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The recent promulgation of pollution abatement regulations for the Electroplating Industry has precipitated some changes in the composition of plating solutions. Some platers have abandoned familiar and reliable solutions and have chosen to experiment with new bath formulations as a means of meeting stringent discharge limits for certain chemicals.

Cyanide is one of the chemicals that has a low allowable discharge limit. The EPA's Proposed Pretreatment Standards for Existing Sources were published in the Feb. 14, 1978 Federal Register. The discharge of cyanide was limited to a maximum concentration of 0.08 mg/l based on an average daily value for (30) consecutive days. This has caused many platers to switch from conventional zinc cyanide plating solutions to non-cyanide formulations such as potassium zinc chloride.

Substituting potassium zinc chloride solution for zinc cyanide can eliminate cyanide from some plant's effluent. The waste treatment system required for potassium zinc chloride is simpler and easier to operate than one needed for zinc cyanide. The contaminated rinse water does not have to pass through a cyanide treatment module. A pH adjustment module is used instead to precipitate the zinc. The result is a substantially lower treatment cost. The value of potassium zinc chloride solution, however, is approximately double that of zinc cyanide, so that recovery and recycle of the plating solution lost to dragout can be economically attractive.

This paper will examine differences between potassium zinc chloride plating solution and zinc cyanide plating solution with respect to plating, bath maintenance, waste treatment, and recovery. A case history of an evaporative recovery system will be presented with before and after chemical consumption data, economics, impurity problems and other considerations.

Chloride zinc plating solutions have been available for several years now; however, the earlier formulations contained a zinc ammonium chloride complex. The presence of ammonia often presented problems for conventional waste treatment system. Fairly stable ammonium complexes can be formed with copper and nickel bearing wastes present in plating effluents. These complexes prevent the precipitation of

these heavy metals and can result in an effluent concentration higher than allowable. Some areas of the country have also placed limitations on the concentration of ammonia in a plant's effluent. In some locations, therefore, the ammonia formulation created unacceptable discharges. Most of today's chloride zinc solutions do not contain ammonia and generally are a formulation of potassium zinc chloride. The following bath composition is for Conversion Chemical/Plating Systems Department's Kenlevel II.

Chemical	Concentration oz/gal
Zinc chloride concentrate	13 fl. oz.
Potassium chloride	30
Boric acid	4.5
KENLEVEL II LEVLR-TB	4 fl. oz.
KENLEVEL II LEVLR-TM	4 ml
pH value 5.5-6.0	
Optimum temperature 75-85°F	

A typical zinc cyanide solution has the following bath composition:

Chemical	Concentration oz/gal
Zinc cyanide	8.0
Sodium cyanide	5.6
Sodium hydroxide	10.5
Addition agent	(as required)
pH value 14	
Temperature 80°F	

A cursory examination of the two plating solutions shows that the cyanide solution is strongly alkaline and the potassium zinc chloride solution is acidic. The change over of solutions, therefore, requires modifications in the materials of construction for equipment in contact with the solutions. Carbon steel is usually acceptable for zinc cyanid but potassium zinc chloride solutions will require more corrosion-resistant materials such as:

Equipment Item	Materials of Construction
Plating and rinse tanks	Plastic or rubber lining
Heating/cooling coils	Titanium
Anode baskets	Titanium
Plating machine superstructures	Plastisol coated or painted
Racks	Plastisol, PVC or rubber coate

Changing to a potassium zinc chloride bath requires basically the same materials of construction as for nickel baths. This is generally a substantial cost albeit a one-time cost. The use of these materials will generally suffice for many plating solutions so that the equipment may never need to be changed again. The investment for corrosion resistant equipment is offset by several considerations, both tangible and intangible. Savings in waste treatment costs, however, can be realized annually.

A conventional cyanide treatment system involves a two-stage alkaline chlorination reaction with chlorine or sodium hypochlorite to completely oxidize the cyanide radical to carbon dioxide and nitrogen. This does not complete the treatment of cyanide bearing waste streams because the associated heavy metals such as zinc must be precipitated from the treated solution. Rinse water containing potassium zinc chloride solution only requires pH adjustment for the precipitation of zinc.

The treatment cost for one gallon of zinc cyanide plating solution is approximately $1.50 versus a treatment cost of approximately $0.10 per gallon of potassium zinc chloride solution. The value of the plating solution being treated is also a part of the total treatment cost. When this is factored in, the net difference in treatment costs is $0.70 per gallon in favor of the potassium zinc chloride solution. For example, this translates to an annual savings of $28,000 when the dragout rate is 10 gph and the plant operates 4000 hours per year.

In addition to possibly eliminating cyanide from the effluent and reducing treatment costs, potassium zinc chloride solutions offer other benefits including:

1) a bright zinc plate finish
2) faster plating cycles
3) up to 50% less electrical power
4) essentially no hydrogen embrittlement
5) the ability to efficiently plate carbonitrided parts
6) less stringent storage requirements for plating chemicals
7) less of a health risk
8) less dragout loss due to relatively low surface tension of the bath

All of these advantages don't appear without the acceptance of me drawbacks such as:

1) a substantial investment in corrosion resistant materials for equipment associated with the plating operation - this also applies to recovery systems

2) parts must be cleaned thoroughly prior to plating

3) chromating the zinc plate may be difficult

Also, the iron impurity concentration level in the bath is critical and must be maintained below 200 ppm by the addition of hydrogen peroxide and filtration. Excessive peroxide treatment may, however, cause problems with the bath's organic chemicals.

Impurity build-up is amplified when an evaporative recovery system is used to recover and recycle plating solution normally lost to dragout. The dragout can no longer act as a purge for impurities because they are recycled to the bath along with the recovered plating solution. Generally this does not present an insurmountable problem and usually only requires an increase in the frequency of the impurity removal operation.

Before discussing the special considerations for the recovery of potassium zinc chloride solution, it may be helpful to have a general review of the evaporative recovery process.

Evaporative recovery separates contaminated rinse water via evaporation into its original components: rinse water and plating solution. It is a physical process as compared to chemical destruction which is a chemical process.

A simple schematic shown by figure 1 illustrates how an evaporative recovery system recovers plating chemicals, metals and water in a closed-loop manner.

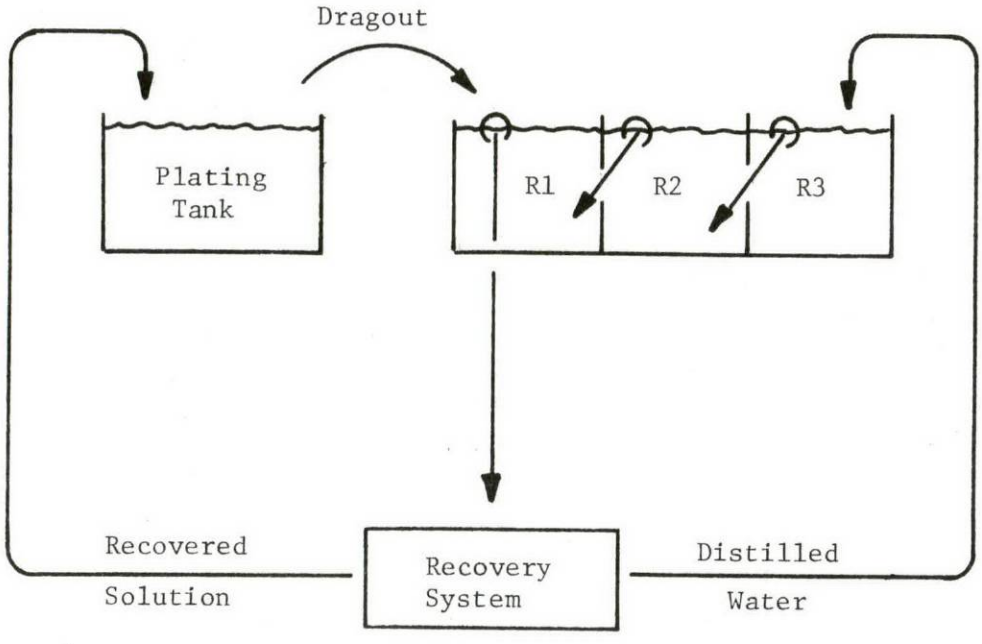

Fig. 1 Closed Loop Recovery

Plated items leaving the plating tank are rinsed in a series of counterflow rinse tanks to remove the adhering plating solution, commonly referred to as dragout. The first rinse tank, R1, has the highest concentration of plating solution. The overflow from the first rinse is sent to an evaporative recovery system where it is separated via vacuum evaporation into distilled water and plating solution. The distilled water is recycled to the final rinse tank, R3, and the plating solution is recycled to the plating tank.

Figure 2 shows a typical, single-effect evaporative recovery system.

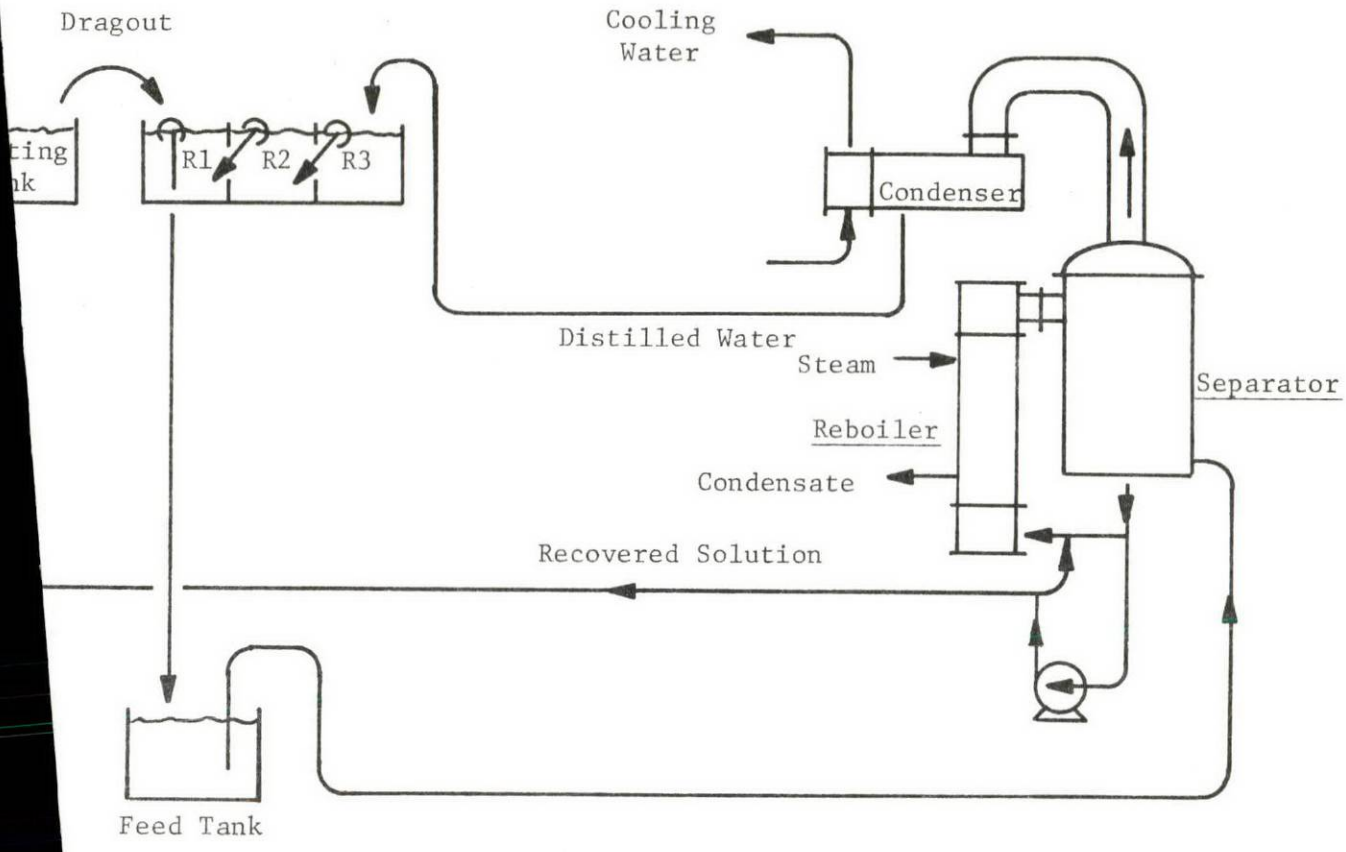

Fig. 2 Single Effect Evaporative Recovery System

Contaminated rinse water overflows by gravity from the first rinse tank to the feed tank. The rinse water is then drawn into the recovery system by vacuum. Water is evaporated from the rinse water by heating it with steam in the rising film reboiler heat exchanger. The boiling solution enters the separator where the water vapor rises through a de-entrainment device to remove entrained droplets of plating solution. The distilled water vapor then enters the water-cooled condenser which condenses it. The distilled water then is transferred to the final rinse tank. The concentrated plating solution remaining in the evaporator is recycled to the plating tank. Virtually no chemicals are added or discharged to the sewer. This concept is referred to as closed-loop recovery.

The key to economic closed-loop recovery is multiple counterflow rinse tanks which concentrate the plating chemicals in the rinse water. This drastically reduces the rinse water flow rate and allows the use of an efficient size recovery system.

Closed-loop recovery is useful when trying to minimize discharges of chemicals which have very low discharge limits such as cyanide and hexavalent chromium. However, closed loop recovery is not imperative. For less restricted chemicals such as those found in potassium zinc chloride plating solutions, a more economical mode of recovery called open-loop recovery can be utilized. Open-loop recovery is schematically shown by figure 3.

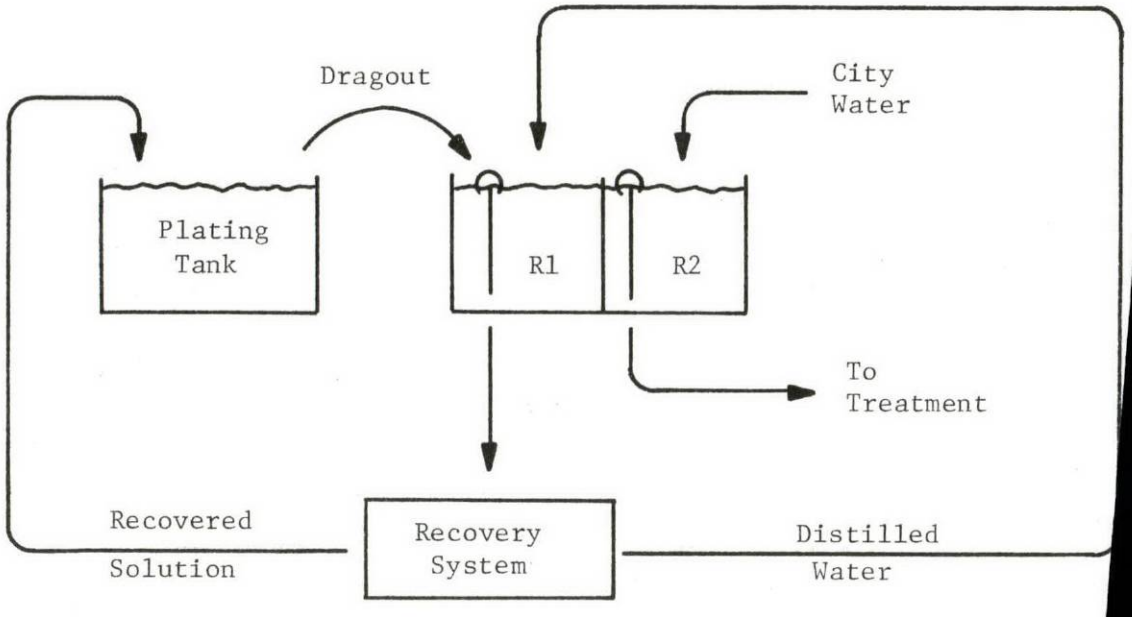

Fig. 3 Open Loop Recovery

Using this approach, about 90% of the dragout can be recovered by operating the recovery system around the first rinse tank only. The remaining 10% ends up in the second rinse tank which uses external water and overflows to waste treatment. Open-loop recovery allows the use of a smaller capacity evaporative recovery system because the system is not required to produce the rinse water for all the rinse tanks; just for the first one. This means lower capital and operating costs which improve the economics for recovery.

Evaporative recovery systems have been used for various cyanide baths for zinc, cadmium, copper, silver and brass; various proprietary chromic acid baths; nickel baths; fluoborate solutions for tin, lead-tin and lead-tin-copper; and potassium zinc chloride solutions.

The recovery of potassium zinc chloride solution will be explored in greater detail as an example. Certain chemical and physical properties of the potassium zinc chloride bath present several unique problems to be overcome for the successful operation of an evaporative recovery system.

Perhaps the most significant consideration is the difference between the bath's dragin and dragout volumes. In most instances, it is not uncommon for the dragin to exceed both the dragout and humidification losses to the surroundings. This happens because the low surface tension of the bath reduces the adherence of plating solution to the work. Thus, the volume of the plating tank actually increases. Periodically, the removal of solution from the plating tank becomes necessary to prevent solution from overflowing onto the floor. This of course precludes the return of any recovered plating solution from a dragout or save-rinse. Although the low surface tension of the bath tends to minimize dragout losses, this property prevents the use of dragout rinses and poses problems for most evaporative recovery systems.

A recovery method has been developed, however, which circumvents this problem and allows the direct recovery of potassium zinc chloride solution from rinse waters.

If the dragout from a bath is less than the dragin to the bath, then it follows that the dragout from the first rinse tank is greater than the dragin from the bath. In fact, the differential volumes between dragin and dragout for the bath and first rinse tank are the same. Therefore, the excess volume of the plating tank will be equal to or less than the volume shortage in the first rinse tank.

The problem is that excess water dragin is diluting the bath. the excess water can be removed it can be accepted by the first nse. A recovery system scheme was developed to accomplish the above d also return recovered chemicals to the bath. Figure 4 schematically ws this recovery system -

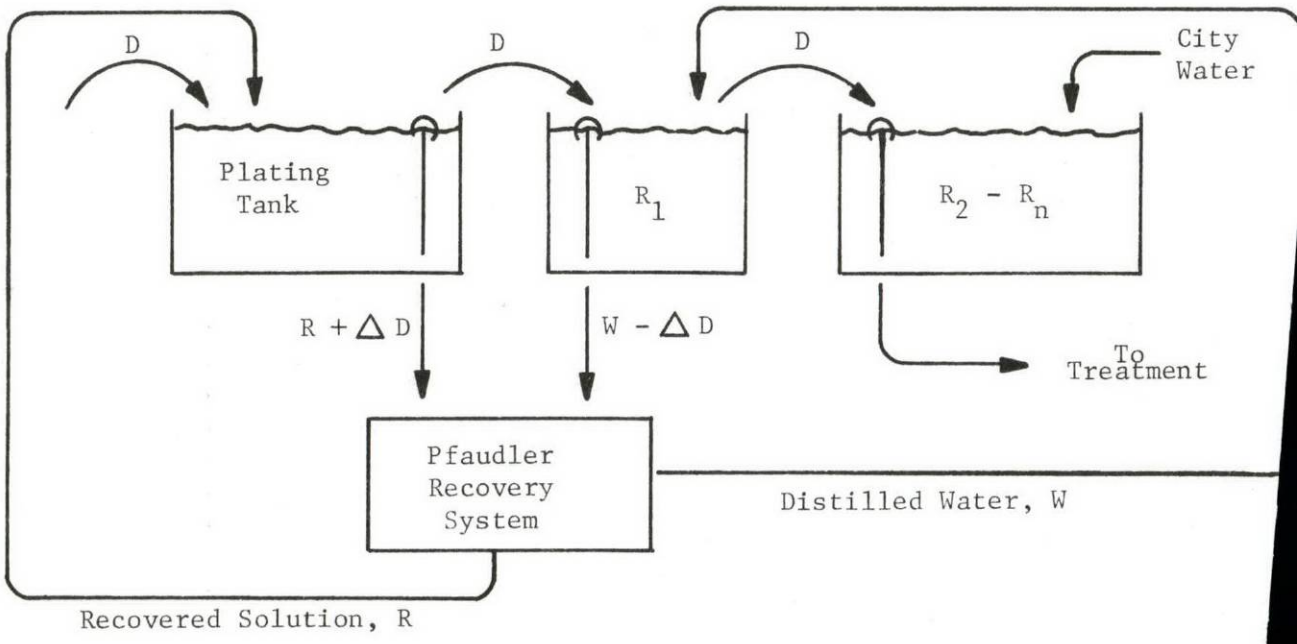

Fig. 4 Potassium Zinc Chloride Recovery System

Briefly, distilled water, W, produced by the recovery system is returned to the first rinse tank. It overflows by gravity at the same rate, W, less the difference between dragin and dragout, ΔD. The plating tank also overflows by gravity at a rate, R, plus the difference between dragin and dragout, ΔD. The volume balance around the recovery system is:

$$\underline{\text{IN}} \qquad\qquad \underline{\text{OUT}}$$

$$(R+\Delta D) + (W-\Delta D) = R + W$$

Thus, the volumes balance and there is no gain or loss. The next consideration is the chemical material balance. This is best illustrated by assigning values to the concentrations and volumes. The aqueous dragout will be 10 gallons per hour (gph) and the bath solution dragout will be 9 gph. The concentration of the bath will be 30 ounces per gallon of potassium chloride. The distilled water flow rate, W, will be 100 gph and the recovered solution recirculation rate, R, will be 100 gph. A material balance around the recovery system is stated by the following equation. (The concentration in the various tanks is designated by C and a subscript.)

$$\underline{\text{IN}} \qquad\qquad\qquad\qquad \underline{\text{OUT}}$$

$$(W-\Delta D)C_1 + (R+\Delta D)\,C_B = RC_R + WC_W$$

C_W = 0

W = 100 gph

R = 100 gph

C_1 = 2.5 ounces/gallon

Substituting .....

$$(100 - 1)\ (2.5) + (100 + 1)\ 30 = 100\ C_R + W(0)$$

$$247.5 + 3030 = 100\ C_R$$

$$C_R = 32.77 \text{ oz./gal.}$$

At first glance it appears that the recovery system is over-concentrating the recovered solution because its concentration is 32.77 oz/gal. versus a bath concentration of 30 oz/gal. This is not the case because when this stream is combined with the dragin of 10 gph, the concentration of the resulting solution will be 29.78 oz/gal. A slight decrease in concentration is expected because the recovery system is not operating as a closed loop and recovering all of the dragout. Instead, it is operating around the first rinse and recovering the major percentage of dragout as described by the following calculation:

$$\% \text{ Recovery} = \frac{D_B\ C_B - DC_1}{D_B\ C_B} \times 100 = \frac{9(30) - 10\ (2.5)}{9\ (30)} \times 100 = 90.7\%$$

It is certainly possible to recover from all of the rinse tanks (i.e. closed loop), and the amount recovered will be 100%. In this instance the concentration of the bath would be maintained at 30 oz/gal.

Another problem peculiar to potassium zinc chloride solutions is the "oiling out" of the organic additive. This is an organic liquid compound which is temperature sensitive and comes out of solution at relatively low temperatures. Even though the recovery system can operate at temperatures below 110°F, "oiling out" still occurs. Fortunately, this is not an irreversible process and a portion of the organic additive does back into solution. The remaining portion floats on top of the plating solution and can be skimmed off periodically. Thus, the usage this chemical may increase after the installation of a recovery system. Its concentration in the plating solution is small and, thus, it has a small effect on the overall economics.

Many platers are apprehensive about utilizing a recovery system for potassium zinc chloride solution because it is a highly wetted solution

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and produces copious quantities of foam when mechanically agitated. The foaming property does not appear to interfere with the operation of a properly designed recovery system or cause carryover which will contaminate the distilled water produced by the system. This potential problem may be held in abeyance due to the lack of air in a recovery system which operates at almost 28-1/2" of mercury vacuum.

Potassium zinc chloride baths do not have the carbonate impurity problem encountered with cyanide solutions, but there are other impurities to be considered. Iron is the most troublesome impurity which must be continually purged from the bath. It is recommended that the concentration of iron be maintained below 200 ppm although in some cases a lower level may be desirable. The use of a recovery system will call for an increase in the frequency of removing iron because the dragout can no longer function as a purge. The iron may be oxidized from the ferrous state to the relatively insoluble ferric state by an oxidant such as hydrogen peroxide. The iron is removed from the bath by filtration.

A case history of a recovery system used for potassium zinc chloride will now be presented. Modern Plating Corp. at Freeport, Ill. is a large job shop plater specializing in plating a variety of items with zinc, nickel, and chrome. They have multiple automatic lines for plating zinc. Operation of a waste treatment system including a two-stage cyanide destructive system for several years has made them painfully aware of treatment costs. They opted to substitute potassium zinc chloride for zinc cyanide because of these costs. The potassium zinc chloride solution also offered other benefits including a) increased versatility for carbonitrided parts; b) no hydrogen embrittlement; c) a 98% efficient bath which meant 50% less electrical power.

Modern Plating switched to the potassium zinc chloride solution for their Udylite VIP Barrel Plater which can plate up to 24 barrels per hour. The plating tank holds 3000 gallons of solution which is maintained at 80-90° by cooling coils. The sequence following plating is:

rinse
rinse
rinse
dil. nitric
either clear chromate or dichromate
rinse
rinse
hot water rinse

Management selected for use, the Kenlevel II solution which was described earlier in this presentation.

Modern Plating maintained a record of chemical additions to the bath during a 23 day period in August, 1977 prior to the installation of the evaporative recovery system. The following data was provided by Mr. Paul Massion, Vice President, Modern Plating.

Average Daily Chemical Additions Before Recovery

Chemical	Amount	Equiv. Bath Volume
Potassium chloride	470 lbs.	250 gal.
Boric acid	73 lbs.	259 gal.
Levlr-TB	7.8 gal.	249 gal.
Levlr-TM	1 gal.	946 gal.
Zinc chloride	3.5 gal.	33 gal.

Based on the recommended concentration of these components in the bath, the equivalent volumes of plating solution in gallons were calculated as shown in the above table.

Three of the components indicate the volumetric losses from the bath were approximately 250 gal/day. The consumption of additive Tm was determined by the bath's ampere-hours and was higher than the amount lost to dragout.

Modern Plating reported they had to remove approximately 25 gallons/day of excess solution from the plating tank prior to recovery because the dragout was appreciably less than the total of dragin plus humidification losses. Subtracting this volume, the dragout rate was calculated to be 11.5 gallons per hour (gph) based on an average operating time of 19.5 hours/day. This figure seems reasonable due to its approximation of a dragout rate of almost 1/2 gallon per barrel of plated work.

Early in 1978 Modern Plating installed a Pfaudler evaporative recovery system for their potassium zinc chloride plating operation.

The system was initially installed to operate in an open loop manner around the first rinse tank only. City water was introduced to the second and third rinse tanks which overflow to their waste treatment facility.

The recovery system operated at the following conditions:

Evaporating temperature	99° F
Evaporating vacuum	29.2 inches mercury
Steam pressure	12 psig
Cooling water	In @ 40° F, out @ 75° F
Distillate rate	80 gph

A record of chemical additions to the bath was kept for 21 days in March, 1978 after the recovery system had been installed. The following were the average daily consumption figures:

Average Daily Chemical Additions

Chemical	Before Recovery	After Recovery	% Reduction
Potassium chloride	470 lbs.	175 lbs.	63
Boric acid	73 lbs.	14.6 lbs.	80
Levlr-TB	7.8 gal.	2.8 gal.	64
Levlr-TM	1 gal.	1.86 gal.	+86
Zinc chloride	3.5 gal.	0	100

The before and after addition figures aren't exactly comparable because after the installation of the recovery system the thickness of the zinc plate was increased and the production rate was also increased. This would increase the dragout rate and make the actual savings greater than shown.

All of the chemical additions declined substantially except for component Tm which actually increased in consumption by 86%. Although this chemical costs more than $14 per gallon, it has a relatively low concentration of 1/2 fluid ounch per gallon in the bath. It accounts for less than 5% of the value of a gallon of plating solution and thus has an insignificant impact on the economics of recovery.

The economics of recovery for Modern Plating were as follows:

Value of solution recovered (A)

160 gal/day @ $1.70/gal. x 300 days/yr = $81,600

Operating costs (B)

Steam 730 lbs/hr x $4.00/1000 lbs x 5850 hrs/yr	$17,082
Electricity 8 kw x $0.03/kw x 5850 hrs/yr	1,404
Cooling water 39 gpm x 60 x $0.10/1000 gal. x 5850 hrs/yr	1,369
Operating labor and maintenance 600 hrs/yr @ $10/hr	6,000
	$25,855

Net annual savings (A) - (B) = $55,745

This figure does not include the savings in waste treatment costs and sludge disposal avoided by recovery. Even without the additional savings, the recovery system's cost was recovered in the first year. Today's cost for a comparable recovery system can be estimated by referring to figure 5 and using a dragout rate of 11.5 gph. Costs of recovery systems for other dragout rates can also be estimated.

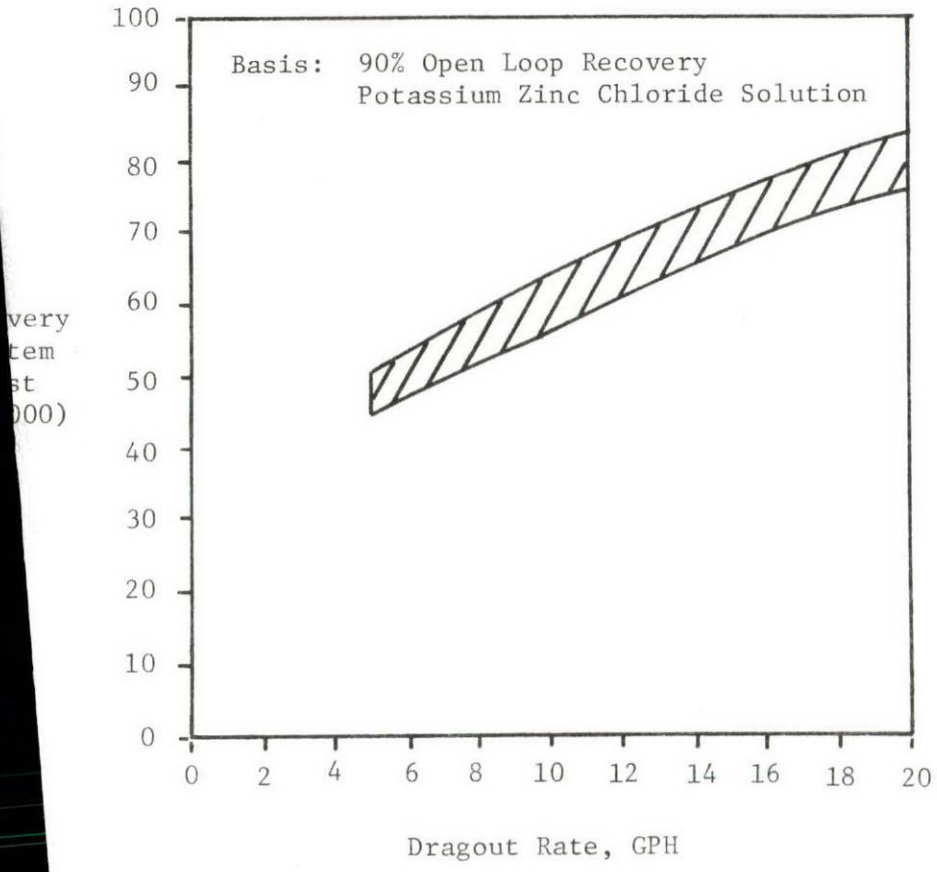

Fig. 5 Cost of Recovery System vs. Dragout

The economics for recovery of potassium zinc chloride solution can be estimated by using figure 6 to determine annual savings.

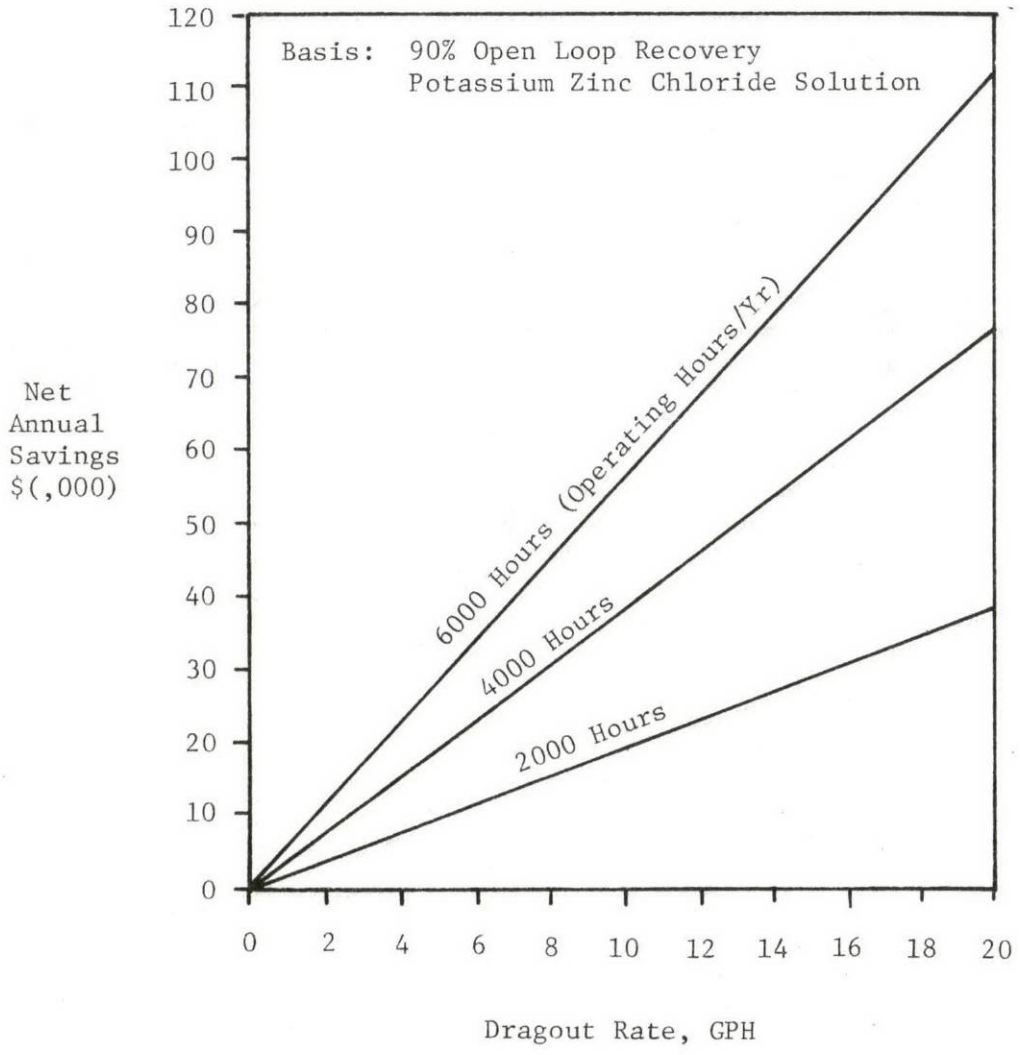

Fig. 6 Economics of Recovery for Potassium Zinc Chloride Solution

In summary, stringent effluent limitations for cyanide are causing many platers to switch to non-cyanide plating solutions such as potassium zinc chloride. The substitution of potassium zinc chloride for zinc cyanide plating solutions can minimize and in some cases eliminate the presence of cyanide in a plant's effluent. Potassium zinc chloride solutions offer other distinct advantages such as brighter plate, elimination of hydrogen embrittlement, ability to plate carbonitrided parts and simplified treatment of waste discharges. These advantages are gained at the expense of costlier plating equipment, more fastidious pre-plate requirements, and possibly troublesome post-plate chromating.

Another important consideration when selecting a plating solution is whether it can be recovered and recycled to the plating tank. Stringent effluent limitations require treatment of toxic chemicals and precipitation of heavy metals. These requirements enhance the economics of recovery.

The value of the potassium zinc chloride solution makes it economically attractive for recovery. A recovery system has been developed and proven in the field for the recovery of potassium zinc chloride. Obstacles to recovery including the usual increase in the plating tank's volume have been successfully overcome.

Q-3

Environmental I
Session Q

The Application of Centralized Industrial Waste Treatment in the U. S.

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Introduction

Centralized treatment and disposal of industrial wastes is not a new concept. The U. S. Environmental Protection Agency is supporting centralized treatment to:

1. Encourage use of regional solutions to metal finishing waste disposal where conditions are conducive.

2. Formalize the methodology necessary to identify safe sites so that industrial wastes do not become "hazardous wastes".

3. Consider use of this approach for other industries made of small companies.

4. Develop technologies applicable to centralized treatment and proper and safe waste management.

5. Enlist assistance of Chambers of Commerce and other trade organizations to support centralized treatment alternatives.

6. Establish compliance schedules on area basis to facilitate group solutions.

The metal finishing industry utilizes more than 100 surface finishing and fabricating operations which require aqueous application and removal of various metals to and from metal and plastic parts. Contained in metal finishing process baths are various cyanides and cyanide complexes, hexavalent chrome, nickel, zinc, cadmium and other metals which must be disposed of once the useful life of the bath has been reached. In addition, rinse waters are generated which contain dilute concentrations of these metals resulting from washing the plated parts during a particular unit operation.

A vast majority of electroplating shops reside in large industrial communities in and around municipalities. Eighty percent of the plants in the electroplating industry discharge to municipal sewers untreated or lightly treated rinse water and plating baths for treatment by the POTW. These pollutants, discharged to POTW's in over one billion gallons of process water per day, are nonbiodegradable, and hence, are ineffectively treated by such systems. Cadmium, chromium, lead, nickel and zinc are not destroyed when introduced into a POTW and will either pass through the POTW or contaminate the sewage sludge. The metal finishing process wastewater pollutants interfere with proper operation of biological systems and restrict the utilization of biological sludges because of their high metal content. This metal content may preclude land application of sewage sludge on food crops; questions also arise regarding sewage sludge disposal by incineration due to the volatility of cadmium and lead.

Institutional Constraints Affecting Centralized Waste Treatment Facilities

Centralized treatment is not a new concept; however, it has not gained complete private and public acceptance in those regions where it is applicable. In order to further quantify the attitudes of municipal and regional officials, the U. S. Environmental Protectio Agency funded a study to determine what the attitudes were regarding centralized treatment. This survey of 22 cities investigated the disposition of metal finishing wastes, the attitudes of these city's officials with regard to assumption of waste disposal by the municipal and the feasibility of centralized treatment of metal finishing wastes

The survey showed that many of these municipalities (11 of the 22 completed the response) had more than 50 metal finishing operation in their jurisdiction. Thirty-six percent of the 11 respondees indic that less than 20% of these plants had pretreatment technology instal Further, 55% of the 11 respondees said that less than 20% of the equipment installed will meet the proposed pretreatment regulations. The survey showed that, even though more restrictive regulations were increasing the quantities of sludge being generated in the areas, there was a general lack of facilities for disposing of these wastes While the municipalities in general felt that the platers and metal finishers in their vicinity would be interested in utility service, they did not feel that their governing body would permit such a syst (even if financed entirely by user chargers) nor that municipal ownership and operation of such a program would lessen the difficul in obtaining a sludge disposal site. Further institutional constra were sited as jurisdictional disputes, and government/industry cooperation.

The conclusions of the study were 1) there is a widespread interest and a general need for a utility type centralized treatme service in order to encourage proper waste management in large metropolitan areas, 2) there is a wide spread need for environment sound disposal sites for both waste sludges and waste processing solutions that has not been met by private industry and 3) the major concern is that jurisdictional disputes, siting of facilitie and location of a sludge disposal site will preclude centralized waste treatment in many areas.

Since the municipal survey contained some anomalies and identified reservations among the municipalities contacted, a tho program is necessary to determine the feasibility of centralized treatment. While the underlying basis and factors affecting thi feasibility might be different for many communities, the basic methodology for site-specific evaluation should be developed tha could be applied to other communities.

Group Treatment at Taunton, Mass.

The requirements for industrial pretreatment in Taunton, Mass. limited the entrance of metals into municipal treatment facilities. Here opportunities for grouping waste streams from several similar companies for combined treatment existed. This project considered three companies from the metal-related field as possible candidates for CWT. The intent was to determine the potential for cost savings with group treatment and to develop the legal and institutional arrangements necessary for successful implementation and operation.

The project was an outgrowth of a Section 208 (PL 92-500) areawide wastewater management plan under development by the Southeastern Regional Planning and Economic Development District (SRPEDD) of Massachusetts as an alternative approach to meeting pretreatment requirements.

The results of the technical evaluation of centralized waste treatment indicated that:

1. Group treatment of process wastewater is feasible for batch discharges.

2. Group treatment of rinses is practical only when companies are close enough to render collection costs insignificant.

3. Wastes suitable for group treatment must be selected by type.

The economic benefits of CWT show that:

1. Significant cost reductions can be realized by greater utilization of batch treatment equipment through multicompany use than by individual company use.

2. Reduction in operating expenses for group treatment facilities can result from salvage of metal values. For this particular study silver was that predominant metal to be reclaimed. If there are increased amounts of raw waste, copper and nickel recovery will become attractive.

3. Group treatment at another location will prove most interesting to the company that is limited in space or personnel and/or is small in size. The prospects for other companies to join, therefore, are enhanced.

4. Group treatment at its site will prove most attractive to the company that has available space and personnel.

The study showed that control of potentially toxic metal finishing wastes is enhanced by centralized waste treatment and that:

1. Group treatment will provide a higher quality of discharge by use of more appropriate technologies, higher qualified personnel and better methods of operation.

2. Optimization of individual plants to evaluate wastes for group treatment can suggest the most appropriate disposal site to match the particular characteristics of waste.

3. Group approaches encourage maximum water conservation techniq and material recovery options in order to minimize transporta costs of materials being treated.

4. Group approaches can present a single solution/site for residual materials disposal rather than a multiplicity of solutions and sites.

5. Group approaches can decrease the number of monitoring point for regulatory agencies.

Institutional issues confronting centralized waste treatment identified at Taunton were:

1. Group arrangements for waste handling and disposal are feas for companies willing to accept responsibility and work tog

2. Financing alternatives will require at least one company w ability to borrow necessary funds.

3. Role of pollution control bonding for group treatment may depend upon IRS acceptance of material recovery for tax exemption within project.

At the conclusion of the final report, the companies believed that group treatment was a technical and institutional arrangement merit.

The three companies, however, did not initiate a CWT facilit One company had committed to most of its batch waste treatment facilities by this time as it had been on an earlier compliance s A second company elected to merge its metal finishing operations another firm within the parent company. The third company, howev has provided its own batch treatment facility using design concep that would permit it to expand capacity on a contract basis, if This may very well be the beginning of a centralized waste treat facility, itself.

Centralized Waste Treatment at Onondaga County, NY

Onondaga County New York State Department of Drainage and Sanitation proposed to demonstrate that a municipality could provide a utility type service to metal platers and finishers in their service area. This service would be structured so that:

a) The municipality would purchase ion exchange units and resins which are specific for certain metals and lease the units to local metal finishers and platers for use in treating rinse waters.

b) The municipality would service these ion exchange units on a regular basis by collecting the resin cartridges for central regeneration and deliver fresh resin cartridges.

c) The municipality would collect spent plating solutions from the local industries for resource recovery where feasible. Treatment would otherwise be provided on a user charge basis.

d) The municipality would collect waste metallic sludges from other industries with treatment and/or pretreatment facilities in operation, dewater them if necessary and dispose of them in Solvay process and acetylene by-product waste beds.

e) The municipality would own and operate both a resource recovery facility and a secure landfill for processing and disposal of metal laden sludges.

The Onondaga County proposed two interesting aspects:

1) Municipal ownership and financing of this system and associated equipment and facilities.

2) The use of abandoned soda-ash and acetylene plant wastebeds as high alkaline environment for sound repository of residual sludges.

The proposal, based on a preliminary study, contended that similar ources of waste alkaline sludges were available in other parts of the nited States, existing at plants manufacturing acetylene as well as at lants which presently or formerly manufactured soda-ash using the Solvay rocess. The United States Environmental Protection Agency subsequently unded a survey to determine both the quantities and locations of such lkaline sludge deposits and the attitude of selected municipal officials ward the assumption of the type of responsibilities proposed by Onondaga unty. This study was mentioned, in part, earlier in this paper.

Industrial Waste Treatment in Palo Alto

In 1964, the city of Palo Alto initiated a chemical industrial was ordinance to prevent the introduction of incompatible materials (cyanid chromium, copper, etc.) to the newly constructed wastewater treatment f Instead of joint treatment of municipal and industrial wastes, the city proposed and built an industrial waste treatment facility that provided for batch neutralization of acids and bases and other chemical/physica treatments for remaining industrial wastes. These wastes were to be h at the point of generation (the plant site) and hauled to the industri waste treatment facility in tank trucks. The design of this plant was on the survey of the types of industrial waste that had been discharg and caused problems with the existing treatment facility.

The region that Palo Alto is located in has a very strong electr community which utilizes acid and alkaline cleaning, electropolishing electrocleaning and electroplating. The industrial waste survey that was initiated in 1964 indicated that, while many of the companies had attempted to properly manage their waste problems, it was expensive a difficult to treat the small amounts of waste that were being generat and simultaneously achieve good removal efficiences. These companie surveyed and a large percentage indicated that the proposed municipa would be welcome, depending, of course, upon the frequency of servic and its costs.

The facilities that were constructed would comingle acid and a wastes to neutralize them and the sludge would be concentrated and as a solid waste. The overflow of the neutralization operation wou be fed slowly to the biological treatment facility. Reduction of h chrome wastes would be completed separately prior to neutralizatio lime or alkaline wastes. Chlorine would be used to oxidize cyanid subsequent destruction by carbon dioxide followed by neutralizatio precipitation of heavy metals.

The city installed and built this industrial waste treatment however, without effective federal pretreatment and solid waste di regulations, the facility was never utilized. It was more economi haul the wastes to a landfill and dump them without any treatment Currently, with these regulations being promulgated, the plant pr and built by Palo Alto 11 years ago would conceivably have some u that the regulations prohibit landfill of some of these wastes ar economics favor centralized treatment over on-site treatment and

Generation and Disposal of Industrial Residues in Allegheny County

The Allegheny County Department of Works, assisted by partial funding from the U. S. Environmental Protection Agency, completed a study of the current nature and trends of industrial waste generation and disposal in this region. The goals of this study were: 1) to identify and classify all industrial wastes produced in the county, 2) to estimate the current generation rate of these residues as well as trends anticipated in the future, 3) to estimate the alternative methods and their associated costs for collection, transportation, treatment where necessary, and disposal of identified industrial wastes, 4) to examine alternatives for administrating, financing, and developing a working industrial waste management system in the county which meets current, pending, and anticipated regulatory requirements for each industry. The importance of industry to economic growth in this area mandated that cost effective means of meeting applicable Federal Water Pollution Control Act, Toxic Substances Control Act, and Resource Conservation Recovery Act requirements be developed. In addition, the secondary effects of waste water treatment (sludge) and air pollution control (dusts, sludges, and slurries) for iron and steel production and ancillary metal finishing and fabricating facilities, (foundries, smelters, etc.) were to be addressed. This portion of the study primarily defined the quantities and characteristics of wastes generated in this area.

The Allegheny County Department of Planning and Development is developing a program to manage and dispose of the industrial wastes identified in its county. It is anticipated that this phase will make recommendations on: 1) handling, treatment and disposal procedures, 2) transportation schemes for transporting wastes to treatment and disposal facilities, 3) facilities and their associated O&M costs for the waste management program, 4) the administrative procedures, user chargers and a preliminary engineering design.

Resource recovery aspects at centralized processing disposal facilities will be considered in this phase. However, a more detailed study of the region and the institutional constraints of siting these facilities is necessary.

Centralized Treatment Considerations in Ventura, California

The Ventura Regional County Sanitation District, in anticipation of pretreatment and solid waste disposal requirements, surveyed local industries to determine the industrial residuals generated in this region. The study showed that food industry wastes, chemical wastes (organic chemical, pesticide, fertilizer, paper, and metal finishing wastes), as well as some petroleum wastes could be disposed of at a centralized facility. The approach conceptualized by this district was to design and construct a centralized facility to truck industrial wastes for treatment. These wastes were to be segregated into compatible classes in order to minimize further generation of wastes and reduce consumption of energy and treatment chemicals, and to maximize current or future reclamation of stockpiled treated wastes.

The program was divided into three phases. The first phase was the feasibility study as preliminary planning to identify treatment processes required by the District in order to treat the industrial community's wastes. The second phase was to include the design and construction of the various centralized treatment and disposal faciliti that would be recommended under Phase 1. The third phase would be to evaluate performance and operation of the facility and the institution factors which impede and promote the utilization of centralized treatme of industrial wastes.

The first phase of the study was partially funded by the U.S. Environmental Protection Agency and partially by the Ventura County Sanitation District. Proposition 13 precluded pursuit of the program beyond the first phase. It was concluded, however, that centralized treatment was a viable alternative to on-site treatment of industrial wastes as proper management of wastes was insured, and the economic condition of the region would not be drastically affected by complian with pretreatment and solid waste regulations.

Centralized Treatment in the Federal Republic of Germany

In 1964, the administrative agency responsible for the water resources of the catchment basin of the Ruhr River (the Ruhrverband) instituted a program to provide treatment for hazardous industrial wastes at a facility located adjacent to the municipal waste treatment works in Iserlohn, Germany. At the same time, a strong effort was instituted to gain control of the disposal of all hazardo industrial wastes being generated in the region. This was accompli by the encouragement of a waste exchange system, strong efforts to provide an acceptable disposal mechanism for any type of industrial waste, and initiation of pretreatment regulations with the ultimate goal of barring incompatible wastes from municipal treatment syste

The initial centralized system provided for:

- o Cyanide destruction
- o Hexavalent chromium reduction
- o Neutralization
- o Clarification
- o Sludge concentration

The treatment options were combined with the establishment segregated area for the disposal of hydroxide sludges, kept sepa for potential future recovery. The waste generating plant store wastes until it was economical to ship them. Funding for plant construction was obtained from local industries, the municipalit and a loan from the federal government which was subsequently re It was managed by a Board of Directors consisting of industrial

governmental representatives. Since that time, the number of both private and public facilities to treat concentrated industrial wastes has increased to the point where all industrial wastes can be sent to facilities specially designed for their treatment or recovery. Facilities are now available for treatment or recovery of:

- o Spent electroplating baths and ion-exchange regenerates
- o Chlorinated solvents
- o Other organic solvents
- o Spent sulfuric pickle liquor (recovery of acid and sale of iron oxide)
- o Spent hydrochloric acid pickle liquor
- o Oil-water emulsions
- o Dilute sludges (concentration and disposal)
- o Concentrated sludges (segregated landfill)

A regular waste pickup service is maintained, similar to that used for municipal garbage. All treated effluents from both private and public industrial waste facilities are sent to a municipal treatment system.

The prices for the industrial treatment service are such that all systems are self-sustaining; in the case of private facilities, they provide a profit. Normal economic forces have forced large facilities (such as chemical plants) to provide their own treatment while smaller facilities use centralized treatment. The treatment technology used at these facilities is similar to that utilized in the United States.

escription of ZEA Iserlohn Plant

Waste acid and waste alkaline containing cyanide are transported Iserlohn in color-coded containers. The contents from small ntainers are stored in 30-cubic-meter tanks. No distinction is made tween alkaline waste containing cyanide and those free of cyanide all are treated for cyanide. Certain pickle liquors and baths ntaining nickel and copper are kept separate because the nickel d copper are sold to a nearby recovery plant which, through ectrodeposition, recovers the metal. Pickle liquors are transferred municipal plants for use as flocculating agents, when possible.

Acid wastes are stored in 30-cubic-meter tanks until a fficient amount is accumulated. The chromate-containing acids to a reaction vessel where ferrous chloride is added as a reducing nt. The effluent from the acid neutralization, chromate reduction,

and cyanide destruction go to a further reaction vessel where lime is added for final pH control. From the neutralization vessel, the effluent travels to what was intended to be a clarifier. The mid-level discharge from the vessel goes to one of three rectangular clarifiers, which are arranged to be operated in parallel but which currently operate individually. A breakthrough of material in one of these clarifiers thus can be valved off as one is normally kept empty. The overflow from the clarifiers is pumped to the municipal treatment system. The sludge overflow at about 2 to 3 percent solids, passes to a filter press where it is dewatered to about 35 to 45 percent. The dewatered sludge then goes to a segregated landfill (to be described).

Waste storage vessels are color coded: red or orange indicate ac blue indicates alkaline. The acid containers come in sizes up to one meter but for larger volumes, tank trucks are used. Since the plant accept concentrated plating baths, no plating baths are discharged to the sewer. The plant also will accept neutralized and detoxified pla baths and rinsewaters if sufficiently concentrated. Neutralized wast are directed to the clarifiers. The final pH was generally kept betw 9 and 10 though pH is not monitored as closely as is common in the U. there is no continuous pH recorder.

It is reasonably neat and well kept, and does not have a signif amount of automation. The only major control is ORP for the cyanide destruction.

An ancillary goal of the centralized waste treatment plant is t collect small amounts of waste that might have value elsewhere if available in sufficient quantity. Although this function occurs th private agreement, no significant amount of exchange takes place at site except in the case of nickel-copper solution. Therefore, the exchange of waste at the plant is not really an extensive portion o throughput.

Chemical waste exchanges are accomplished through a series of newsletters that list wastes for sale. These are published weekly the German Chamber of Commerce. Initially, this list was quite ex but sufficient contacts had been made so that only a relatively fe wastes need be marketed.

An important facet of the centralized treatment concept are hydroxide sludge landfills. The district has established a sludg disposal site for handling hydroxide sludges from any type of met plant. This facility accepts dewatered sludges only, and single- sludges are kept separate for possible future recovery. The slud are deposited in a specially designed landfill probably equivale U.S. Class I landfill. Any leachate or runoff drains to the bot the area and is returned to the treatment plant by gravity. Cur

recycling of these sludges is not extensive, although such sludges are available free and occasionally, a manufacturer having need for a certain type of metal will take a small amount of the sludges.

In summary, it can be said that the Iserlohn plant does not utilize any new technology. It is the application of existing technology in an insightful manner to solving the waste problems of electroplaters in the Essen area.

A Preliminary Analysis of the Applicability of CWT to the United States

Of greater interest is the application of CWT in the United States, taking into account U.S. costs and environmental requirements. One of the striking assets of centralized treatment in any industrial region is the large number of possible configurations

When evaluating centralized treatment from an economic viewpoint, balancing the decreased capital and plant operating costs resulting from the economics of scale against the transportation costs for delivering the wastes to the centralized treatment plant is necessary. To evaluate the feasibility of centralized waste treatment in a regional area, one must know:

1. The sources of industrial waste.

2. The characteristics of the waste being generated.

3. The technology currently installed in the generating facilities.

4. Special factors that would affect the ability of the manufacturer to become involved in centralized waste treatment.

5. The pretreatment requirements.

A thorough examination of the economics requires a specific study for the local situation. Major savings in capital costs occur with as few as 5 to 10 plants participating; and the bulk of the capital savings are realized with 25 plants participating. This is the basic effect of size on capital costs. This type of capital savings in scale-up is well known and does not depend on any significant assumptions.

The Metals and Inorganic Chemicals Branch Program on CWT of Metal Finishing Wastes

The Metals and Inorganic Chemicals Branch is developing the procedures to determine, on a case-by-case basis, the feasibility of centralized treatment facilities (CTF) for metal finishing wastes. This plan addresses the usage of the CTF for disposal and management of the following metal finishing wastes:

- o Concentrated, metal bearing wastewaters including those containing CN and chrome.

- o Metal bearing sludges resulting from application of on-site pretreatment technology.

- o Metal bearing sludges resulting from application of on-site direct discharge treatment technology.

As currently proposed, this detailed plan provides for:

- o Assessment of prior work on centralized treatment.

- o Screening feasibility studies for 5 regions, describing the factors affecting siting and the approach used for choosing those sites.

- o A detailed study of one region resulting in a comprehensiv design of the collection and disposal system.

- o A retrospective analytical evaluation of the siting proced

Future programs will consider:

- o A demonstration of the system designed.

The primary output from the first two phases will be the case s and the protocol for evaluating potential sites and a "blueprint" fo struction of a CTF at a particular site. Detailed activities for ea these four phases is contained in available materials.

This program will:

- o Provide EPA and U. S. industry with a cost effective app to remedy impacts to industry derived from complying wi pretreatment regulations and sludge disposal regulation both industrial pretreaters and direct dischargers.

- o Use municipal or regional governments, as a point of co with local industries, for technology and associated co information that will enable industry to economically meet regulations.

- o Utilize personnel dedicated to CTF operation to operat CTF's to ensure the long-term control of industrial wa water discharges and ultimate safe disposal of sludges

- o Provide, through scale of economy, economical treatme metal finishing wastes without hampering potential re recovery of industrial residues, such as recovery of strategic metals from metal finishing wastewaters and

- o Promote segregated disposal of metal finishing sludges.

- o Provide an effective solution to industrial waste disposal in many regions throughout the United States, and reduce impacts associated with conscientious waste disposal.

Though the proposed program specifically focuses on the metal finishing industry, a widespread, complex industry for which impacts from pretreatment and RCRA regulation implementation are anticipated to be extreme, it will contain latitude to include other industrial categories into subsequent analysis.

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Q-4

Environmental I
Session Q

Operating a Regional Waste Management And Land Reclamation Center

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PERATING A REGIONAL WASTE MANAGEMENT AND LAND RECLAMATION CENTER

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ABSTRACT

nvironmentally acceptable methods for ultimate disposition of oxic and hazardous wastes is becoming an area of increasing tudy and concern for U.S. industry. A process technology to nswer this need has been in commercial operation for over ve years in the United Kindgom and through its application, azardous wastes have been converted to a rock-like material at is structurally sound and environmentally compatible and eful for land reclamation. Information shall be presented ncerning operating experience and process economics associated th the technology.

BACKGROUND

Raw materials necessary to produce an inert rock-like land reclamation material can be found in several areas as a result of industrial activity. These raw materials are produced by various industries as waste by-products of their operations. Most of these, some of which are potentially toxic or hazardous, are often disposed of indiscriminately and in an environmentally unacceptable manner.

In the early 1970's, researchers and engineers working at an environmental control laboratory, discovered and developed what is now a patented process that converts many of these by-product wastes to useful land reclamation-type material that exhibits exceptionally good environmental compatability and structural integrity. The process, through which the synthetic rock material is manufactured, relies on a crystal capture mechanism wherein waste by-product raw material forms chemical bonds with additives creating a polymer-like matrix characteristic of a rock-like substance.

The first Process Plant and Land Reclamation Area was the English Midlands. The Plant, started up in late 1974, had a 50,000 ton per year capacity and was designed to accept waste feed stocks from the automotive, metal finishing, plating, and chemical industry within that geographical region. Utilizing patented technology, the facility has successfully treated several hundred thousand tons of material and is close to completing its first land reclamation area.

Local and regional governments, as a result of the public hearing process, approved of additional facilities located adjacent to the first site in 1977, and the second facility was erected. Its annual capacity is 100,000 tons per shift-year. Total plant capacity for the Midlands of England is well in excess of 200,000 tons per year.

A third Waste Management and Land Reclamation Center serving the metropolitan London area was conceived in 1976. Several areas east of London were evaluated since many parts of that region contained abandoned chalk quarries that were not destined for land reclamation. These pits represented wasted space to the township. Township representatives recognized that clean fill was too expensive for land reclamation and recontouring was a poor answer to the problem. It was proposed that a facility be established serving that geographical area and patterned after the successful Midlands experience.

Because many of the abandoned chalk pits are overlying extremely permeable strata, the environmental consultants to the township recommended that the inert processed material be subjected to a series of leachate tests to be performed by an independent laboratory.

Based on the test results and with reconfirmation of a successful Midlands operation, the people and local council of West Thurrock (about 20 miles from London) approved the proposal to begin operation through construction of the largest and most modern plant ever constructed to convert waste and manufacture a land reclamation material.

This plant began operation in early 1978 and was formally opened by HRH The Prince of Wales in July 1978. Since the plant started-up, it has successfully passed through its facilities many different wastes characteristic of those produced in the London vicinity.

As the English based company's experience increased, it began to receive inquiries from companies associated with its British clients. Many of these companies were U.S. parents or subsidiaries of its customers. Company representatives followe these inquiries through a series of visits to the U.S. to deter the potential market. These exploratory visits culminated in a decision to establish a U.S. Corporation to pursue the creation of Regional Waste Management and Land Reclamation Centers.

REGIONAL PLANT DEVELOPMENT

A facility designed to treat various industrial wastes mu located in an area central to their source. This assures that costs associated with pollutant transport are minimized. It i important to site the facility such that it is located near or adjacent to an acceptable land reclamation area in which the converted, non-toxic material may be placed. This virtually eliminates charges associated with the transport of the final and these savings are passed on to the waste producing custom

Locating the facility near an area in need of restoratio allows the Waste Management Center Operator to perform a need service to the community in which the conversion facility is located. With the price of clean fill steadily increasing, i becoming difficult to provide economic fill material in most needing land reclamation.

The regional center must be located such that transport of materials to the facility does not have adverse impact on community. It is important to take every possible step to l a facility near a major interstate, state, or federal highwa and to provide access roads to the facility so they are as r possible to the service ramps of the highway. The number of vehicles entering the facility must be carefully controlled insure that needless traffic delays and tie-ups due to truc are no longer a factor. This helps reduce the transport im

The facility's aesthetic value must be considered. Un no circumstances should it be an eye sore. It should be de to blend in with the surrounding area so that it does not d from the land's natural beauty. If possible, it should enh the area's scenic attributes.

WASTE MANAGEMENT FACILITY OPERATION

There are several steps that must be followed for the successful operation of a Regional Waste Management and Land Reclamation Center. These steps illustrated in Figure 1 are:

Screening the Waste: Before agreeing to accept a manufacturers or processors waste materials for conversion to inert, synthetic rock at the facility, samples of the candidate wastes are subjected to chemical and physical analyses in a regional laboratory and a waste profile is prepared. Trial formulations are then carried out to determine if the waste can be converted in an acceptable fashion to an environmentally compatible final product. The resultant product is then subjected to one or more nationally recognized standard leachate tests. Only upon successful completion of the above procedures, is an agreement to accept the waste completed, delivery scheduled, and a price set.

Additionally, a hazard code is assigned to each waste so that the plant operators can handle the material properly on receipt.

Waste Reception: Wastes are received at the facility in tank trucks, dump trucks, and drum carriers. Wastes are only accepted from duly authorized carriers. On entering the facility, the transport vehicle passes over a weigh scale for determination of delivered waste quantity. A sample of waste is taken for immediate lab analysis to confirm the waste delivered corresponds to the initial waste profile prepared. The in-plant analysis is compared to previous data and if within an acceptable range, is accepted for treatment. A checklist is then prepared by the plant chemist which ensures that the material has been adequately tested to ensure compatibility with the process.

For bulk liquid deliveries, the truck is directed to an unloading point by the plant operator. The plant operator, having obtained a key, unlocks the proper valve necessary to off-load a tanker insuring the truck is coupled to the proper tank. After discharge, the operator will insure that the hose connecting the truck to the discharge point is emptied prior to disconnect. At that point the operator closes and locks the receiving valve to insure that no further material may be off-loaded without approval.

In the case of bulk solid delivery,vehicles are directed to specific off-loading solid bays where material is stored in covered areas.

A similar procedure is followed for drummed wastes. However, after the drums are moved to their storage area, the plant operator indelibly labels each drum with the following information:

.. Date received
.. Control form number
.. Type of material

The entire waste reception area is paved, curbed, and graded to contain any spilled waste. Run-off is directed to a drainage system which discharges to a central sump. Sumped material is introduced to the process to make certain no contaminants are discharged to the environment.

Waste Storage: Liquid wastes are stored in tanks fabricated with appropriate materials. Bulk solid wastes are stored in separate bins which are covered for protection from the elements. Waste received in drums are palletized and stored in a segregated section of the waste reception area.

Pretreatment: Appropriate quantities of compatible liquid waste material are blended in a battery of pre-treatment vessels. Certain materials either from bulk solid waste storage or drum storage are passed through a solids preparation operation to reduce the particle size of the material to the desired specification Following the size reduction operation, compatible solid waste materials are blended in a large pretreatment tank where appropriate quantities of additives are blended to prepare the mixture for the final product preparation phase. At this point, samples are taken from the pre-treatment facility and tests are run to determine if that batch has the required characteristics necessary to produ satisfactory final product.

Product Preparation: After the plant chemist performs tests to insure the quality of the final material prepare from the pretreatment batch is acceptable, the product preparation run begins. This consists of mixing a weighed quantity of pretreated materials with pre-weighe quantities of additives to produce the final product.

Product Placement: Following completion of the product preparation phase, the product is conveyed, usually by pipeline, to discharge in an adjacent land reclamation placement area. If pipeline placement is not possible, then truck transport is utilized. On setting, the fina product, which is a hard rock-like material with a co-efficient of permeability on the order of 10^{-7} centimet per second and with a compressive strength of 200 psi o more, is an excellent material for land reclamation pur poses. Water falling on the placed material tends to r off the surface and is directed to a sedimentation basi

where it is sampled prior to discharge to insure its environmental compatibility.

Environmental Characteristics: Despite the extremely low permeability of the Stablex synthetic rock, it is conceivable that a small proportion of the mass of product produced could be exposed to water with the passage of time. It is therefore important to assess the risk of water pollution in rigorous laboratory leaching tests. Among the tests that have been performed with the Stablex product are:

The Equilibrium Leachate Test, ELT: In this test, product samples are ground to a fine powder and immersed in ten times their weight of distilled water at a pH of 4.5 to 6. The particles are totally wetted for one hour in a magnetically stirred vessel. The leachate is then separated by filtration and analyzed by atomic absorption spectrophotometry, emmission spectroscopy, volumetric or colorometric methods. For pollution by organic components, standard tests such as the TOC analysis can be carried out on the filtrate. Constituents leached are reported in parts per million. Figures 1 through 5 display tests of unstabilized waste material and pulverized stabilized product. These tests were performed with a modified equilibrium test such that each of the samples was exposed to several days of contact with the leaching solution. For example, the first sample represents a 24-hour exposure, the second, third, and fourth samples represent 7, 14, and 28 days exposures. During each day of exposure, samples were mixed vigorously by a magnetic stirrer for one hour.

ASTM Procedure (Method D 19.12 Method A): This method is used for leach testing of raw waste and processed waste. Samples of material to be tested are immersed in four times their weight of distilled, deionized water. Continuous contact with gentle agitation is accomplished for 48 hours. Liquid is then decanted and filtered and analyzed. The test may be continued if desired by repeating the first steps. Data for a Zinc Phosphate Primer Waste before and after treatment are shown in Tables 6 and 7.

Japanese Standard Method Article 3, Cabinet Order 5, 1973 - Japan Environmental Protection Agency Notice No. 13: The sample is first ground to a powder 0.5 to 5 mm diameter and mixed with ten times its own weight of water at 20° C. The pH of the water is adjusted to 5.8 to 6.3 by the use of Hydrochloric Acid, Carbon Dioxide, Sodium Hydroxide, or Sodium Carbonate. When sea disposal is considered, the pH is adjusted to 7.8 to 8.3. The mixture is shaken for six hours, filtered through a Type 5C paper and the filtrate centrifuged at 5000 rpm for 20 minutes. Data for several wastes before and after conversion are shown in Tables 8 and 9.

On-Site Tests: Product material has been placed for years in a land reclamation area. To confirm the material's stability the local water authority extracted cores from the placement area and performed the following leachate test:

Four inch core samples were ground to a fine powder. 150 grams of core were placed in contact with 1500 ml of distilled water. The sample/water mixture was agitated for a few minutes each working day over a seven day period. A sample of the aqueous phase was then taken and analyzed. The same procedure was repeated for a further period of seven days after which time a second sample of the aqueous phase was taken and analyzed. The same procedure was repeated again for a five day period after which the mixture was stirred continuously for eight hours on each of two subsequent days. A third sample of the aqueous phase was then taken and analyzed.

In addition to the core tests, the local water authority also routinely takes samples of surface water which was in contact with the treated product and is collected and sampled prior to discharge to insure its quality. These tests have been done for the last five years and in no case was there any evidence of anything but satisfactory quality run-off.

Materials treated in commercially operating facilities include those listed in Table 10, and the leachate test results on extracted cores are shown in Table 11.

OTHER PROPERTIES

The land reclamation material also exhibits other important environmental properties including: non-biodegradability, non-flammability, odorless, and unattractive to pests and vermi

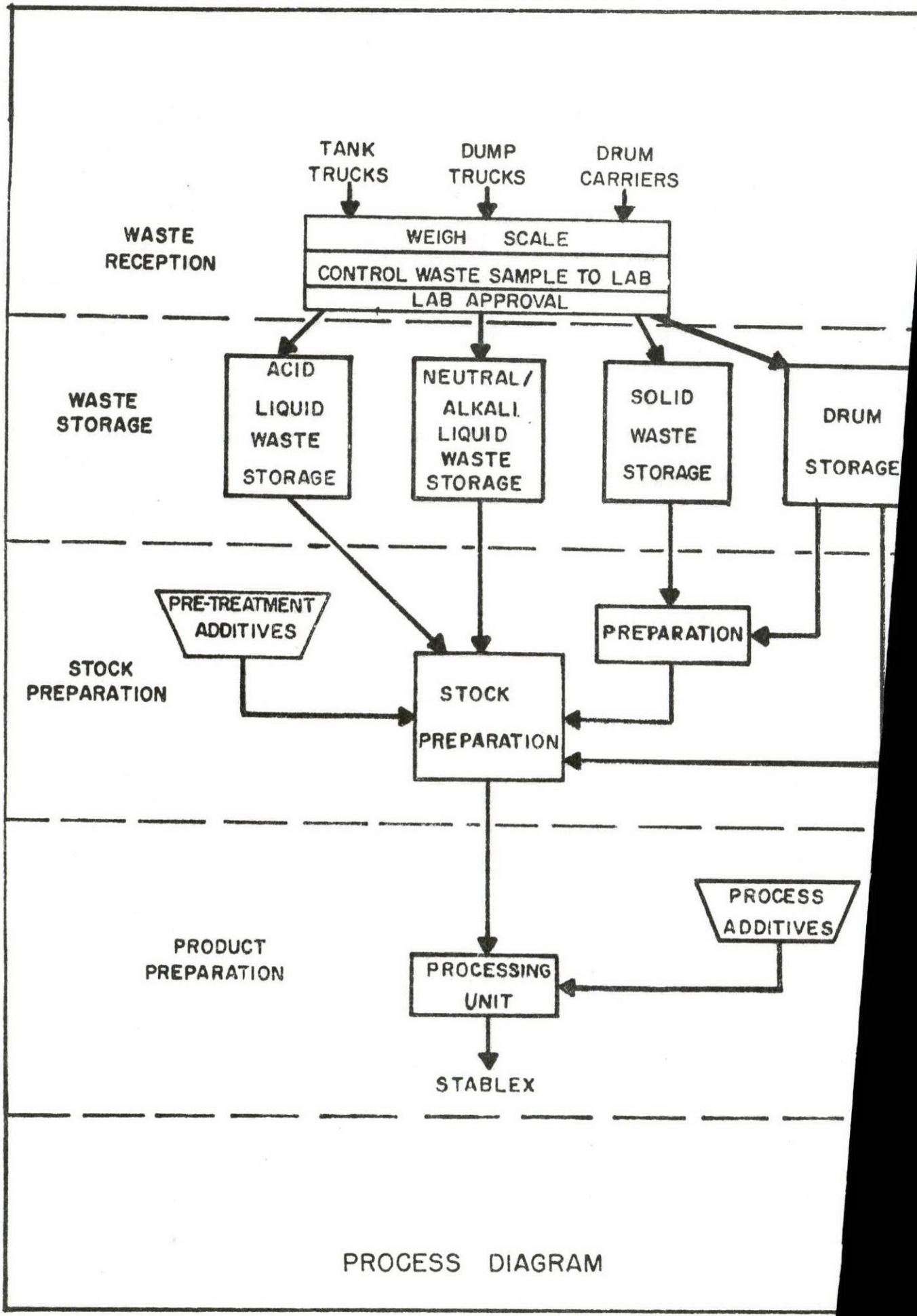
ECONOMICS

For the past five years, wastes from more than 2,000 different industrial sources have been successfully treated. S of these are shown in Table 10. The process is particularly successful in the disposal of arsenical, mercury, cyanide, and other noxious wastes. Environmental claims which were made an proved before launching the process in 1974, have been substan by many statutory authorities, and there has been no case of p tion or serious injury to personnel since its acceptance.

The cost of waste treatment by the process varies considerable according to the type and quantity of waste proc A typical Regional Treatment Plant costs several million

dollars, and may be capable of handling several hundred thousand tons per annum of wastes. The size of the plant, however, is designed according to need and according to transportation considerations. Plant location is not subject to the same geological restrictions of normal landfill operations because of the high quality of the final product. Overall, it can be expected that the combined transport and processing costs are competitive with existing methods of landfill disposal. Typical prices for plant conversion of waste materials may vary from as little as $20 per ton of material received to over $200 per ton, depending on the volume of waste and the degree of difficulty to treat the specific waste in question.

FIGURE I



PROCESS DIAGRAM

TABLE I

ELT - PROCESSED NICKEL WASTE

Parameter	Raw Sludge	PROCESSED MATERIAL			
		1 Day	7 Days	14 Days	28 Days
TOC, mg/l	110	<1.0	<1.0	1.0	<1.0
COD, mg/l	397	<25	<25	<25	<25
Al, mg/l	30.0	3.00	0.300	<0.005	0.010
Cu, mg/l	220	<0.002	0.003	<0.002	<0.002
Ni, mg/l	2,900	<0.005	0.010	<0.005	<0.005
CN, mg/l	9.14	0.03	0.04	<0.03	<0.03
ODOR	N/A	A (1)	A	A	A

(1) Acceptable

TABLE 2

ELT - PROCESSED CHROME WASTE

		PROCESSED WASTE			
Parameter	Raw Sludge	1 Day	7 Days	14 Days	28 Days
TOC, mg/l	45	< 1.0	< 1.0	< 1.0	< 1.0
COD, mg/l	103	< 25	< 25	< 25	< 25
Cr, mg/l	1,750	0.090	0.100	0.030	0.005
Ni, mg/l	40.0	< 0.005	0.050	< 0.005	< 0.005
Zn, mg/l	100	< 0.005	0.600	.020	< 0.005
ODOR	N/A	A (1)	A	A	A

(1) Acceptable

TABLE 3

ELT - PROCESSED COPPER WASTE

		PROCESSED WASTE			
Parameter	Raw Sludge	1 Day	7 Days	14 Days	28 Days
TOC, mg/l	520	3.0	1.3	<1.0	<1.0
COD, mg/l	2,000	<25	28	<25	<25
Al, mg/l	50	8.00	0.060	<0.005	<0.005
Cu, mg/l	7,500	0.020	0.020	0.008	<0.002
Se, mg/l	0.360	0.020	0.005	<0.001	<0.001
Cl, mg/l	10,650	390	81.7	7.1	< 3.5
CN, mg/l	5.80	0.04	0.40	< 0.03	< 0.03
ODOR	N/A	A (1)	A	A	A

(1) Acceptable

TABLE 4

ELT - PROCESSED ZINC PHOSPHATE WASTE

		PROCESSED WASTE			
Parameter	Raw Sludge	1 Day	7 Days	14 Days	28 Days
TOC, mg/l	21,500	2.9	1.9	<1.0	<1.0
COD, mg/l	201,000	97	<25	<25	<25
Cr, mg/l	20.0	0.300	0.020	<0.002	<0.002
Fe, mg/l	2,500	0.010	0.030	<0.005	<0.005
Pb, mg/l	18.0	<0.005	<0.005	<0.005	<0.005
Mn, mg/l	150	<0.005	0.020	0.030	0.010
Hg, mg/l	2.0	<0.002	<0.002	0.002	0.002
Ni, mg/l	800	<0.005	0.100	0.070	0.030
Zn, mg/l	21,250	<0.005	2.6	0.7	0.2
F, mg/l	3,000	6.3	8.8	8.2	2.6
NO_3, mg/l	5,010	2.2	4.8	0.4	<0.4
P, mg/l	10,400	0.1	<0.05	<0.05	<0.05
ODOR	N/A	A (1)	A	A	A

(1) Acceptable if sludge density 1.3 g/cc

TABLE 5

ELT- PROCESSED WASTE WATER TREATMENT

		PROCESSED WASTE			
Parameter	Raw Sludge	1 Day	7 Days	14 Days	28 Days
TOC, mg/l	144,000	77.6	36.9	6.1	4.6
COD, mg/l	277,000	806	209	71	48
Al, mg/l	750	2.20	1.07	0.200	0.500
As, mg/l	0.7	< 0.005	< 0.005	0.020	0.020
Cr, mg/l	120	0.070	0.050	0.050	0.002
Fe, mg/l	500	0.005	< 0.005	< 0.005	0.010
Pb, mg/l	70.0	0.010	< 0.005	< 0.005	0.006
Mn, mg/l	100	0.010	0.005	0.006	0.010
Zn, mg/l	9,500	< 0.005	< 0.005	0.060	0.200
CN, mg/l	114	0.03	0.04	< 0.03	< 0.03
ODOR	N/A	A (1)	A	A	A

(1) Acceptable if sludge density 1.13 g/cc

TABLE 6

ASTM LEACHATE TEST - RAW ZINC PHOSPHATE WASTE

		UNPROCESSED WASTE				
Parameter	Sludge Analysis	Exposure 1	Exposure 2	Exposure 3	Exposure 3	Exposure 4
TOC, mg/l	21,500	4.4	<1.0	<1.0	1.5	<1.0
COD, mg/l	201,000	47	< 25	< 25	< 59	< 25
Cr, mg/l	20.0	0.080	0.020	0.020	0.020	0.003
Fe, mg/l	2,500	10.0	1.10	2.00	0.40	0.20
Mn, mg/l	150	4.50	1.60	1.10	0.90	0.80
Hg, mg/l	2.00	<0.002	<0.002	<0.002	<0.002	<0.002
Ni, mg/l	800	50.0	14.0	5.00	5.00	26.0
Zn, mg/l	21,250	226	138	112	276	134
F, mg/l	3,000	188	65.0	170	65.0	42.8
NO_3, mg/l	5,010	0.9	2.2	34.3	10.6	3.1
P, mg/l	10,400	264	132	104	76.0	62.9
ODOR	N/A	A (1)	A	A	A	A

(1) Acceptable if sludge density 1.3 g/cc

TABLE 7

ASTM LEACHATE TEST - PROCESSED ZINC PHOSPHATE WASTE

rameter	Sludge Analysis	PROCESSED WASTE Exposure 1	Exposure 2	Exposure 3	Exposure 4	Exposure 5
OC, mg/l;	21,500	8.2	1.8	< 1.0	1.4	< 1.0
)D, mg/l	201,000	67	41	< 25	< 25	< 25
, mg/l	20.0	0.060	0.020	0.007	0.003	0.002
mg/l	2,500	< 0.005	0.030	< 0.005	< 0.005	0.010
mg/l	18.0	0.030	< 0.005	< 0.005	< 0.005	< 0.005
mg/l	150	0.020	< 0.005	0.006	0.009	< 0.005
mg/l	2.00	0.003	< 0.002	< 0.002	< 0.002	0.002
g/l	800	< 0.005	0.010	0.010	0.010	0.030
g/l	21,250	< 0.005	0.100	0.200	0.300	0.700
/l	3,000	50.0	30.0	8.1	5.9	2.9
g/l	5010	< 0.4	29.9	8.4	2.2	< 0.4
	10,400	< 0.05	0.02	0.10	0.30	0.20
	N/A	A (1)	A	A	A	A

eptable if sludge density 1.3 g/cc

TABLE 8

TOTAL ANALYSIS OF INDUSTRIAL WASTES
INCLUDED IN JAPAN ENVRIONMENTAL PROTECTION AGENCY TEST

TOTAL ANALYSIS OF INDUSTRIAL WASTES					
	Electroplating Waste	Humus Sludge	Paint Sludge	Latex Sludge	Acid Tar
Sample	4860	6622	8651/5	4585	6817
Total Solid Matter %	44.7	1.5	3.7	55.0	93.3
Ash on Ignition %	46.5	0.3	2.4	0.1	1.3
pH	<1	6.1	9.0	8.1	<1
Cyanide	0	0	0	0	0
Cadmium (ppm)	5	<1	1	<1	<1
Chromium (ppm)	120,000	3	1,000	13	18
Copper (ppm)	11,600	25	20	40	146
Iron (ppm)	--	340	7,200	24	60
Lead (ppm)	220	19	32	50	4,08
Nickel (ppm)	2,200	1	220	5	1
Zinc (ppm)	3,200	300	2,200	11	2,4

TABLE 9

JAPAN ENVIRONMENTAL PROTECTION AGENCY LEACHING TEST

JAPAN ENVIRONMENTAL PROETECTION AGENCY LEACHING TEST					
	Electroplating Waste (ppm)	Humus Sludge (ppm)	Paint Sludge (ppm)	Latex Sludge (ppm)	Acid Tar (ppm)
Sample No.	4860	6622	8651/5	4585	6817
Cyanide	< 0.007	--	--	--	< 0.007
Cadmium	< 0.01	< 0.01	< 0.01	< 0.01	0.02
Chromium	< 0.01	--	< 0.01	< 0.01	< 0.01
Copper	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Lead	< 0.3	< 0.3	< 0.3	< 0.3	0.37
Nickel	< 0.1	--	< 0.1	< 0.1	0.1
Total Mercury	--	< 0.0005	< 0.0005	< 0.0005	--
Organic Phosphorus	--	< 0.02	--	--	--
Arsenic	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001

TABLE 10

Industrial Wastes Treated by SEALOSAFE Service Facilities

Mine Tailings	Tannin Residues	Vanadium Powders
Dyestuff Liquors	Acid Tars	Asbestos Wastes
Spent Catalysts	Zinc Sludges	Solid Cyanides
Sulphide Wastes	Spent Acids	Paint Wastes
Pickling Acids	Chrome Solutions	Barium Sludges
Incinerator Ashes	Fluorides	Scrubbing Liquo
Tin Solutions	Cadmium Liquors	Arsneic Solids
Mercury Salts	Sewage Sludges	Nickel Salts
Filter Cakes	Latex	Antimony Resid
Copper Sludges	Alkaline Solutions	Aluminum Sludg
Cobalt Salts	Cyanide Solutions	Phosphates
Thicoyanates	Ion Exchange Resins	Lead Solution
Effluent Treatment Sludges	Electroplating Residues	Foundry Sand

TABLE II

LEACHATE TEST RESULTS - CORE SAMPLES

	EXPOSURE TIME		
	After 7 Days	After 14 Days	After 21 Days
N. Ammoniacal	.02	0.12	0.7
TOD	107	111	140
CN	< .01	.03	.01
SCN	< .01	.09	.01
Phenols	0.3	0.3	0.3
Cd	< .001	< .001	< .001
Cr	.06	.02	0.15
Cu	< 0.10	0.34	0.14
Pb	.01	< .01	.04
Hg	.001	--	--
Ni	.06	.025	< .02
Zn	.02	1.85	.02

NOTE: Test results reflect continuously more concentrated leachate since samples extracted from original liquid.

Q-5

Environmental I
Session Q

An Improved Treatment For Complex Effluents

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BACKGROUND

The Scovill Manufacturing Company, Apparel Fastener Division, decided to merge their operations at one facility with those at another existing facility. A complete review of the wastewater situation at both plants was necessary to insure State approval of the expected combined flow. The factory where the consolidation was to occur, built in 1970, had a State approved treatment system for plating rinses (Table 1). These treated waters were discharged into a small brook, while untreated cleaning and burnishing wastewaters were directed to the sanitary sewer.

The existing treatment system was of the integrated type. Plated parts were directly immersed in the recirculating treatment solution. Subsequent rinses were piped through a neutralization stage, and out to a holding tank located at the rear of the building. The holding tank was designed to provide two hours of settling time for suspended solids removal. Overflow from this tank went to a small sump. Two centrifugal pumps in the sump returned a portion of the treated water to the plant for reuse in non-critical areas. Waters in excess of reuse demand overflowed to the brook.

The "reuse water" was employed within the plant for cooling, non-critical plating rinse operations, and oblique barrel cleaning and tumbling. The cooling water and the non-critical rinse waters formed a closed loop system with the holding tank. The water once used for oblique barrel cleaning, deburring, and burnishing, was not reused again, but discharged directly to the sanitary sewer after removal of only heavy fines in a small settling pit. When the plant was built, it was felt that this flow could be safely directed to the sanitary sewer. More recent regulations cast doubt upon this practice.

PLANNING

The existing plating effluent treatment system had been operating satisfactorily for over seven years and met most of the Connecticut Department of Environmental Protection requirements during this period (Table 1). It was determined that this system could handle most of the combined plating rinses. Modifications would be needed to handle increased spill and batch dump requirements. The anticipated increase in nickel plating and the modification of the automatic plating line would require elimination of one of the integrated rinse tanks. Therefore, the nickel rinses would have to be included in any new treatment plan. The rolling operations area was the next discharge source to be reviewed. The operations performed in this area included cleaning, deburring, polishing, oxidizing, relieving, pickling, and burnishing. These operations were performed on brass, aluminum, steel and stainless steel. The combined facility would have 68 oblique

tumbling barrels, 10 horizontal barrels, and 3 vibratory tubs. The anticipated discharge from this equipment was estimated to be 100,000 gallons per day. Typical chemical inputs are alkaline cleaners, chelated burnishing and polishing compounds, pumice, waxes, acids, etc.

Another area considered during this planning stage was the sludge bed underdrain from the integrated treatment system. This flow was originally discharged directly to the stream, but on numerous occaisions this effluent had metal concentrations in excess of the Department of Environmental Protection limits.

Faced with the above information and a 15 month deadline, Scovill contacted independent consultants, designer-suppliers, and proprietary suppliers for conceptual designs and estimates. After careful evaluation of the designs submitted, they chose Aqualogic Inc.* of Bethany, Connecticut as the system designer-supplier.

Waste characterization studies were immediately started. Composite samples from the two existing plants were studied in the expected flow ratio. The composition of the effluent is shown in Table 2. Due to the tight completion schedule, the treatability studies were performed parallel to the characterization studies and the preliminary engineering report was issued in only 6 weeks.

Aqualogic pioneered the application of multiple stage treatment of difficult industrial effluents. They found that metal finishing wastewaters respond well to such treatment. At first, it involved providing a separate mixing tank and related equipment to produce properly flocculated metal hydroxides after the neutralization stage. It was subsequently discovered that a third treatment tank preceding the neutralization tank would provide greater reliability and flexibility to the treatment format. This third stage of treatment was termed either pretreatment or coagulation, depending upon the purpose of the chemicals being added. Addition of simple chemicals such as calcium chloride, or certain proprietary formulations, at this early stage of treatment aids in the removal of emulsified oils and grease, the breaking of chelate complexes, the reduction of detergent loadings, the removal of phosphates and fluorides, the reduction of BOD and COD, and, in some cases, the filterability of subsequent sludges produced. Some of these attributes have long been associated with the use of lime in some neutralization processes, however, it has been found that the use of a soluble coagulant can have many of these features without the attendent sludge bulk normally associated with lime usage.

*Aqualogic, Inc. is a registered trademark

Very early in the treatability studies on the combined Scovill effluents, it was observed that the triple treatment tank format produced an outstanding effluent over the entire range of anticipated compositions. Subsequently, Scovill elected to employ this format to insure compliance with the strict Connecticut Department of Environmental Protection discharge standards (Table 1A).

Upon acceptance of the Preliminary Engineering Report, preparations of the final engineering report, plans, and specifications were begun. The close client input of detailed processing steps, surge loading, and production requirements led to customizing the Scovill system for their particular circumstances. The knowledge of not only the processes, but also individual skills and work rules within the plant were also considered by the consultant in his choice of treatment equipment and methods (Fig. 1). It was also during this stage of the project that Scovill decided that a new building annex would be required to house the treatment system. The building and installation contractors were hired and their thoughts incorporated into the final plan. This early involvement between owner, contractor, and supplier led to cost saving modifications and speeded construction.

Once the final plans and specifications were approved by the State D. E. P., a schedule for completion was developed. Equipment delivery was inter-locked with building construction, so that as heavy pieces of equipment were delivered, the construction men were available for installation direct from trailer bed to final location. Each piece of equipment was timed to arrive in order of placement, eliminating multiple movements. The contractor was working on building completion and interconnecting piping and wiring as the equipment arrived so no special work crews were required, nor was time lost waiting for deliveries.

OPERATION

In June 1978, the system started up. The filter press was not completely installed at start-up, however, a few days were needed to accumulate sufficient sludge for it to operate. The start-up was extremely smooth, building up to the design flow of 200 GPM on the first day of operation. The only problem that arose during start-up was the discovery of a slight leak around a flange on the settling tank. The next week the filter press was placed in operation with similar success.

A key item in the success of this treatment plant is the equalization basin which collects the plant wastes by gravity flow. The tank collects the contaminated rinse waters, which can have an

instantaneous pH from 1 to 14 and equalizes the composition with a 20 HP turbine mixer. The equalization basin 35' x 35' x 12' deep (110,000 gal.) was sized to give an effective volume of one day's production. Therefore, the basin not only averages out flow peaks, contamination, and pH, but also acts as an emergency holding basin in the event of a plant malfunction. This basin also provides a capability for system shut-down and batch treatment of the contents in the event of an unauthorized dump (Fig. 2).

The equalized effluent is pumped from the basin through twin alternating 10 HP self-priming centrifugal pumps. This is the only stage in the treatment system where the effluent is pumped. The flow of the effluent throughout the entire treatment plant is by gravity into the sewer. This method stops all flow through the system in the event of power failure and automatically prevents the discharge of untreated wastes. The Aqualogic automatic pump controls also monitor the basin level and provide a high level alarm. Flow valves inserted in the discharge lines provide adjustable effluent flow into the system. The inlet flow is measured by an open flume with an electronic readout.

The first reaction tank is designed for 20 minute residence time. Liquid 40% calcium chloride (4.7 #/gal.) and 27% aluminum sulfate (2.8 #/gal.) are metered into the reaction tank from 5000 gallon storage tanks. In addition to the capability of adding both aluminum sulfate and calcium chloride to the pretreatment tank, it was decided to include pH adjustment capability. Since caustic was to be fed from an Aqualogic pressure feeder system to the neutralization tank, a few feet of PVC pipe and a solenoid valve extends the caustic feed to pretreatment. A sulfuric acid storage tank had been assigned to neutralization; an additional small chemical feed pump is used to supply the pretreatment tank. Addition of an Aqualogic high-low pH controller automated the pH adjustment in the pretreatment stage. This produced an added element of reliability to the system, particularly on those occasions when unanticipated strong dumps and spills would upset most systems.

The second tank, Neutralization, is designed for 18 minute residence time. In this tank, pH is adjusted to 10, which was found to be optimum for precipitation of metals in this system. The neutralization stage is controlled by a standard Aqualogic controller having both acid and caustic control. The addition of caustic is by means of the Aqualogic pressure feeder system mentioned previously and has a backup capability that opens a second valve to increase the flow of caustic, should the pH fall below a preselected level. The controller has visible and audible alarms for high pH, low pH, and mixer failure.

The pressurized caustic supply system has an audible low level alarm to signal when the supply has fallen to within one day of being empty. Refilling is by means of a transfer pump from an existing bulk caustic storage. Since the storage tank is inside, a 50% sodium hydroxide solution is used year round.

The third reaction tank, Flocculation, is designed for 8 minute residence time. Polyelectrolyte solution is added to the flocculation tank from an Aqualogic tandem chemical feeder station. The station has two independent 250 gallon compartments with mixers, allowing one batch of polyelectrolyte to be prepared and aged while the other is in use. A single variable stroke piston pump with pick-up from either compartment feeds the solution to the treatment tank. The treated effluent from the flocculation tank passes through a "splitter box" to two equivalent settling tanks.

The settling tanks are designed for 2.5 hour residence, and are little more than flat bottomed, rectangular, welded steel tanks. There is a reverse weir at the outlet end to prevent floating sludge and/or oil from escaping. The secret behind the simplicity of these tanks is the Aqualogic automatic sludge collector, a "T" shaped sludge collector-thickener suspended from a travelling bridge. These collector-thickeners travel the length of the settling tank at the rate of 1 ft./min. This gentle stirring of the sludge provides thickening. At pre-timed intervals, pumps on the bridge are activated and the thickened sludge is withdrawn into a 4500 gallon holding tank. The pumps used are a rubber diaphragm type with a D.C. speed control to adjust the amount of sludge withdrawn on each pass. The sludge collected averages 2% to 5% dry solids, by weight (Fig. 3).

The clear effluent from the settling tanks flows over the discharge weir into a pH adjustment tank. This tank was incorporated because the optimum pH for precipitation and settling may not fall within the final effluent pH limits. This final tank adjusts the pH to meet State and Federal requirements. Final pH adjustment is controlled by a small Aqualogic high-low controller similar to the one described for the pretreatment stage. Sulfuric acid is supplied by a chemical metering pump from a small day tank, while liquid caustic addition is controlled by a solenoid valve on a line from the same pressure system mentioned previously. Overflow from the final pH adjustment tank passes through a flow measuring weir. The instantaneous flow rate is displayed on a meter at the pH control panel. The flow is also recorded and totalized on a remote circular chart recorder located in the laboratory, adjoining the treatment room.

An often neglected part of most systems, included in this one, was a small, fully equipped laboratory-office. The laboratory included an atomic absorption spectrophotometer as well as balances, glassware, and other necessities. Scovill felt that no effluent treatment plant could be considered fully equipped unless there was adequate provision for analyzing the effectiveness of the treatment. A remote alarm board in the laboratory displays high-low pH alarms, mixer condition for each stage of treatment, as well as high level and pump failure alarms for the equalization tank. As mentioned before, the laboratory also houses the circular chart recorder for flow and final pH, both of which are required for a permit.

SLUDGE DEWATERING

One outstanding feature of this system is the facilities for sludge handling and dewatering. The heart of this system is a high pressure recessed plate filter press. Through the first six months of operation, this machine has consistently produced a filter cake with 50% dry solids by weight. In operation the 2-5% sludge from the sludge holding tank is pumped to a sludge reconditioning and ballast tank, and from there is pumped into the filter press through a progressive cavity type pump at a pressure of 225 psi. Rapid cycling of the pump is eliminated by use of a pressure vessel in the line to maintain a constant pressure. As the press dewaters the sludge, the time between the on and off cycles of the pump lengthen. At a preset off time, the press shuts down and it is ready for emptying.

The discharge of the cake is simple and rapid. The filter plates are recessed and have no outer shell, as do most other pressure filters. The operation consists of withdrawing the hydraulic ram, and starting the automatic plate shifting mechanism. As each plate is shifted, the filter cake drops from the recessed chamber into a standard 2 cubic yard dumpster below. Occasionally, a sludge cake will not drop freely from the plate and the operator will give it a nudge to release it. The entire operation is complete in about five minutes and the press is ready for the next cycle (Fig. 4).

The sludge dewatering cycle takes between 1 to 2 hours. The tim is dependent upon the concentration of the sludge from the settlin tanks. The one hour cycle is with 5% solids and the 2 hour cycle i with the 2% solids sludge. Each cycle of the filter press produce approximately 680 lbs. of filter cake. After drying at 250 F to r further weight loss, the average filter cake was found to contain 5(water. Each cycle of the press produces 340 lbs. of dry solids. Fou of these loads, one day's production, will fill a standard two cub yard dumpster. The analysis of the typical sludge is shown in Table

RESULTS

The effluent quality from this system has been excellent. The total concentration of four metals - copper, iron, nickel and zinc is consistently below 1 ppm. In fact, the typical zinc concentration (less than 0.1 ppm) has been so low, that Scovill spent almost one month reevaluating their analytical procedures before believing the results. The results of several analysis on the effluent are in Table 3. Connecticut is currently updating their effluent guidelines and this system is expected to easily meet the anticipated regulations (Table 1A).

There have been a few problems since start-up. The chelating agents remaining in a spent nickel stripper solution after batch treatment for cyanide caused havoc. The accidental addition of 200 gallons of stripper into 80,000 gallons of mixed effluent in the equalization basin resulted in levels of copper and zinc over 8 ppm, and it was almost two weeks before the system returned to normal. The use of unauthorized chemicals (i.e. chromic acid), resulted in many hours of investigation before one of the workers admitted using it in a non-chrome area.

One problem with the system was that of rising sludge in the settling tanks. The continuous mixing in the equalization tank was aerating the effluent, and the air was being trapped in the settling sludge. As the temperature of the liquid in the settling tank changed, the sludge would float to the top and form a blanket over the tank. A wide mesh screen attached to the traveling sludge collector acting as a mechanical deaerator, substantially improved this condition. A small amount of floating sludge that the screen does not hit remains at a constant volume, and does not cause any problems. The reverse weir configuration mentioned previously eliminated the discharge of floating particles.

One problem that has not yet been solved, is that of foaming in the final neutralization tank. It was felt that a silicon defoamer would solve the problem, but now studies are underway to solve the problem by eliminating it, rather than adding an additional contaminant to control it. The foam is only a cosmetic concern and is not reflected in the COD and TOC of the discharge.

COSTS

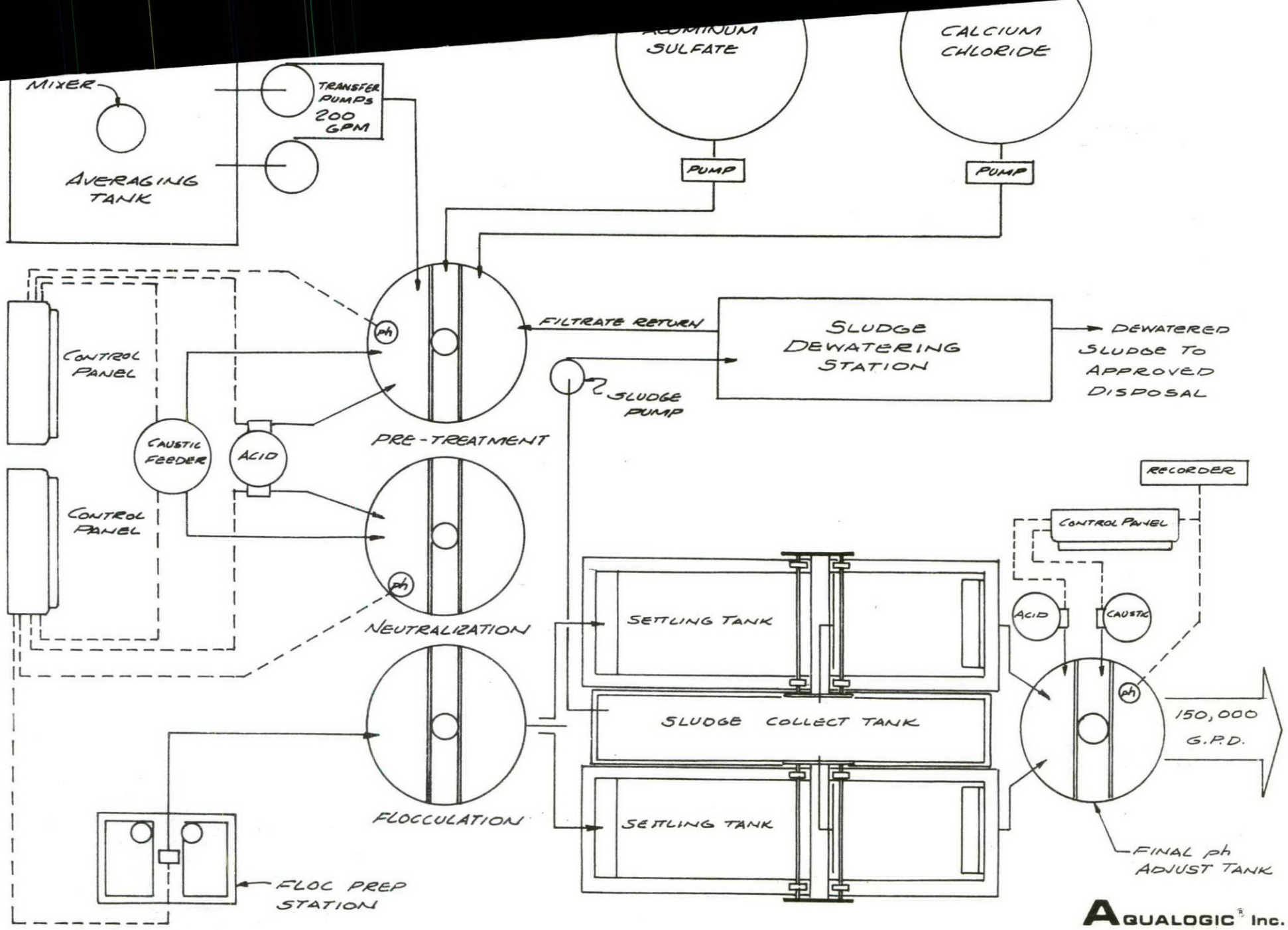
There is a full time operator for the system. His duties include calibration of controls, chemical ordering, equipment lubrication, and effluent analysis. He performs daily analysis, not only on this system, but also on the integrated treatment system. He also records daily flow, chemical use, sludge production, etc. A maintenance log is kept on each piece of equipment to pinpoint problem areas, so appropriate action may be taken.

The 1978 costs for the system came to a total of $565,000 complete. Engineering services were $18,000, equipment totaled $263,000, spare parts $15,000, laboratory equipment $20,000, and building and installation $249,000. Chemical operating costs are tabulated in Table 5.

SUMMARY

Scovill is very happy with the system operation at this point. They have found some excess operating capacity in this system and plan to incorporate some of the more troublesome parts of the integrated treatment system into the new system. The first major area is the elimination of the porous concrete block gravity sludge bed. They plan to pump the sludge from the integrated treatment reservoirs into the equalization basin, because the sludge is not thick enough to feed the filter press directly from the reservoirs.

When conceiving this project, we attempted to look as far into the Environmental Protection Agency regulatory future as possible. In our planning, we considered some of the "advanced systems" such as membrane filtration for sludge thickening. After evaluating these systems, we concluded that under optimum conditions, some might, at times, produce a slightly better effluent, but in the final analysis, the best system is the one that can consistently produce a high quality effluent that meets all State and Federal regulations. Long-term consistency also requires that the system's functioning is easily understood by operating and maintenance personnel. Using these criteria, we believe this system meets the 1983 requirements.



AQUALOGIC® Inc.
S.P. 12/26/78



Fig. 2—Equalization basin & pump house.



Fig. 3—Treatment & settling tanks.

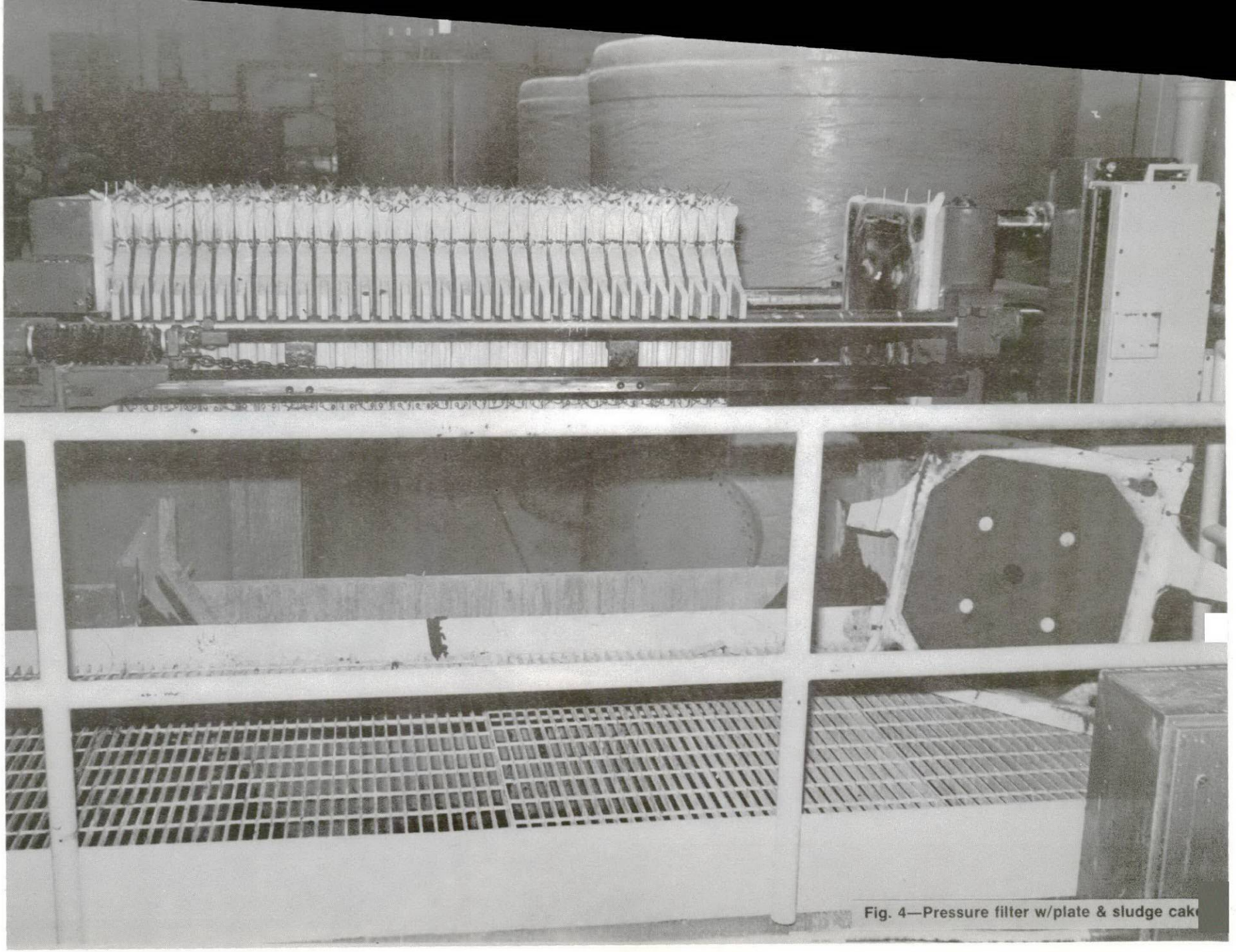


Fig. 4—Pressure filter w/plate & sludge cak

TABLE 1

1970 CONNECTICUT EFFLUENT LIMITS

PARAMETER	AVERAGE DAILY CONCENTRATION
Aluminum	2.0 mg/l
Chrome (Hexavalent)	0.1 mg/l
(Total)	1.0 mg/l
Copper	1.5 mg/l
Iron	1.0 mg/l
Nickel	2.0 mg/l
Tin	1.0 mg/l
Zinc	2.0 mg/l
Cyanide (Amenable to Chlorination)	0.1 mg/l
(Total)	1.0 mg/l
Total Suspended Solids	25 mg/l
pH	7-10

TABLE 1A

STATE OF CONNECTICUT

DEPARTMENT OF ENVIRONMENTAL PROTECTION

EFFLUENT LIMITATIONS

August 1, 1978

PARAMETER	EFFLUENT LIMITS (mg/l)
Cyanide, Amenable to Cl_2	0.08
Cyanide, Total	1.00
Aluminum	2.00
Chromium, Hexavalent	0.09
Chromium, Total	1.00
Copper	1.00
Iron	Varies (1.0-3.0)
Nickel	1.00
Tin	2.00
Total Suspended Solids	20.0
pH	6.0-9.0

TABLE 2

Composition of Effluent in Equalization Basin

Element	Min.	Max.
Copper	9.7 mg/l	31.7 mg/l
Iron	7.8 mg/l	27.3 mg/l
Nickel	8.2 mg/l	27.8 mg/l
Zinc	5.8 mg/l	33.3 mg/l
T.S.S.	103 mg/l	437 mg/l

TABLE 3

Final Effluent Analysis (mg/l)

October, November, December 1978

Copper	Iron	Nickel	Zinc	Total Metals
.16	.20	.13	<.01	.49
.17	.17	.13	.02	.49
.10	.05	.12	.01	.28
.45	.28	.13	.02	.88
.52	.26	.11	.02	.91
.34	.79	.09	.01	1.23
.15	.39	.17	.04	.75
.09	.25	.23	.03	.60
.13	.71	.12	.03	.99
.19	.26	.20	.02	.67
.16	.50	.23	.03	.92
.18	.25	.13	<.01	.56
.14	.46	.13	.01	.74
.11	.26	.18	<.01	.55
AVERAGE				
.21 mg/l	.35 mg/l	.15 mg/l	.02 mg/l	.72 mg/l

TABLE 4

TYPICAL SLUDGE ANALYSIS

52.7% Water 47.3% Solids

SOLIDS ANALYSIS

Al	3.0%
Ca	9.6%
Cu	1.45%
Fe	2.34%
Ni	3.93%
Zn	2.32%
Non Digested	26.4%
Oxide, Hydroxide etc.	Bal.

TABLE 5

COST ANALYSIS

Effluent Flow	70,000 Gal/Day
Sludge Production (Dry)	1,350 Lbs/Day

	Gal/Day	Lbs/Day	Chem. Cost	Cost/Day	Cost/M Gal
$CaCl_2$ (40%)	120	560	.0814/lb.	$45.58	$ .651
$Al_2(SO_4)_3$ (27%)	62	175	.209/Lb.	$36.61	$ .523
Floc (2%)	70	1.4	2.30/Lb.	$ 3.22	$ .046
H_2SO_4 (Conc)	10	150	.030/Lb.	$ 4.50	$ .064
Caustic (50%)	5	32	.096/Lb.	$ 3.05	$ .044
			Total	$92.96	$1.328

R-1

Electroless II
Session R

A New Look at the Chemistry of Electroless Copper Plating Solutions

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A New Look at the Chemistry of Electroless Copper Plating Solutions

by

C. Courduvelis & G. Sutcliffe

Extended Abstract of Paper to be Presented at the Sur/Fin 1979 in Atlanta, GA

Most electroless copper plating solutions used commercially today employ:

1) a copper salt, such as sulfate, chloride, nitrate,
2) formaldehyde as the copper ion reducer,
3) sodium hydroxide to keep the solution alkaline, and
4) a chelator of copper to prevent copper hydroxide precipitation in the alkaline solution.

In addition, a variety of other substances may be present to ensure solution ability, desired plating rate and superior deposit characteristi cs.

Electroless copper solutions are operated at either room temperature -85°F) or higher temperature (110-160°F.). Sufficient solution agitation provided at all times by means of pumping recirculation or air bubbling, both. The agitation is known to improve the stability of the solution against mical decomposition, to increase the plating rate and to maintain deposit kness uniformity.

In order to deposit one gram-atom of copper, two moles of formaldehyde and four moles of sodium hydroxide are consumed along with one gram-atom of copper ions in the solution:

$$Cu^{++} + 2CH_2O + 4OH^- \longrightarrow Cu^\circ + H_2 + 2H_2O + 2HCOO^-$$

At the same time one mole of hydrogen is produced, which escapes and two moles of sodium formate and one mole of sodium sulfate (or two moles of sodium chloride or nitrate, in the case where chloride or nitrate is the copper salt of the solution).

Once an electroless copper plating solution is made up it is used to plate load after load over many weeks, when the consumed ingredients are properly replenished. As more plating is performed the level of formate and sulfate (or the other salts mentioned above) of the solution rises continuously and it may reach the point where it affects the plating. This usually will determine the end of the life of the plating solution. One may calculate the level of such salts from the amount of replenishments, or plating, and fr the amount of plating solutions lost to drag out and bail out.

Besides the plating reaction there are other side reactions or change taking place, which will make the composition of an old plating solution diffe from the calculated one. These are:

1. The Cannizzaro Reaction

   $$NaOH + 2CH_2O \longrightarrow HCOONa + CH_3OH$$

   consuming NaOH and formaldehyde to produce sodium formate and methanol.

2. Evaporative loss of formaldehyde

3. Air oxidation of formaldehyde to sodium formate

4. Reaction of the CO_2 of the air with the NaOH to convert it to sodium carbonate.

It is one of the objectives of this research to determine the extent and the significance of these four processes.

The following results were obtained from our study:

1. The carbonation reaction is very significant for an electroless copper solution operated at room temperature with continuous air bubbling during plating and when the bath is at rest. Thus, over a 24 hour period as much as 40% of the make-up amount of 10-11 g/l of NaOH can be converted to carbonate while only about 10% of the make up amount is used up in the Cannizzaro reaction.

Many plating solutions, like the ones used in plating on plastics, plate only 1 or 2 metal turnovers (MTO) per day. Such solutions will build significant amounts of carbonates if operated at room temperature. For example, assume an electroless copper solution operated at room temperature with moderate air agitation, a make up of 10 g/l $CuSO_4 \cdot 5H_2O$ and 10-11 g/l NaOH, is plating 1 MTO of copper a day. This solution will produce about 3 g/l of sodium carbonate and a total of about 4.4 g/l of sodium formate (2.7 g/l from the plating and 1.7 g/l from the Cannizzaro). During a shut down (such as over a weekend) the ratio of carbonate to formate increases to more than 50:50. Thus, one may expect to find a ratio of more than 1 to 3 carbonate to formate in an old electroless copper solution of this kind. The ratio is even

greater in some slow electroless copper solutions used in printed circuits. There are solutions plating in some installations at the equivalent of 1/2 MTO of 10 g/l of $CuSO_4 \cdot 5H_2O$ per day at a NaOH concentration of 12-15 g/l.

The rate of carbonation of the sodium hydroxide is greater at faster air bubbling and at higher NaOH levels in solution. A three-fold increase in this rate is common by going from low to fast rate of aeration.

In a warm electroless copper solution the carbonation reaction is as important, but the Cannizzaro reaction is much more significant. Although the carbonation is only slightly faster at higher temperatures, the Cannizzaro reaction going from room temperature to 120°F. or 140°F. appears to accelerate 5-10 fold.

The air oxidation reaction of the formaldehyde is insignificant in the materials balance.

The evaporative loss of formaldehyde is also insignificant in the mate balance in solutions operated at room temperature. In warm solutions formaldehyde is lost only when some of the solution evaporates. The evapor solution normally takes along only 1/3 of its original formaldehyde.

Samples of various old electroless copper solutions were received fr production installations and subjected to complete salt analysis. The salt levels are in agreement with the above experimental results.

R-2

Electroless II
Session R

High Speed Electroless Copper Plating At Room Temperature

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HIGH SPEED ELECTROLESS COPPER PLATING AT ROOM TEMPERATURE

by
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A year ago the Photocircuits Division of Kollmorgen Corporation had sharply increased the capacity for subtractive plated through hole printed wiring boards. Drilling capacity was expanded. Because the additive printed wiring board production had moved entirely to a new plant in Riverhead the necessary extra printing capacity was available at the Glen Cove Plant. However, the electroless copper plating between the drilling and the printing steps proved to be a real bottleneck. This line was operated three shifts, seven days/week and still was barely meeting their commitments.

The Table below shows the electroless copper line cycle and processing times. The rinses are omitted for brevity, but including the various rinses between each step, the total cycle per rack was one hour and 45 minutes. Obviously, the electroless copper bath was the major portion of the bottleneck.

TABLE 1

Electroless Copper Cycle

Hot Alkaline Clean	10 minutes at 70°C
Sodium Persulfate	30-60 seconds
Activator Predip	5 minutes at 25°C
Activator	5 minutes at 25°C
Accelerator	4 minutes at 25°C
Electroless Copper	1 hour at 28°C
Total with Rinses	1.75 hours

As the first step, the engineer in charge of this process went outside the Kollmorgen organization looking for an electroless plating system that would solve this problem. He contacted many of the commercial suppliers. Some of their electroless baths were ruled out because they would not cover CEM base material adequately, producing blisters and voids. One of the fast electroless baths offered commercially failed because of occasional poor copper adhesion to the stainless steel racks.

The only suitable alternative seemed to be a commercially available, elevated temperature bath working in the 45-55°C range. This bath covered the holes in the CEM material very well; there were no signs of blisters or voids. But because Photocircuits Division had always been a user of home-brewed electroless plating baths, the bath supplier requested a 6 month contract; and insisted on a new electroless copper plating tank designed to his specifications. He recommended lower panel loadings of 1.5 sq. ft/gal (4 sq. dm/l) as compared to loadings of up to 2-1/4 sq. ft/gal (5.4 sq. dm/l) used with the then operating FD-400 bath.

This means that the electroless copper line would have to be broken down and a new larger tank installed with the incumbent delay period. In addition, promised delivery of the new tank was daily pushed back. Ultimately the use of this commercial bath was rejected because of the new tank, its delivery delays, the lower panel loadings and the 6 month commitment.

At that time the engineer in charge was in a desperate position. However, there had been some experimentation in the PCK Technology laboratory with electroless baths which had copper deposition rates up to six times faster than the FD-400 bath used for a number of years in Photocircuits Division production line. The production schedule for manufacture of subtractive printed wiring boards called for a sharp scale-up within the next two months which required moving a laboratory curiosity into a production tank within such a short period, certainly a tall order.

The first step was to convert an old rinse tank available on the production floor into an electroless copper plating tank. Fortunately, this new fast electroless copper bath was a room temperature bath and heating was no problem. This "pilot plant" tank was set up with an overflow weir, panel rack agitation to move the panels back and forth in the solution and an air agitation system.

The intial work established the addition rates on scrap copper material. Although the experimental FRT-450 bath had been six times faster than the FD-400 bath in the laboratory operation, it became obvious that in the larger scale operation deposition rate four times faster was more real

The method used to monitor the copper deposit thickness in hole metallization operation at Photocircuits is the so-called "burn-out" method. This method has been described before, but briefly: a rapidly increasing DC current is passed through a 1 millimeter diameter hole (0.040 in.) with an electroless film on the hole wall. The thin copper film on the hole wall quickly reaches a temperature where it fuses and an open circuit interrupts the flow of the DC current. The current value at which this occurs is proportional to the copper deposit thickness in the hole. Typically after deposition of 1 hour in electroless copper plating the FD-400 bath would give burn-outs of 18-25 amperes before the hole wall is fused. The same criteria applied to the FRT-450 bath gave burn-outs of 25 amperes after only 20 minutes plating.

Since the plating rate was so much higher, the bath must be absolutely stable especially during non-operating periods. The problem was solved by maintaining air agitation both in the tank and in the weir when the bath solution circulation system was turned off. In addition, a stirrer was used to help mix the solution.

After a few days operation with scrap material, production boards were run through the "pilot line". It was at this point that one of the major advantages of the new bath showed up. The difficult to plate CEM material was being plated rapidly and reliably. The pilot plant work continued for three weeks. However, it should be pointed out that at 4 sq. ft/gal the amount of hydrogen evolved is substantial. One of the modifications we did have to make to the plating tank was an adequate exhaust to safely remove the hydrogen. Another addition was a cooling coil, since temperature rises of up to 2.5^{o}C/hr had been observed in the course of a working day.

The old 400 bath was stabilized with cyanide compounds. This produced a clear, bright copper and an excellent base for further electroplating. It should be noted that in the new FRT-450 bath the cyanide stabilizers were replaced by other proprietary stabilizers. As a result, a much faster plating rate is achieved but a much darker copper is deposited. Extensive tests were necessary to convince ourselves this was not going to affect quality of copper nor the adhesion of subsequent electroplate. However, it was found that a simple dip in sulfuric acid brings this dark deposit up to the pink copper color.

In mid-November we were ready to put the bath into the production line tank. The cooling system, the air mixing sparge and the improved exhaust were in place in the production line tanks. Also, a lip had been built around the edges of the tank to prevent the bath from splashing on the floor when the air mixing was on.

The production schedule allowed only two days to start the full production operation of this new FRT-450 bath in the line. If unsuccessful, on the third day the old bath had to go back in. As might be expected with any new process, the first morning was very difficult, but by the middle of the afternoon the bath was running smoothly except that the operators were being run ragged due to the faster plating cycle. Eventually, the platers from the second and third shifts had to be added to the day shift to handle the work coming off the line.

This is not to say that the FRT-450 bath doesn't have its disadvantages. The major problem has been storing the bath over the night shift and especially over weekends. At the present time this problem is solved by the cooling coil which had been installed in the bath to maintain the operating temperature below 30°C. Using this cooling coil the bath is cooled to 10°C for storage over the weekend. In addition air mixing or vigorous stirring is maintained. For storage overnight the bath is continually stirred by air from sparges in both the plating tank and in the overflow weir compartment. If it is necessary to clean the plating tank, the bath is pumped in to a storage tank after cooling it to 10°C and is maintained in the storage tank with vigorous stirring while the plating tank if cleaned.

One other advantage comes out of cooling the bath. After one or two shifts operation at high panel loadings the bath contains substantial quantities of by-products salts. These salts crystallize out at 10°C and can be simply scooped out and discarded.

One caution must be observed when starting a cold bath that has been stored over the weekend. At temperatures below 19 or 20°C the deposit becomes brittle and there is a possibility that some of the copper in the plated through hole may blister causing hole wall separation. For this reason, in addition to the cooling coil, a heater is included so that the bath solution can be heated rapidly to 25° before starting the plating work.

Actually, these brittle deposits have been noticed even at normal operational temperatures in the initial rackload when starting a freshly prepared solution. This has been eliminated by dummying a brand new bath, freshly installed in the plating tank, where a load of 2 sq. ft/gal of scrap panels are plated first in the new bath for a period of 40 minutes. This quie the bath down and stops the brittle deposit. Perhaps, as in electroplating dummying operations, some trace impurities are also removed from the bath.

In summary, this FRT-450 bath seems to solve many of the problems experienced by users of electroless copper plating systems desiring thicker deposits.

Among these problems are:

a) Slow plating rates
b) Relatively low loading capacities (1-1.5 sq. ft/gal)
c) Difficult to control
d) By-product build up, causing short bath life
e) Pollution and no means of reclamation
f) Voids and blisters
g) High overflow
h) High operating cost

The newly developed FRT-450 bath exhibits properties and performance characteristics which bypasses the shortcomings of presently used copper baths, since it provides:

a) High plating rate
b) High loading capacity
c) Ease of operation
d) Long bath life
e) Premixes or bulk chemical makeup and additions system
f) Low overflow with capabilities of reclamation and recycling of chemicals

During its operation in regular production line for the past seven months, this FRT-450 bath plated consistantly in excess of 1/20 oz/ft^2 (14 g/m^2) of uniform cohesive copper in 15 minutes. This permits up to four cycles per hour as compared to two or three cycles per hour with the high temperature electroless plating systems presently available on the market. These plating rates are achieved with plating bath operations between 25-27°C. Higher deposition rates, though not recommended or needed, can be achieved by operating the bath at 30-32°C temperature levels.

Unlike other conventional electroless copper plating baths, with the FRT-450 bath the loadings as high as 3.5 to 4.0 square feet of surface area per gallon of working solution are obtainable. With automatic or time controlled addition systems even higher loadings can be achieved. A bath operating at such high, 3.5 - 4 sq. ft/ gal, loading level will deplete between 30% and 35% of its consummables in 15 minutes and requires corresponding replenishments.

The use of this bath has entirely eliminated blisters and voids occasionally observed on CEM type laminates or laminates with high flame retardant material content or on the punchable grade laminates which have less uniform hole walls.

The bath is highly stable and can be stopped overnight or over extended periods of time with simple procedures. It has high tolerance limits of fluctuation of all its constituents which allows that occasional mistakes of production personnel will have little detrimental effects on the plating

performance of the bath. This high tolerance and ease of shut-down is an essential attribute for its use on production floor with lower qualification personnel.

Another desirable feature of the bath is its ability, without any complicated procedure, to remove some of the by-products which are built up during the plating process. This feature not only allows for control of the bath density which is important for its steady state operation, but also gives the bath an extended life since it reduces plating problems commonly caused in the industry by accummulation of by-products.

We feel that this bath is a major breakthrough in electroless copper reduction field and will modernize the industry by allowing increased plating capacity without increasing the deposition facility. Other applications of FRT-450 bath, still in the development stage, will use this bath for:

a) Semi-additive plating
b) Multilayer plating
c) Plating on plastics

S-1

Environmental II
Session S

A Case History of Reverse Osmosis Used for Nickel Recovery In Bumper Recycling

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Paper not available at time of printing of proceedings.

S-2

Environmental II
Session S

Solution Drag-out and Rinsing After Chromium Plating

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SOLUTION DRAG OUT AND RINSING AFTER CHROMIUM PLATING

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INTRODUCTION

Rinsing after electroplating is one of the most important operations in a plating room, yet has been explored very little until recently. Although rinsing had not been studied directly, it was examined indirectly in attempts to determine factors responsible for variations in solution dragout. Soderberg's work (1) on drag out has long been accepted as a guide in the metal finishing industry for understanding the gradual contamination of rinses. Kushner's work (2) on drag out attempted to establish a relationship between the speed of part withdrawal and solution viscosity on the amount of carry over into the sequential steps of rinsing. Tallmadge and Gutfinger (3) attempted to make some order out of the literature describing drag out; they summarized the work dealing with the process of drainage, withdrawal, and removal from liquids, on the volume of liquid carried to the next process step. Much of their work dealt with fluids such as molten glass, waxes, motor oils as well as water. Tallmadge and Barbolini (4) studied the influence of part orientation and speed of removal and drainage time on the volume of solution drag out and found significant variations dependent on the variables.

Approaching the problem from another viewpoint, Grube and Clifton (5) explored plating from less concentrated CrO_3 solutions in an effort to reduce chemical loss through drag out. S. Konishi and M. Tadagoshi (6) reported about similar studies with dilute chromium plating baths to determine the properties of Cr deposits from solutions containing only 25-50 g/L CrO_3.

Although causes for solution drag out have been reasonably well identified, little rinsing technology has been developed beyond the introduction of the counterflow rinsing principle which employs connected rinses running counter to the direction of the work traveling through. In spite of this major advance, large volumes of rinse water are still being consumed, and if we are to make further progress, factors responsible for solution drag out and removal from parts must be explored in more detail.

Addressing this problem at the GM Research Laboratories, a miniature automatic plating apparatus was developed to provide reproducible continuous solution drag out, and the tests that were run are described in this report.

EXPERIMENTAL

Several sets of small cathodes, mounted on the conveyor of the automatic plater, were transported through a series of plating and rinsing steps. Twe cathode specimens were carried through chromium plating and rinsing and wer recycled automatically for replating. Conductivity of the rinses was monito using small tungsten or platinum probes and the signals were displayed poten metrically on a strip chart.

Plating and Rinse Assembly

The assembled conveyor and tanks are shown in Fig. 1. The tanks were constructed of acrylic to contain 1.5 L and were all mounted in a straight line. The conveyor was a continuous length of roller chain that traveled over a series of small sprockets. After the final rinse, the parts were carried back to the HCl strip, rinsed and then were rechromium-plated. Stripping the chromium after each plating cycle achieved a uniform substrate for chromium plating, resulting in a consistent drag out volume from cycle to cycle.

A schematic drawing of the apparatus is shown in Fig. 2. The first tank was the strip solution containing 50% HCl for removal of the chromium and activating the nickel substrate for chromium deposition. The second tank was a fast flowing rinse to wash the HCl from the cathodes. The third tank contained a chromium plating bath; lead anodes were attached to the front and back walls of this tank. The fourth tank was a stagnant or drag out (DO) rinse. The last three tanks R1, R2 and R3 were additional rinses. The volume of the tanks was 1.5 L, but in some trials the volume was reduced using acrylic displacer blocks to promote faster buildup of rinse contamination.

Operating Conditions

Table I gives the operating conditions that were held constant. Conveyor speed was maintained at 16.5 cm/min providing a total immersion time of 75 s. Chromium deposition was done at 195 mA/cm^2 for 20 s on each panel. The cathode support arms attached to the chain were made of plastic to insulate them from each other. Cathode contact was made through a small gold plated slider on the ends of the support arms and a wire fixed horizontally above the plating tank. Current connection was made immediately after the part was completely submerged in the electrolyte, and was broken just prior to the part being lifted out of solution.

Chromium Electrolyte and Rinses

Compositions of the plating electrolytes are shown in Table II. Tests were run with 80 and 250 g/L CrO_3 solutions, at a $CrO_3/SO_4^{=}$ ratio of 100:1 and temperature of 43°C. Deionized water at a conductivity of 2 µS/cm was used for the rinses.

Cathodes

Six different sets of cathodes were used; they had comparable surface area but differed slightly in orientation or shape as shown in Fig. 3. Sets A, B, C, D and E had a surface area of 26 cm^2 and set F had 24 cm^2. The cathodes were made of flat steel, polished and buffed to a smooth finish, then plated with bright copper and nickel. Sets A and B differed only in orientation; set A was held vertically and set B was tilted at about 30°, so that the panel entered the solution at one corner. Sets C and D were similar in comparison except these panels had an "L" shaped profile. Set E panels were flat squares with a cylindrical cup attached to one side, and entered the solutions at one corner. Set F cathodes were flat strips with a series of holes and scalloped edges. With the exceptions of the holes, this set was similar to the A cathodes.

Measurements

Conductivity of the rinses was measured with a conductivity bridge using a tungsten sensor. Conductivity readings were taken at the end of e 20 part cycle, and at the completion of 5 cycles (100 parts). Samples we taken of each rinse for Cr^{+6} analysis by atomic absorption spectrophotome Volume of electrolyte drag out was calculated from the Cr^{+6} analyzed in the rinses divided by the number of panels run.

RESULTS AND DISCUSSION

Chromium deposition was uniformly bright from both electrolytes. Deposition completely covered the flat panels, but the deep recesses of the cup area of the type E panels were not plated as well as the low current density bend of the "L" shaped cathodes (C and D). Figure 4 is a plot showing the conductivity of the DO rinse versus parts rinsed after plating type C panels in the 80 and 250 g/L CrO_3 baths. Conductivity increased linearly to 2.1 mS/cm after 140 panels were rinsed out of the dilute 80 g/L bath contrasted to conductivity increasing to 2.8 mS/cm after rinsing only 100 panels plated in the 250 g/L CrO_3 bath.

Figure 5 gives the conductivities of the DO rinse after rinsing 100 of the six cathode sets from the 80 g/L CrO_3 bath. The type C bent cathodes carried out the largest amount of electrolyte, increasing linearly. The other sets of cathodes dragged out less than 50% of the volume carried by the C panels. Figure 6 shows the conductivity of the DO rinse following rinsing out of the 250 g/L CrO_3 bath. Sets C and E panels dragged out more electrolyte than was obtained from the 80 g/L bath. Sets A, B, D and F carried only about 30 to 50% of the electrolyte transferred by the C and E panels. Since less total CrO_3 was dragged out of the dilute 80 g/L bath, it is estimated that 2-3 times the number of panels plated in the dilute bath could be rinsed before the electrolyte drag in of the DO rinse would reach the level produced during rinsing after plating in the 250 g/L CrO_3 solution.

The drag out electrolyte was transferred from the plating bath without any extraneous dripping between tanks and therefore was distributed to all four rinse tanks. The largest fraction of the drag out was retained however, by the first rinse (DO) after plating and only a small portion was divided into the last three rinses.

Table III gives the relationship of the chromium found in the dragout rinse compared to the concentrations found in the following three rinses combined. The analysis indicates that 99% + of the total Cr^{+6} carried out of the bath, remained in the dragout rinse and that only 1% or less was carried further down stream. At least for the conditions of this experiment, the DO rinse was the most effective. Thus at this stage, inhibiting increased buildup would mean less contamination of subsequent rinses.

Table IV gives the concentrations of Cr^{+6} found in each of the four rinses after trials with the six sets of cathodes. The Cr^{+6} in solution ranged between 15 and 633 µg/mL in the DO rinse after rinsing 100 parts from the 80 g/L CrO_3 and up to 13 µg/mL in the following rinses. Electrolyte carried from the 250 g/L CrO_3 bath by the different panel sets ranged between 47.5 to 2000 µg/mL in the drag out rinse and accumulated to 47.5 µg/mL in the R1, R2, and R3 rinses.

Drag Out vs. Panel Shape

Drag out from the bath was as a thin film and as drops and pools on the edges and in crevices. The volume of drag out depended on the orientation during removal of the panels as well as shape. Figure 7 is a histogram showi the relative electrolyte volumes carried by each of the six panel types. Set carried the least volume of drag out and type C panels carried the most. Al the A and B panels were the same size and shape, "A" cathodes carried about more than B cathodes. Although the area of the set F panels was slightly le than the A panels, approximately 40% more plating solution was dragged out

the F panels. Thus, variations in orientation and shape contributed the most significant differences in drag out volume. Cathodes emerging from the plating bath or rinses were wetted with a thin liquid film, and upon separating from the liquid surface a drop or bead formed on the lowest extremity of the parts; dependent on the area or size of that extremity, variations in volume of the hanging drops were noted. A large continuous bead usually formed on a flat edge was seen on the type A panels as illustrated in Fig. 8. However, different orientation of the same part, represented by the B type cathodes, resulted in only a corner touching the liquid surface at the moment of panel-liquid separation; consequently, only a small droplet was formed as shown in Fig. 9. Assuming the same rate of drainage down both panels, the difference between volumes of electrolyte carried by the two cathodes seems related to amount of surface area in contact with the liquid at the moment of separation.

Set C cathodes carried out a comparatively large volume of electrolyte, noted as a pool on top of the horizontal step along with a large hanging drop on the bottom of the step. This was contrasted to the relatively small volume carried by the similar cathodes (set D) differing only in orientation during removal. The small tilt given to the D cathodes, which again caused only a small area to remain in contact with the liquid surface at the moment of panel-liquid separation, permitted more complete run off of the electrolyte and thus decreased the size of the hanging drop. This concept is summarized by the illustration in Fig. 10. The liquid tends to cling to the panel at the air-solution interface and, when separation between the panel and liquid occurs, the volume of fluid carried appears to be proportional to the panel area last contacting the liquid. This agrees, in part, with the work reported by Tallmadge and Barbolini (4) where they showed a dependence on shape to drag out, claiming at least 50% of the adhering fluid was in the form of bottom drops.

Comparing results of electrolyte volumes transferred by A and B panels, only 15% of the total drag out could be attributed to the thin film and the remainder was caused by the electrolyte clinging as a continuous bead on the bottom edge. A similar comparison was noted between the volumes carried by type C and D panels.

The E panels transferred a moderate volume of electrolyte which was carried over as a small pool in the cup area, in addition to the thin film that wetted the parts. A small droplet also formed on the bottom corner as shown in Fig. 11. Rinsing appeared to be nearly complete in the cup recess immediately after the part was submerged in the rinse. Electrolyte was seen streaming out as it was displaced by the water.

The type F panels dragged out small pools of electrolyte that tended to collect around the holes and in the scalloped sides as shown in Fig. 12. The holes inhibited run down of the electrolyte and consequently 37% more electrolyte was carried by this type panel compared to the volume obtained with the type A panels having the same basic shape and orientation. Thus, the increase was attributed to pools that accumulated around the holes and along the sides.

In conclusion, it appears that the pools and drops adhering to the edges and crevices of the parts contributes a significantly greater amount of the total drag out than the thin film wetting the majority of the area. In addition, the size of the drops adhering to bottom edges was not only controlled by the shape of the part, but by its orientation relative to the surface of the liquid at the moment of panel-liquid separation. Parts oriented so that only a small surface area contacted the liquid surface at parting, resulted in less volume of solution carried out. Removal of the drag out solution was nearly complete during the first rinse after plating, and only a small fracti was carried to the downstream rinses.

REFERENCES

1. G. Soderberg, Am. Electroplaters' Soc. Proc., 24 233 (1936).
2. J. B. Kushner, Metal Finishing, 49 (12), 58 (1951).
3. J. A. Tallmadge and C. Gutfinger, Industrial and Engineering Chemistry, 59, (11) 19-34 (1967).
4. J. A. Tallmadge and R. R. Barbolini, JWPCF, 38 (9) 1461 (1966).
5. W. L. Grube and F. L. Clifton, American Electroplaters' Society Monthly Review, 34 140-153 (1947).
6. S. Konishi and M. Tadagoshi, Metal Finishing, 71 49-52 (1973).

TABLE I

OPERATING CONDITIONS

° Conveyor Speed	16.5 cm/min
° Immersion Time	75 s
(26.5 s down)	
(22 s horizontal)	
(26.5 s up)	
° Cathode current density	195 mA/cm^2
° Plating Time	20 s
° Parts per cycle	20
° Parts per hour	54
° Rinse tank volumes	
DO	1260 mL
R1	770 mL
R2	1010 mL
R3	1190 mL

TABLE II

ELECTROLYTE COMPOSITIONS

	Dilute	Conventional
CrO_3 (g/L)	80	250
H_2SO_4 (g/L)	0.8	2.5
Ratio ($CrO_3/SO_4^{=}$)	100:1	100:1
Temperature (°C)	43	43

TABLE III

RELATIONSHIP OF THE Cr FOUND IN THE DO RINSE TO THE COMBINED THREE OTHER RINSES

Area Plated (dm^2)	Chromium in Rinses (µg/mL)		% Cr (CrO_3)
	DO	R1, R2, R3	DO Rinse
37	265	0.94	99.6
105	875	4.75	99.4
263	1925	12.5	99.3
26	300	1.4	99.5
26	275	1.26	99.5
26	2100	7.5	99.6
37	1100	0.8	99.9
79	2735	0.3	99.9
42	1815	0.46	99.9
37	1815	0.2	99.9
42	945	7.4	99.2
42	1300	8.3	99.3
42	1250	11.4	99
42	1700	0.2	99.9
42	1535	0.4	99.9
42	1758	0.6	99.9
89	3450	0.3	99.9
74	700	0.4	99.9
42	695	2.58	99.6

TABLE IV

Cr^{+6} CONTENT OF THE RINSES AFTER PLATING IN THE 80 AND THE 250 g/L CrO_3 BATHS

CrO_3 in Bath (g/L)	Panel Set	Parts Run	Cr^{+6} (mg/mL) in Rinse			
			DO	R1	R2	R3
80	A	100	107	0.7	0	0*
250			286	1.33	0	0
80	B	100	15	0.58	0	0
250			47.5	0.9	0	0
80	C	100	633	13	0.73	0.08
250			2000	47.5	1.8	Trace
80	D	100	181	0.975	0	0
280			265	1.45	0.04	0
80	E	100	312	2.23	0.25	Trace
250			850	5.5	1.075	0.375
80	F	100	243	1.2	0	0
250			307	2.1	Trace	Trace

ero values were no detection of Cr
detection limit for Cr by AA is 0.02 µg/mL).


Cathode Specimens On Conveyor
Conveyor
HCl Strip
Rinse
Chromium Plating
Drag Out Rinse
Rinses: R1, R2, R3
LOW PRESS. AIR

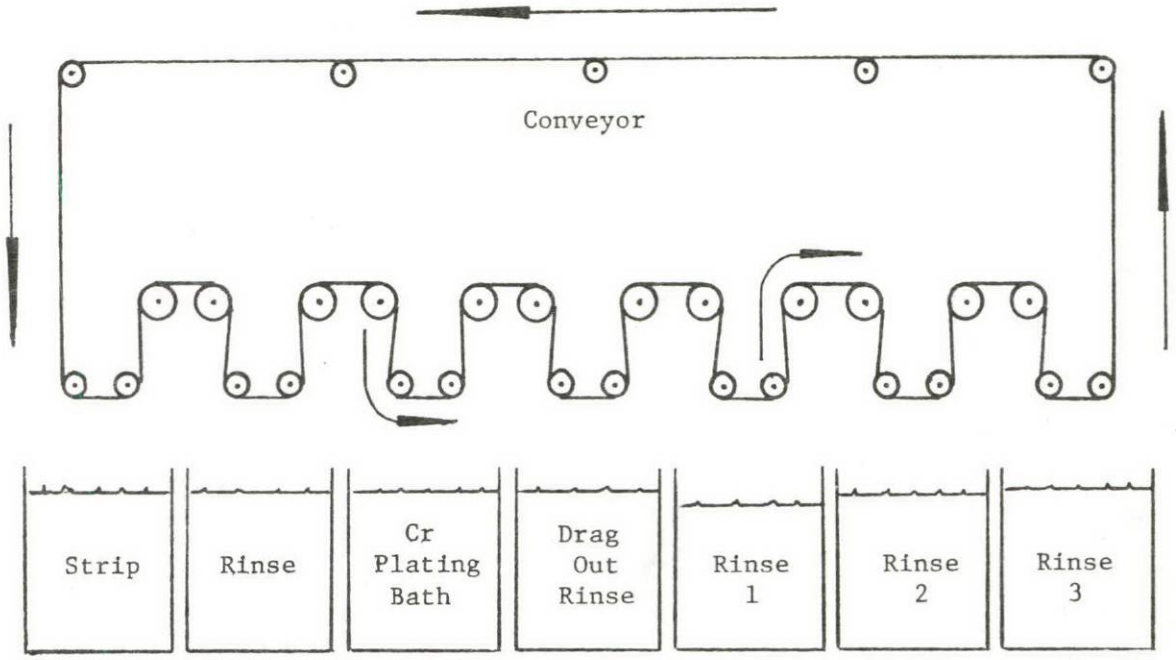


Fig. 2. Schematic of the plating conveyor and tanks.

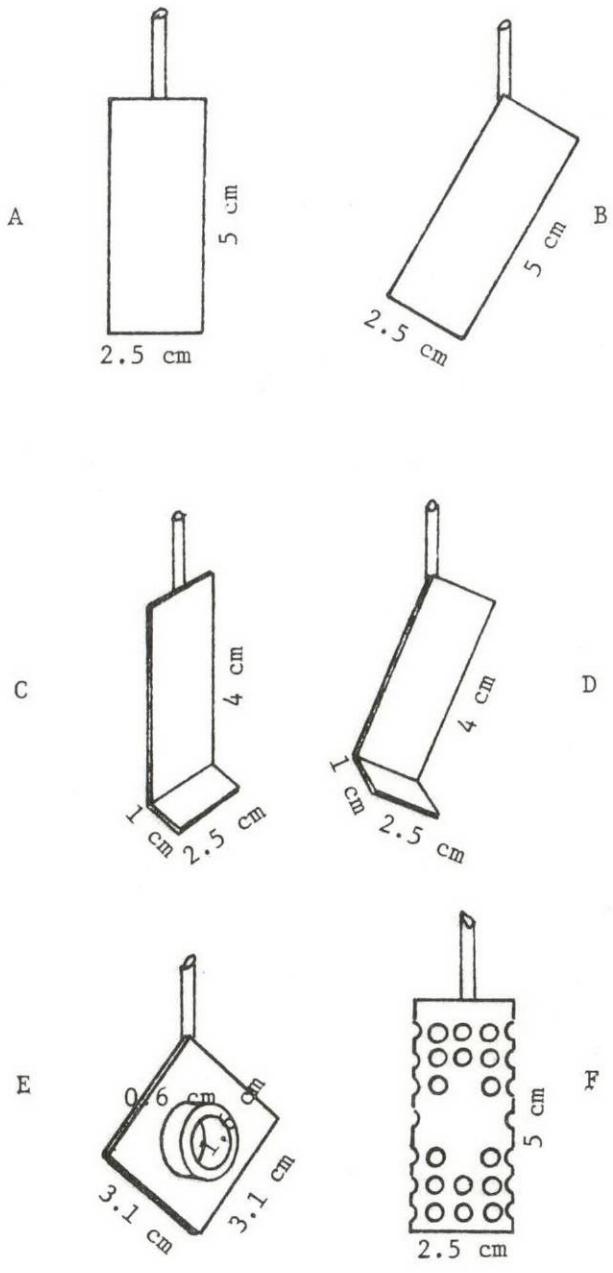


Fig. 3. Cathodes used in chromium plating drag out studies.

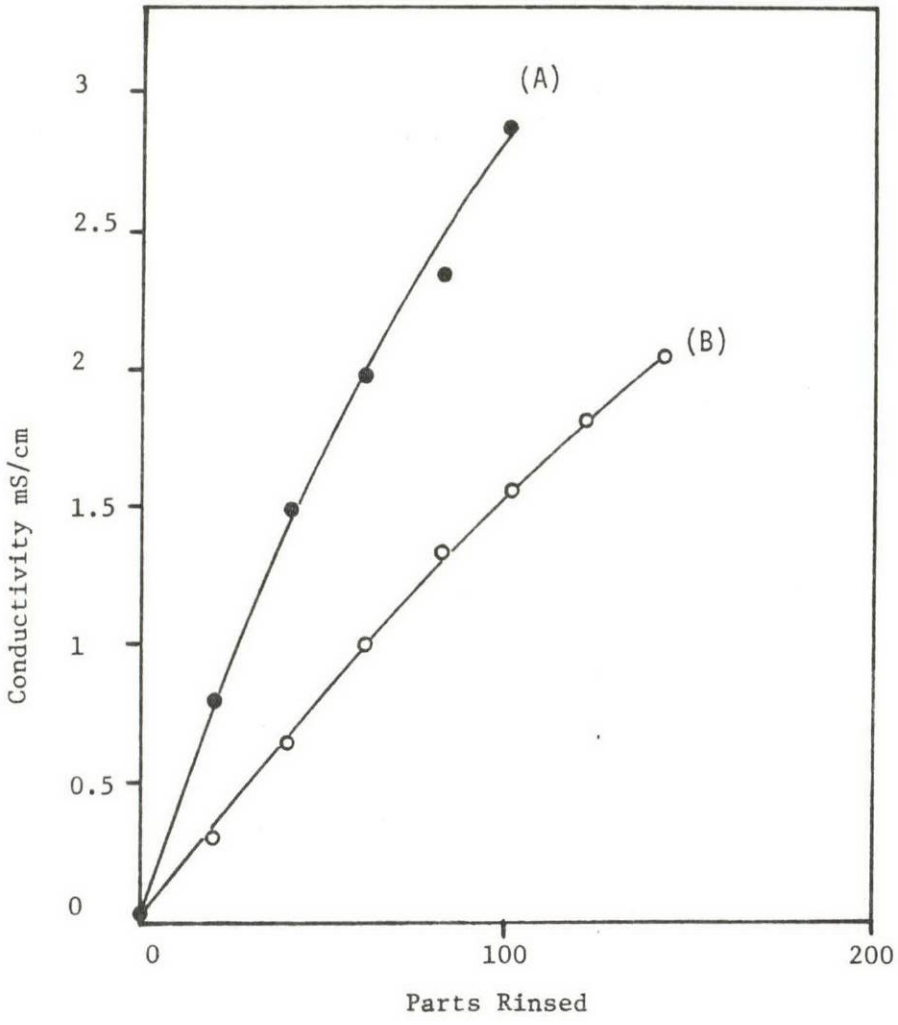


Fig. 4. Conductivity of drag out rinse vs. number of parts rinsed after plating in (A) 250 and (B) 80 g/L CrO_3 baths.

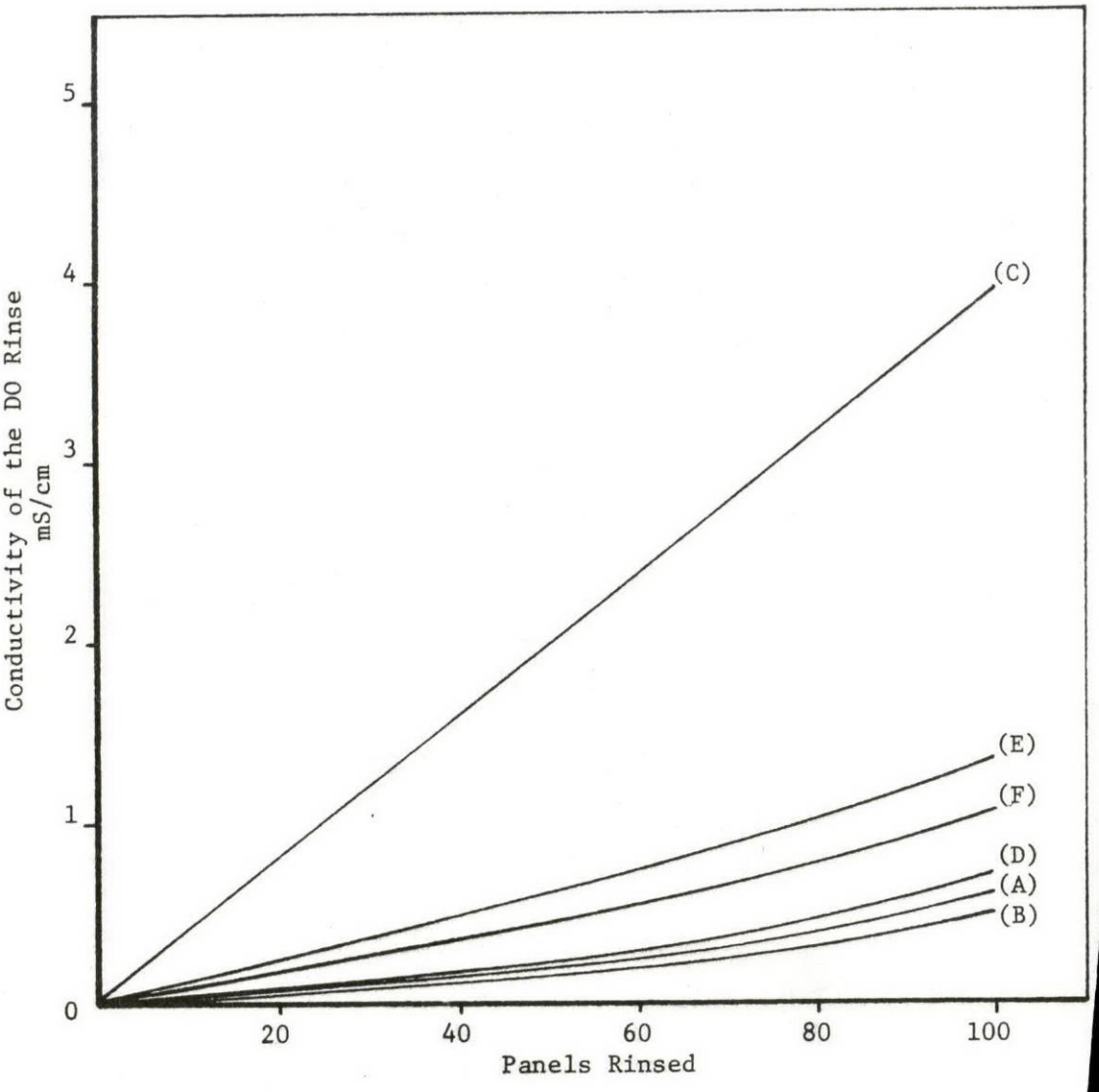


Fig. 5. Conductivities of the DO rinses vs. number of panels rinsed, after plating panel sets A-F, in the 80 g/L CrO_3 bath.

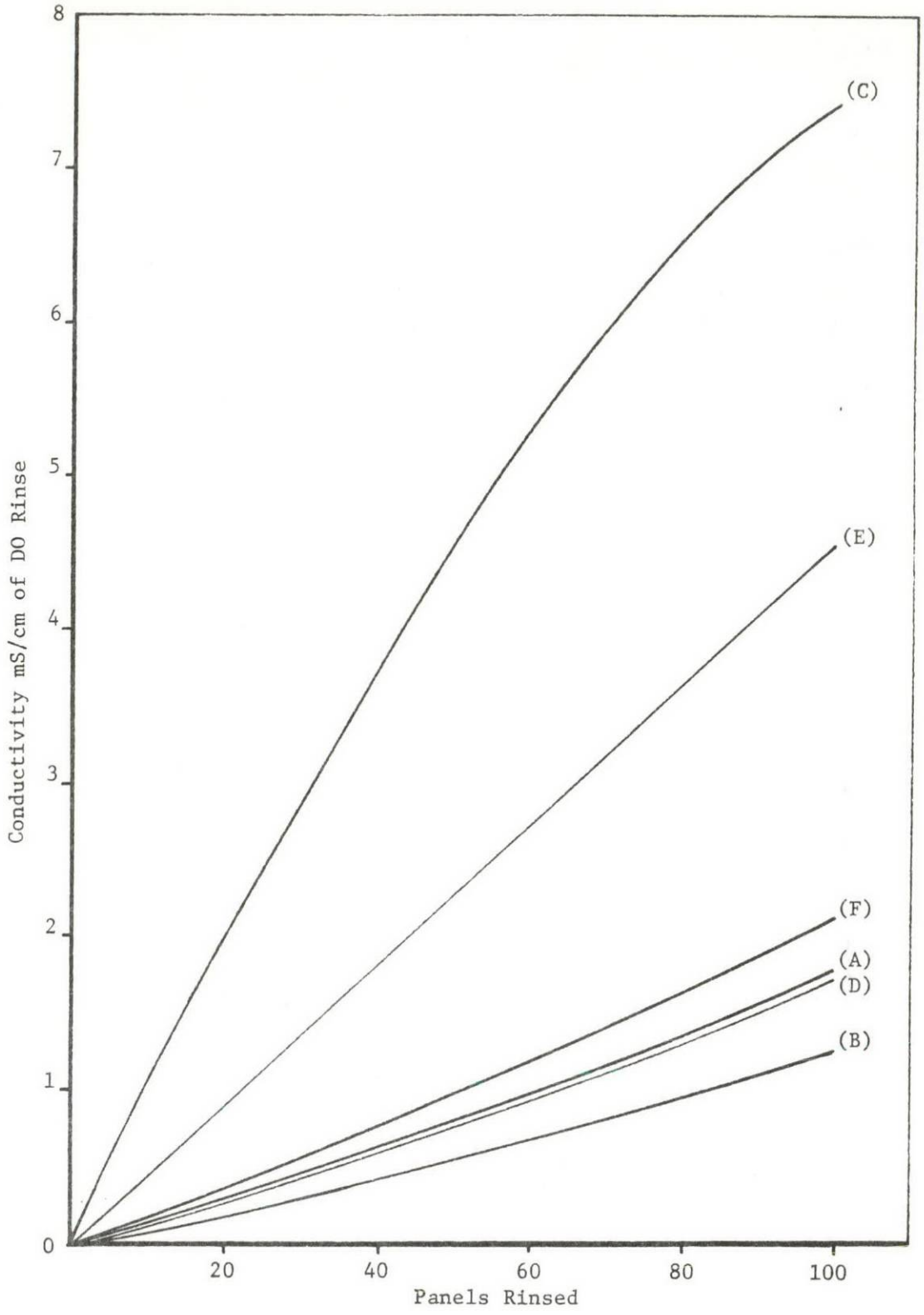


Fig. 6. Conductivities of the DO rinses vs. number of panels rinsed, after plating panel sets A-F, in the 250 g/L CrO_3 bath.

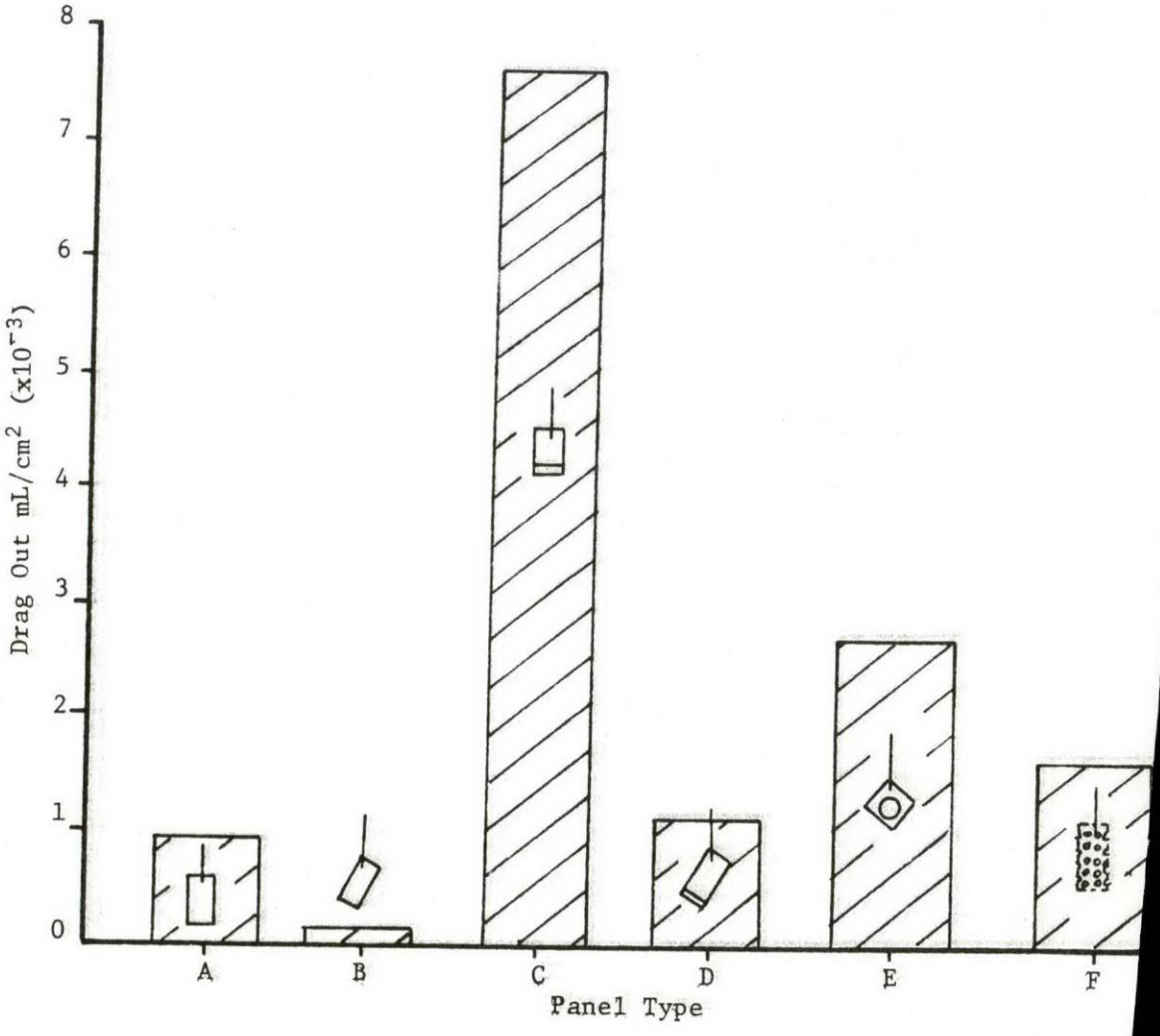


Fig. 7. Histogram of electrolyte drag out volume with each panel type.

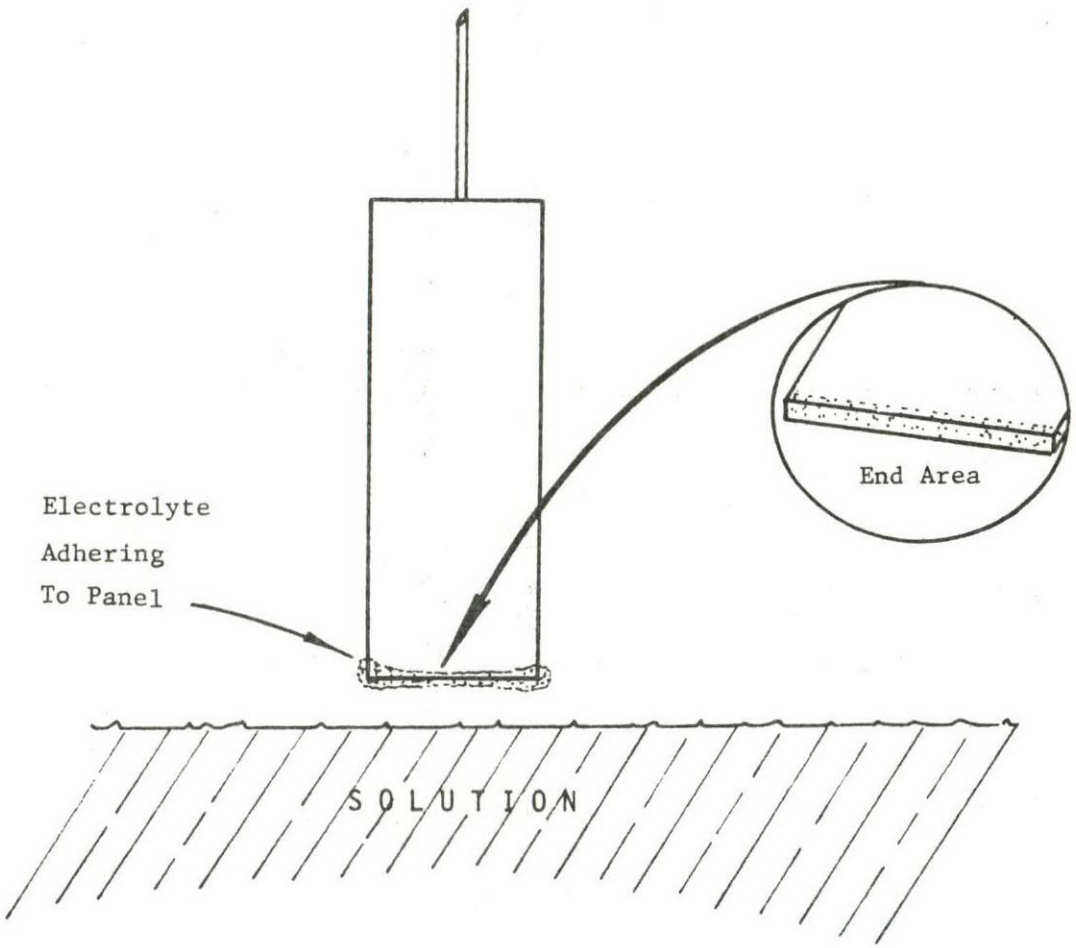


Fig. 8. Area contacting the liquid when the end of the part is parallel to the electrolyte surface during withdrawal from solution.

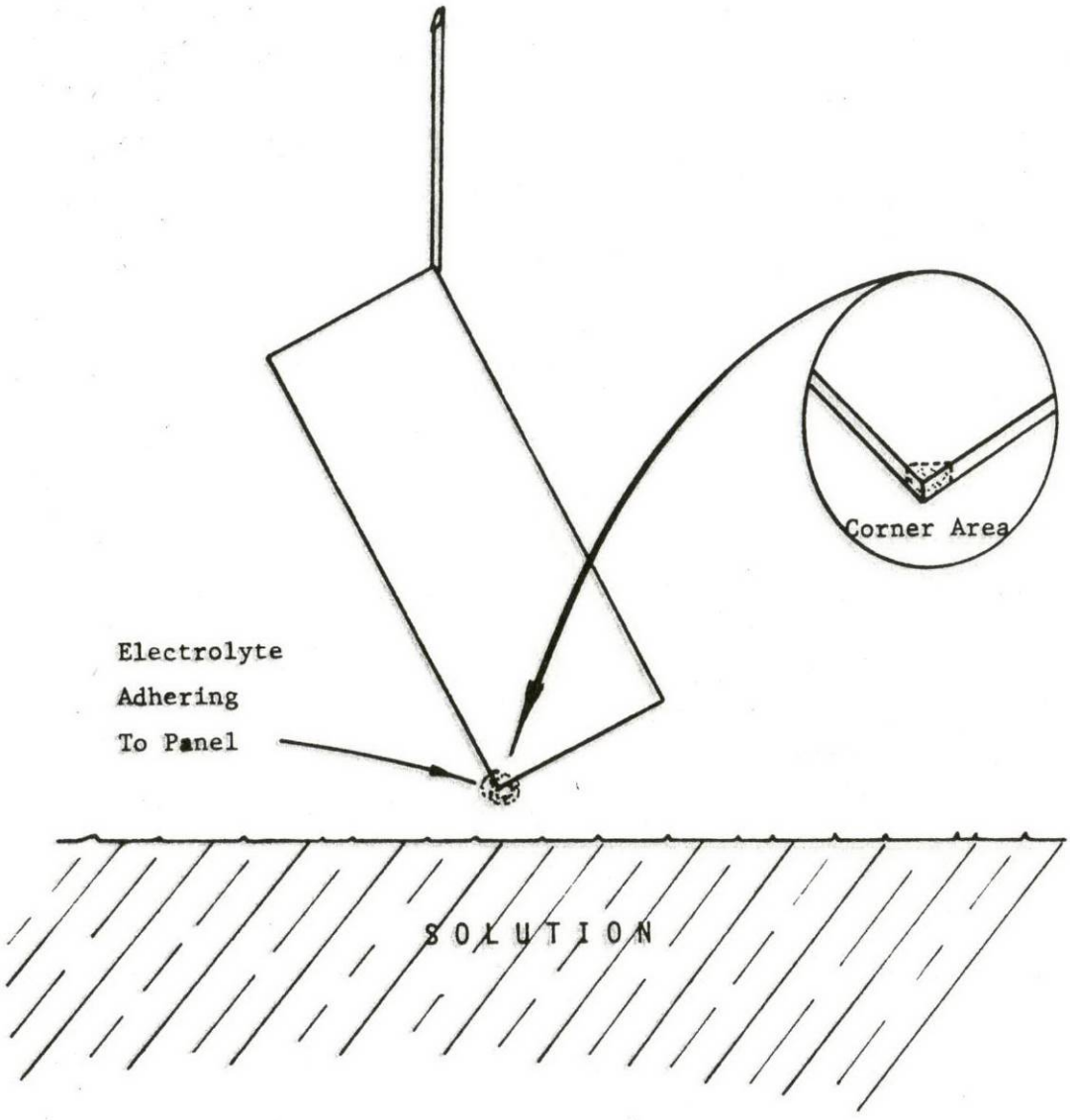


Fig. 9. Area contacting liquid surface with part tilted about 30° from the vertical during withdrawal from solution.

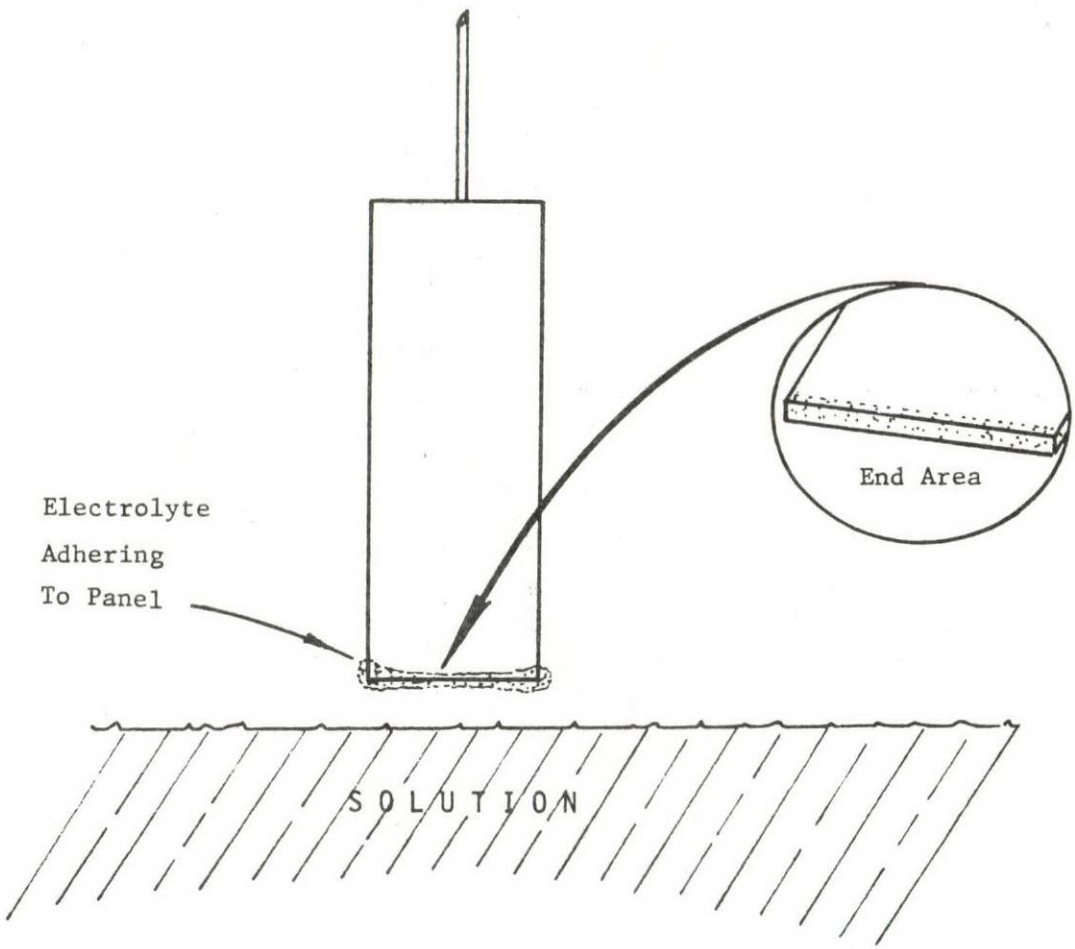


Fig. 8. Area contacting the liquid when the end of the part is parallel to the electrolyte surface during withdrawal from solution.

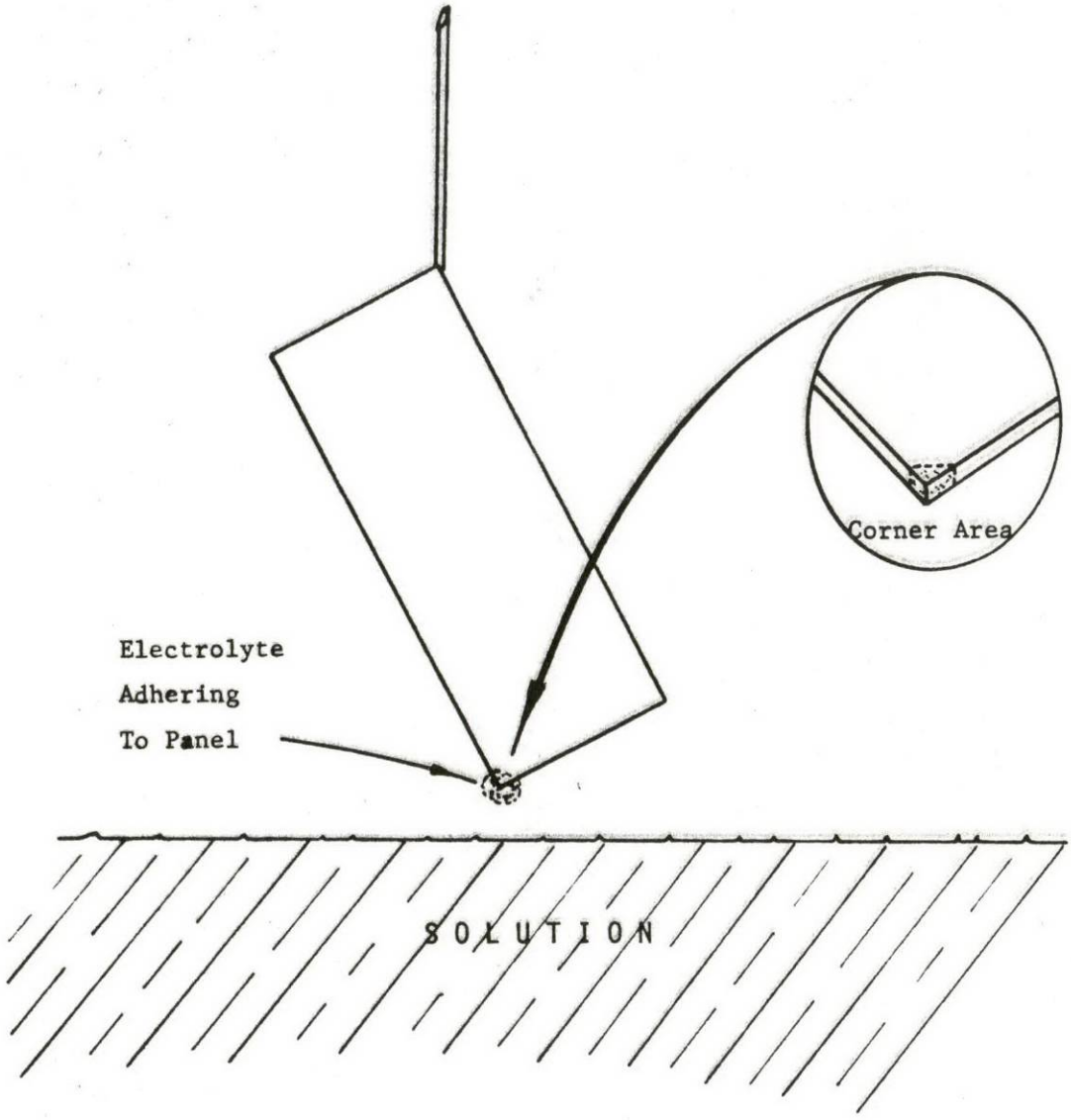
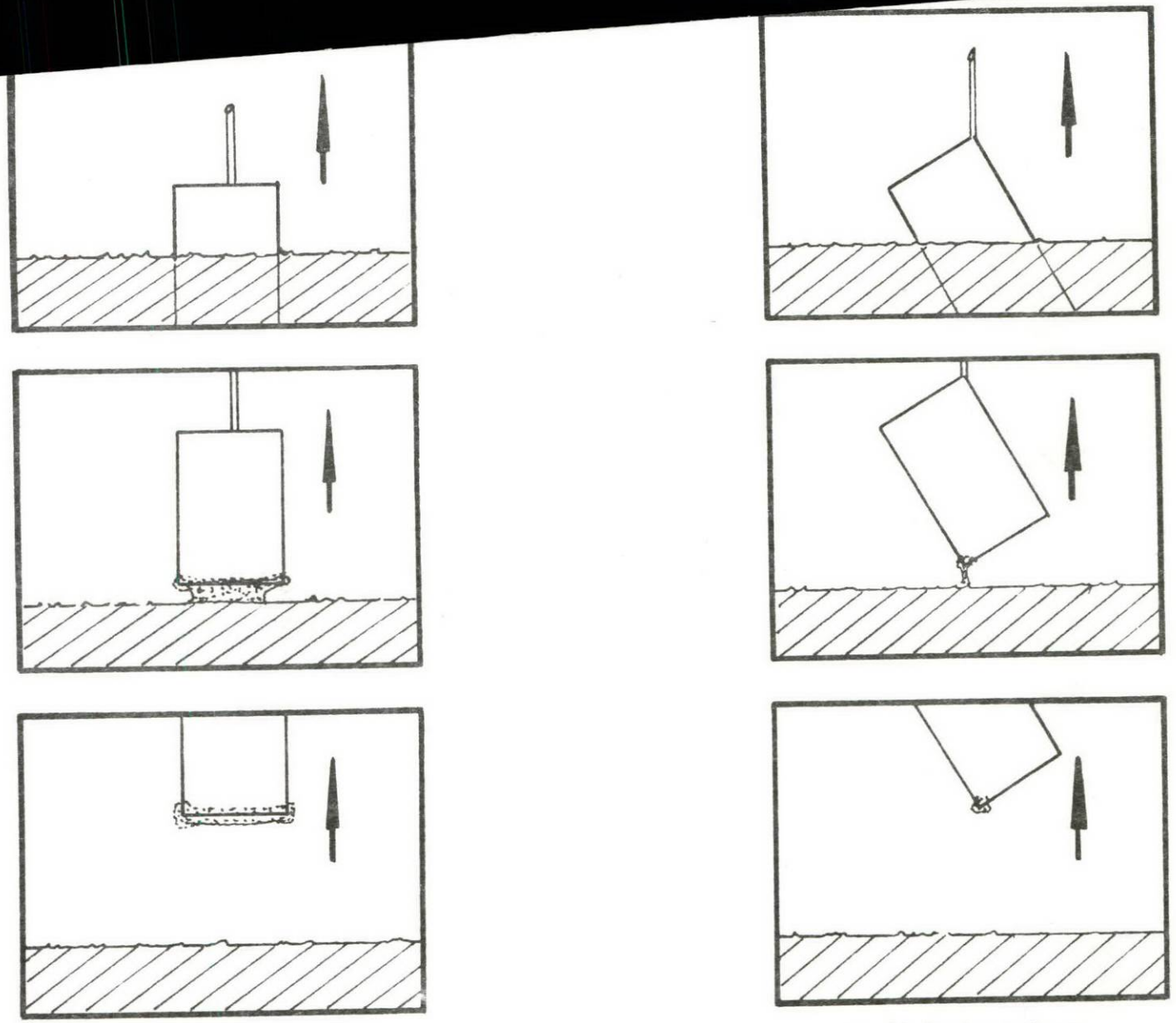


Fig. 9. Area contacting liquid surface with part tilted about 30° from the vertical during withdrawal from solution.



Large contact area

Small Contact Area

Fig. 10. Sequence during separation between the cathode and the solution surface, showing relative volumes of liquids adhering to the contact areas.

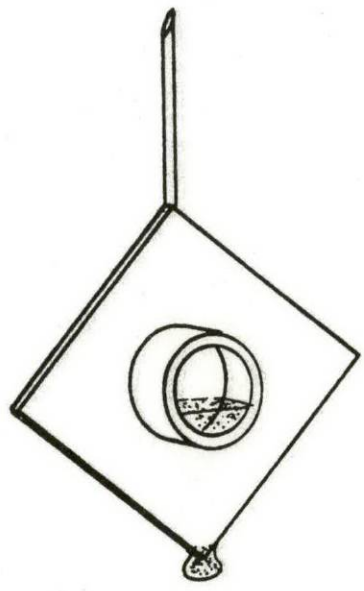


Fig. 11. Appearance of the type E panels with clinging drag out electrolyte.

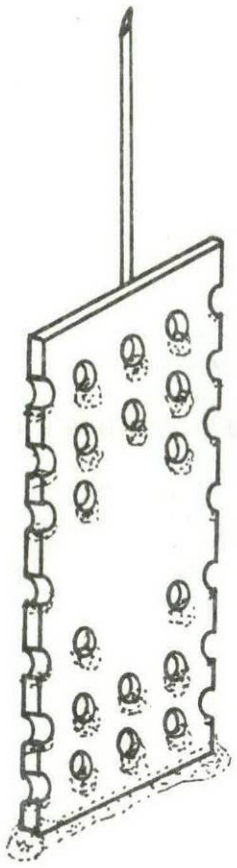


Fig. 12. Appearance of the Type F cathodes with clinging drag out electrolyte.

Figure Captions for "Solution Drag Out and Rinsing After Chromium Plating", by A. J. Wallace.

1. Apparatus for plating, drag out, and rinsing studies.

2. Schematic of the plating conveyor and tanks.

3. Cathodes used in chromium plating drag out studies.

4. Conductivity of drag out rinse vs. number of parts rinsed after plating in (A) 250 and (b) 80 g/L CrO_3 baths.

5. Conductivities of the DO rinses vs. number of panels rinsed, after plating panel sets A-F, in the 80 g/L CrO_3 bath.

6. Conductivities of the DO rinses vs. number of panels rinsed, after plating panel sets A-F, in the 250 g/L CrO_3 bath.

7. Histogram of electrolyte drag out volume with each panel type.

8. Area contacting the liquid when the end of the part is parallel to the electrolyte surface during withdrawal from solution.

9. Area contacting liquid surface with part tilted about 30° from the vertical during withdrawal from solution.

10. Sequence during separation between the cathode and the solution surface, showing relative volumes of liquids adhering to the contact areas.

11. Appearance of the type E panels with clinging drag out electrolyte.

12. Appearance of the Type F cathodes with clinging drag out electrolyte.

S-3

Environmental II
Session S

Case History Reports On Heavy Metal Removal Process

Dr. R. E. Wing
U. S. Department of Agriculture
Peoria, Illinois

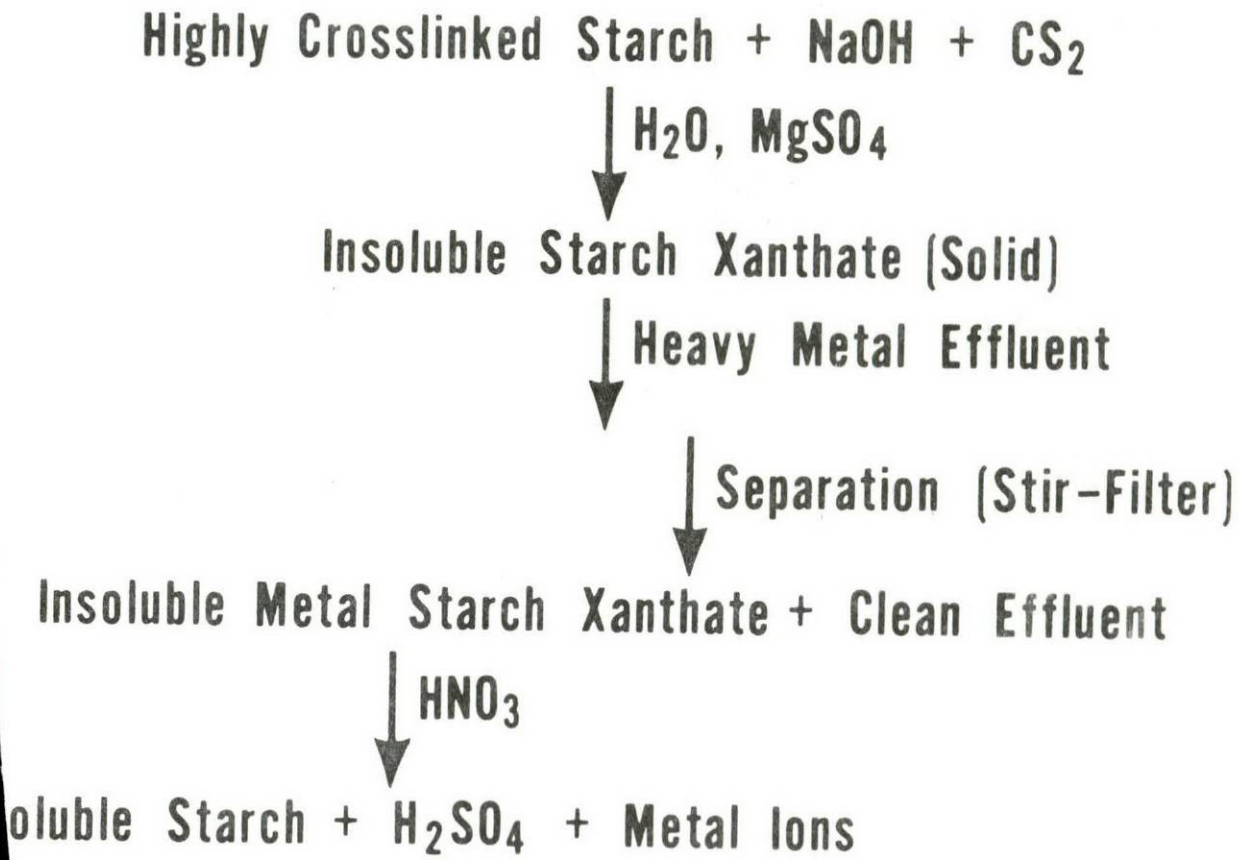


Figure 1. Preparation and use of insoluble starch xanthate (ISX).

TABLE 1. REMOVAL OF HEAVY METAL CATIONS FROM WATER WITH ISX*

Metal	Initial conc., mg/l	ISX, g	Residual conc., mg/l	Illinois discharge limit, mg/l
Ag^{1+}	53.94	0.32	0.016	0.005
Au^{3+}	30.00	0.50	<0.010	---
Cd^{2+}	56.20	0.64	0.012	0.050
Co^{2+}	29.48	0.64	0.090	---
Cr^{3+}	26.00	0.64	0.024	1.0
Cu^{2+}	31.77	0.32	0.008	0.020
Fe^{2+}	27.92	0.32	0.015	1.0
Hg^{2+}	100.00	0.64	0.001	0.0005
Mn^{2+}	27.47	0.64	0.015	1.0
Ni^{2+}	29.35	0.64	0.160	1.0
Pb^{2+}	103.60	0.64	0.035	0.100
Zn^{2+}	32.69	0.32	0.294	1.0

* Synthetic solutions (1,000 ml) containing the individual metals as the indicated concentration were treated with the indicated amount of ISX (capacity = 1.56 meq metal ion/g) at pH = 3.7. Solutions were stirred for 5-60 min at a final pH of 8.9. After filtration, the residual metals were determined by a Varian Techtron AA 120. The theoretical weight of ISX for a divalent metal is 0.64 g. Value listed with less than (<) was below detection limit.

TABLE 2. REMOVAL OF METALS FROM DILUTE SOLUTION WITH ISX*

Metal	Initial conc., mg/l	Residual conc., mg/l
Cd^{2+}	5.62	0.001
Co^{2+}	2.95	<0.010
Cr^{3+}	2.60	0.026
Cu^{2+}	3.18	<0.005
Fe^{2+}	2.79	0.001
Hg^{2+}	100.00	0.0007
Mn^{2+}	2.75	0.010
Ni^{2+}	2.93	<0.050
Pb^{2+}	10.36	<0.031
Zn^{2+}	3.27	0.007

* A synthetic solution (1,000 ml) containing a mixture of heavy metals of the indicated concentrations at pH 3.5 was treated with ISX (capacity = 1.56 meq metal ion/g, 0.32 g) to a final pH = 8.9. After filtration the residual metals were determined by a Varian Techtron AA 120. Values with less than (<) were below detection limits.

etching baths. Rinse waters from these etching operations contain the $Cu(NH_3)_4^{+2}$ complex for which most conventional treatments are ineffective. Some recent reports (20-37) are available which show that these rinse waters are treatable.

ISX (11) was evaluated (Figure 2) on several synthetic and industrial rinses, and the copper concentration was lowered from 28-54 mg/liter to less than 0.1 mg/liter. ISX precoated on filters was also successfully evaluated for these rinses.

ISX Treatment of Other Copper Complexes

Copper in complexed form (EDTA, Quadrol, tartrate, etc.) is very commonly used for electroless plating in alkaline solutions. Treatment of rinse waters from these plating baths has caused considerable problems. Recently (11) ISX was evaluated for copper removal from these rinses, and Figures 3-4 show its effectiveness. Acidification of the rinse in the range of pH 3-6 assists in weakening or dissociating the bonds of the copper complex, and allows more complete removal (Figure 3). Figure 4 shows copper removal by various amounts of ISX. The best results with copper-Quadrol rinses were always obtained when the rinse was adjusted to pH 3, ISX added, and pH readjusted to 3.

Chromium (VI) Removal with ISX

Commercial anion exchange resins containing tertiary amine and quaternary ammonium groups are very useful in removing heavy metal anions from industrial wastewater. Initial cost to install these exchange resin systems has limited the industrial application of this anti-pollution technique. The main reason for the high cost is that these resins are petrochemically based; because of the present petrochemical shortages, these products will likely increase in cost and may even be limited in supply.

A possible solution to this cost problem might be to use a naturally occurring, annually renewable, low-cost polymer such as starch. Previously we have shown that cationic starches were effective in chromium(VI) and ferro- and ferri-cyanide removal (7,13).

The use of chromates and dichromates in plating and as corrosion control agents in cooling water systems is quite extensive. Chromium(VI) is very toxic and must be removed from industrial wastewaters before discharge. Chromium(VI) level allowed in waste effluents which are discharged to natural waterways has been established at a maximum concentra of 0.09 mg/l. Rinse waters of plating operations may vary in composition, but they usually contain 20-100 mg/l Cr^{+6} and have a pH of 2-3. These rinses are treated for three reasons: (1) pollution control, (2) water reuse, and (3) Cr^{+6} recovery.

Treatment for Cr^{+6} usually involves chemical reduction to Cr^{+3} with sulfur dioxide, sodium bisulfite, sodium metabisulfite, or ferrous salts at pH 2-3 (38-42). The Cr^{+3} is then precipitated at alkaline pH's as the hydroxide with caustic or lime. Nonreductive treatments of Cr^{+6} include anion exchange (43-48) and activated carbon (49).

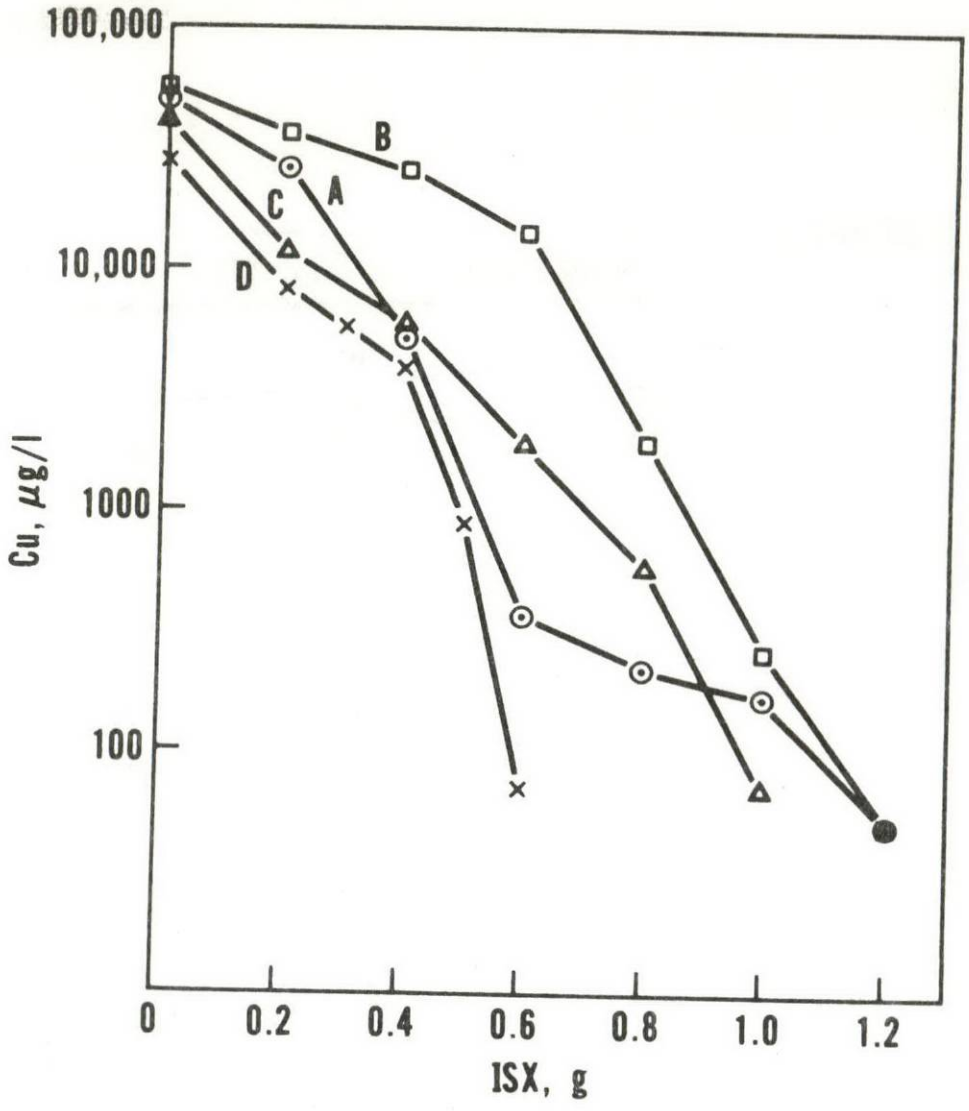


Figure 2. Copper ammonia complex removal with ISX.

pper ammonia complex solutions (1000 ml) were treated with increasing ounts of ISX (capacity = 1.5 meq metal ion/g). Aliquots (10 ml) of e supernatant were removed for copper analysis 5 min after each addition. eoretical weight required is 1.02 g for the 50 mg/l copper ammonia ution.

Curve A. $Cu(NH_3)_4^{2+}$ standard solution (50 mg/l as Cu-initial); oretical weight ISX required is 1.02 g.

Curve B. $Cu(NH_3)_4^{2+}$ commercial rinse (53.63 mg/l Cu-initial); retical weight ISX required is 1.09 g.

Curve C. $Cu(NH_3)_4^{2+}$ commercial rinse (41.77 mg/l Cu-initial); retical weight ISX required is 0.85 g.

Curve D. $Cu(NH_3)_4^{2+}$ commercial rinse (28.35 mg/l Cu-initial); etical weight ISX required is 0.58 g.

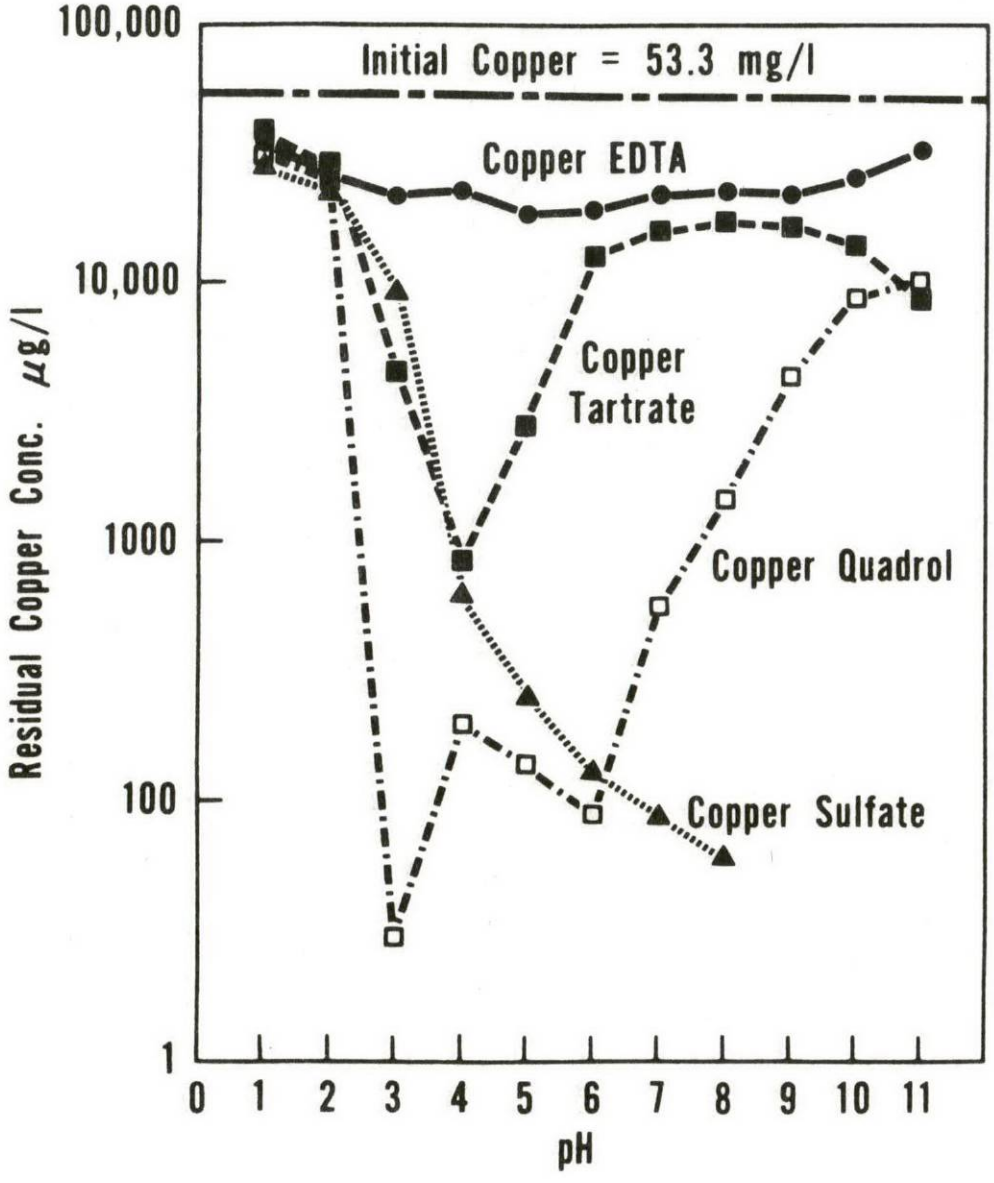


Figure 3. Treatment of copper complexes with ISX vs pH.

Solutions (1000 ml) containing copper (53.3 mg/1) in complexed form were adjusted to the indicated pH. ISX (1.0 g, 1.5 meq metal ion/g) was added and the pH was readjusted. After 30 min, aliquots were removed and filtered for residual copper analysis.

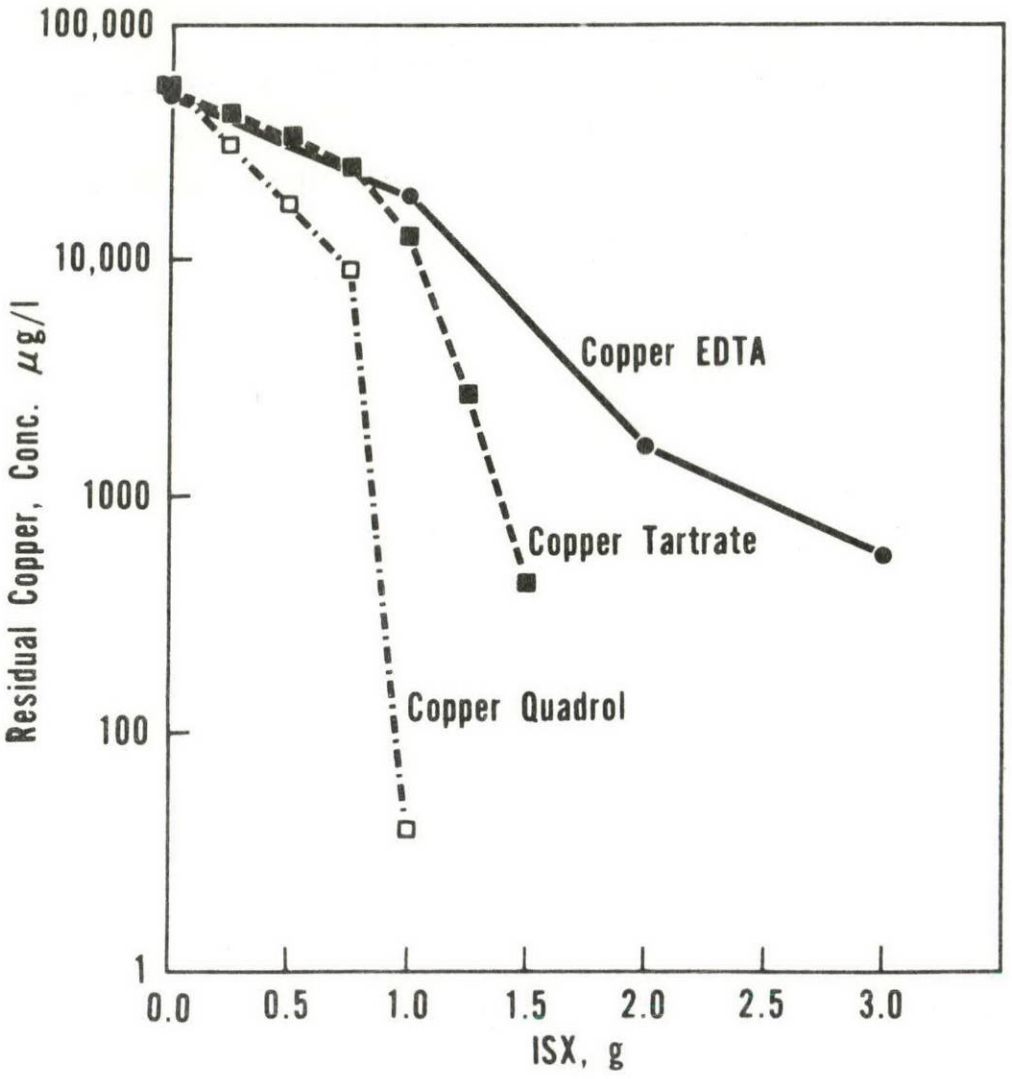


Figure 4. Treatment of copper complexes with ISX.

Solutions (1000 ml) containing copper (53.3 mg/l) in complexed form were adjusted to pH 3 for quadrol, pH 4 for tartrate, and pH 5 for EDTA. ISX (1.5 meq metal ion/g) was added in the quantities shown. After 30 min, aliquots were removed and filtered for residual copper analysis.

ISX was evaluated in Cr^{+6} removal with surprising results. Since ISX and chromium(VI) species are both negatively charged, it would seem unlikely that any removal would occur. Figure 5 shows that optimum removal occurs below pH 3 after subsequent neutralization to pH 8. The following equation shows that in acidic media an oxidation-reduction occurs which allows chromium removal with ISX. Upon neutralization to

$$2CrO_4^{-2} + 16H^+ + 6\ \underset{\text{ISX}}{\text{Starch-O-}\overset{\overset{S}{\|}}{C}\text{-S}^-} \longrightarrow 2Cr^{+3} + 8H_2O + 3\underset{\text{Starch xanthide}}{(\text{Starch-O-}\overset{\overset{S}{\|}}{C}\text{-S-})_2}$$

pH 8 with caustic, the chromium(III) is removed as the chromium(III) starch xanthate or chromic hydroxide. An advantage of this process is that as the pH is raised above 7, the starch xanthide reconverts into ISX to aid metal removal. Figure 6 shows the extent of chromium(VI) removal with increasing amounts of ISX, whereas Figure 7 shows the rate of the chromium(VI) to chromium(III) reduction. Similar results were obtained for dichromate and selenium removal with ISX (50).

ISX Case History Report

A plating company in the Northeast has been making and using ISX for 3 years as a filter precoat to treat rinse waters from three plating lines. Residual metal concentrations after the rinses are passed through the ISX-filters are copper (0.06 mg/liter), nickel (0.57 mg/liter), and tin-lead (0.33 mg/liter-0.09 mg/liter). The water is recirculated from the three filters back to the rinse tanks for reuse. ISX has saved the company as much as $180,000 over conventional treatment systems.

ISX is commercially available in solid form from at least one supplier. Another company is promoting the on-site preparation of ISX to be used in conjunction with precoated filters for heavy metal removal. A 2-week evaluation last summer at a company that discharges 0.2 mg Cu/liter at 300 liters/minute showed a lowering to 0.01 mg Cu/liter when ISX was incorporated. Incorporation of the ISX process at this plant would cost less than $600 for equipment and treatment facility modification. The weekly chemical cost would be approximately $10. Figure 8 shows that ISX has limited stability in solution, so it would have to be prepared every few days and diluted daily for use.

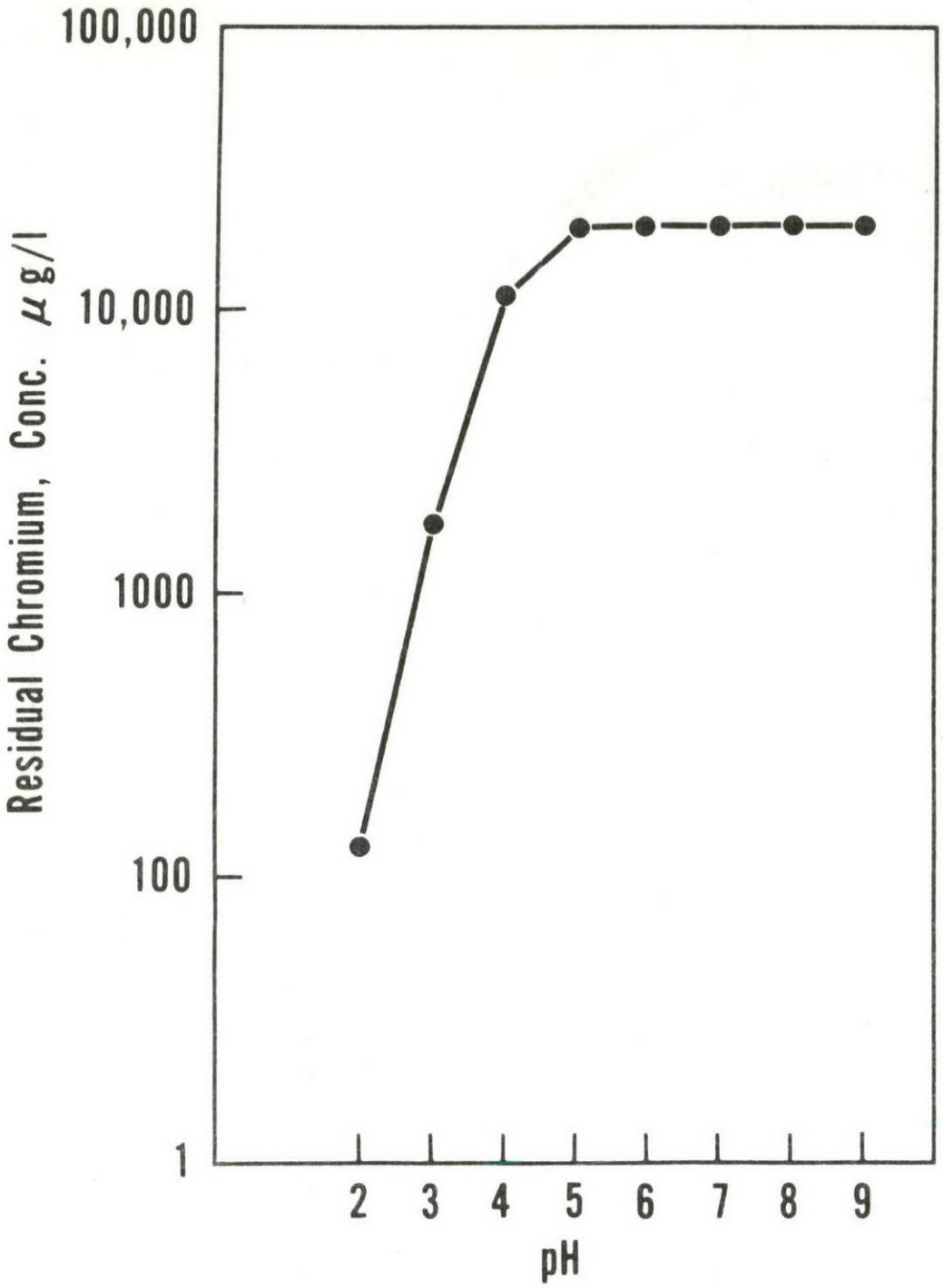


Figure 5. Effect of pH on chromium(VI) reduction with ISX.

Solutions (1000 ml) containing chromate (20 mg/l as Cr^{+6}) were adjusted to the indicated pH. ISX (1.0 g, 1.5 meq metal ion/g) was added and the pH was readjusted. After 30 min, the pH was raised with caustic to 8.0 and aliquots were removed and filtered for chromium analysis.

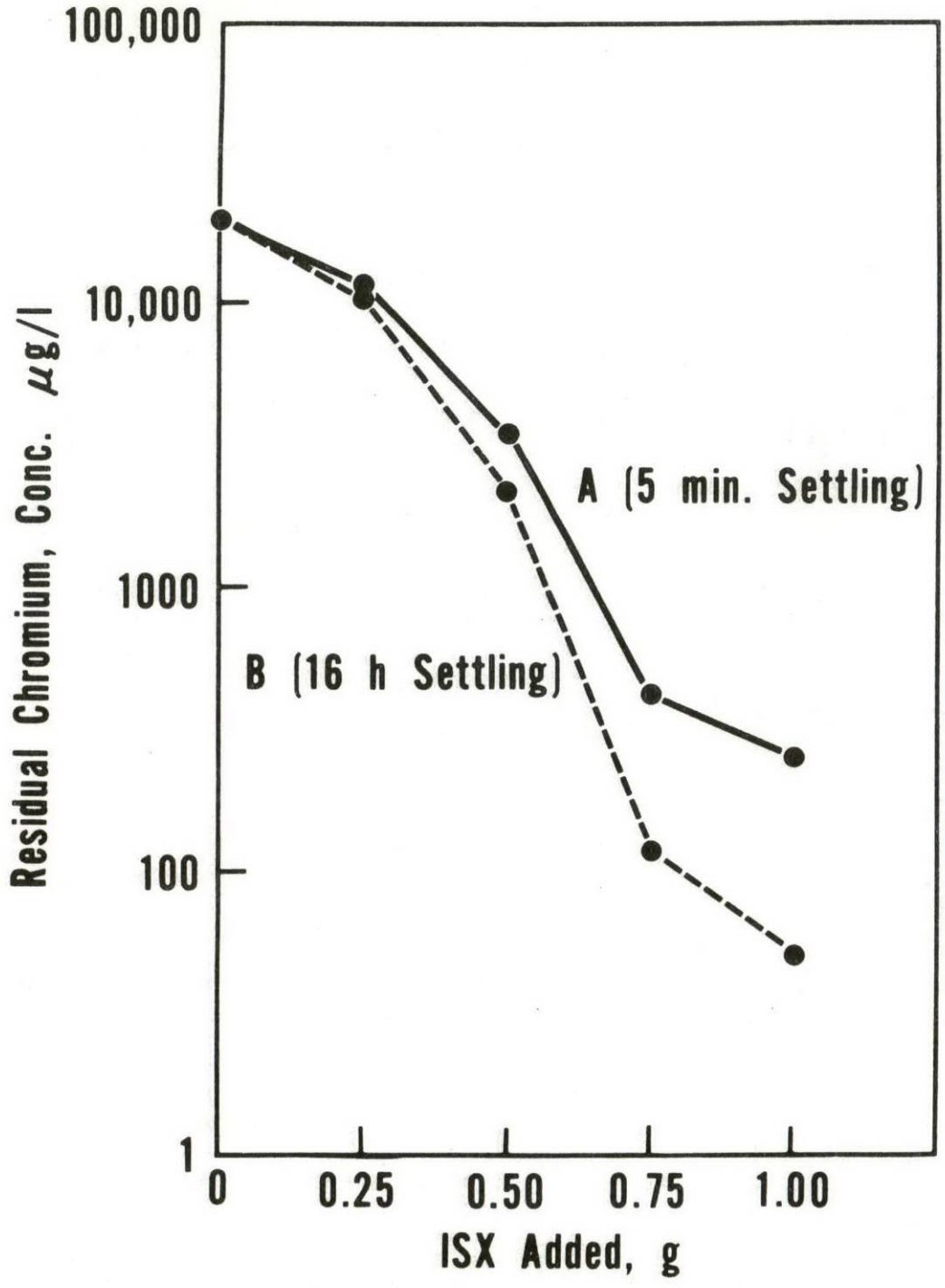


Figure 6. Effect of chromium(VI) removal with ISX.

Solutions (1000 ml) containing chromate (20 mg/l as Cr^{+6}) were treated with the indicated amounts of ISX at pH 2.5. After 30 min, the solutions were adjusted to pH 8.0 with caustic and aliquots were removed and filtered for residual chromium analysis.

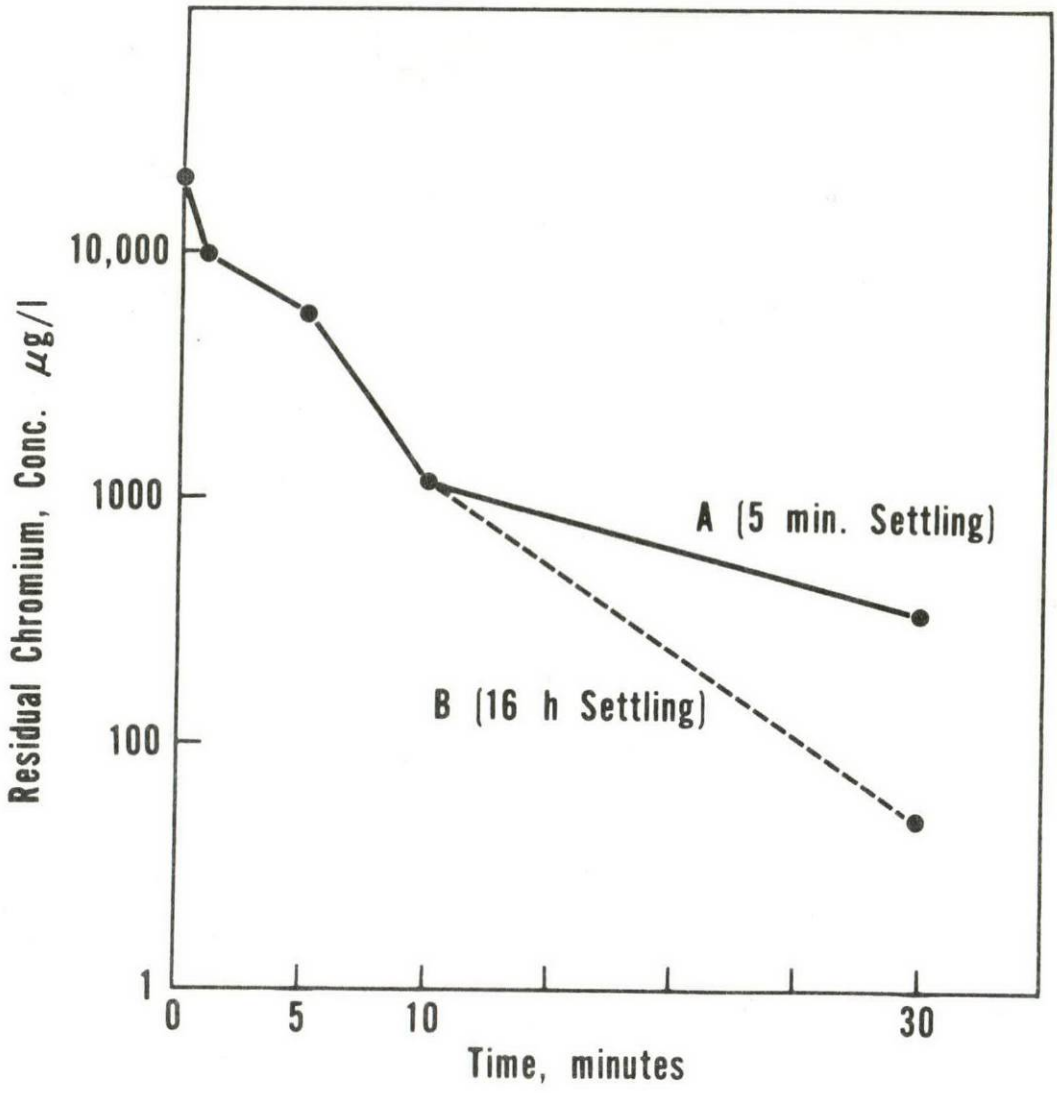


Figure 7. Chromium(VI) reduction rate with ISX.

Solutions (1000 ml) containing chromate (20 mg/l as Cr^{+6}) and ISX (1.0 g, 1.5 meq metal ion/g) were stirred at pH = 2.5 for the indicated time. The solutions were adjusted to pH 8.0 with caustic and aliquots were removed and filtered for residual chromium analysis.

High pH-Lime Treatment of Electroless Copper Plating Rinse Waters

The electroless plating of copper on printed circuit boards and plastics is usually an autocatalytic formaldehyde reduction of a complexed alkaline copper (51-55). Suppliers to the plating industries use proprietary organic complexing agents for copper. For concentrated plating baths (55), treatments such as (a) raising the temperature to 50-65°C, (b) adding excess formaldehyde (1.5%) (56), (c) adding palladium activator (1-50 mg/liter) (56), and (d) lowering the pH have all been used successfully in decomposing the copper complexes. After plating is completed, it is necessary to rinse the plated articles. The rinse waters derived therefrom contain complexed copper which must be removed to prevent possible undesirable ecological effects as a result of introducing the copper to receiving waters or biological sewage treatment systems. These rinses usually contain 20-100 mg/liter of complexed copper around pH 10.9. Usual chemical treatment is not effective on these rinse waters; therefore, special treatments are required that involve segregation of these solutions from the main process waters. Recently a treatment method for removal of copper from these complexed copper rinse solutions was reported (24,57,58). Other reports on the treatment of spent baths, rinses, and chelants have also appeared (59-80).

The treatment involves the addition of a soluble calcium compound, i.e., calcium hydroxide, lime, calcium chloride, or calcium sulfate, to the rinse at pH 11.6-12.0 to precipitate copper hydroxide. The structure of the complexing agents determines the effectiveness of treatment. The order of copper removal for several complexing agents is EDTA > NTA > HEDTA > NDA > tartrate ∿ citrate > gluconate. The replacement of an acetate by a hydrogen or a hydroxyl diminishes removal of copper considerably Tables 3 and 4 show copper removal data from synthetic and actual industrial rinse baths.

Some general observations and comments about this treatment process are:

(a) Good removal is obtained over a pH range of 11.6-13.5 in the presence of excess calcium ion (greater than 2.5 mmoles calcium ion/1.0 mmo copper).

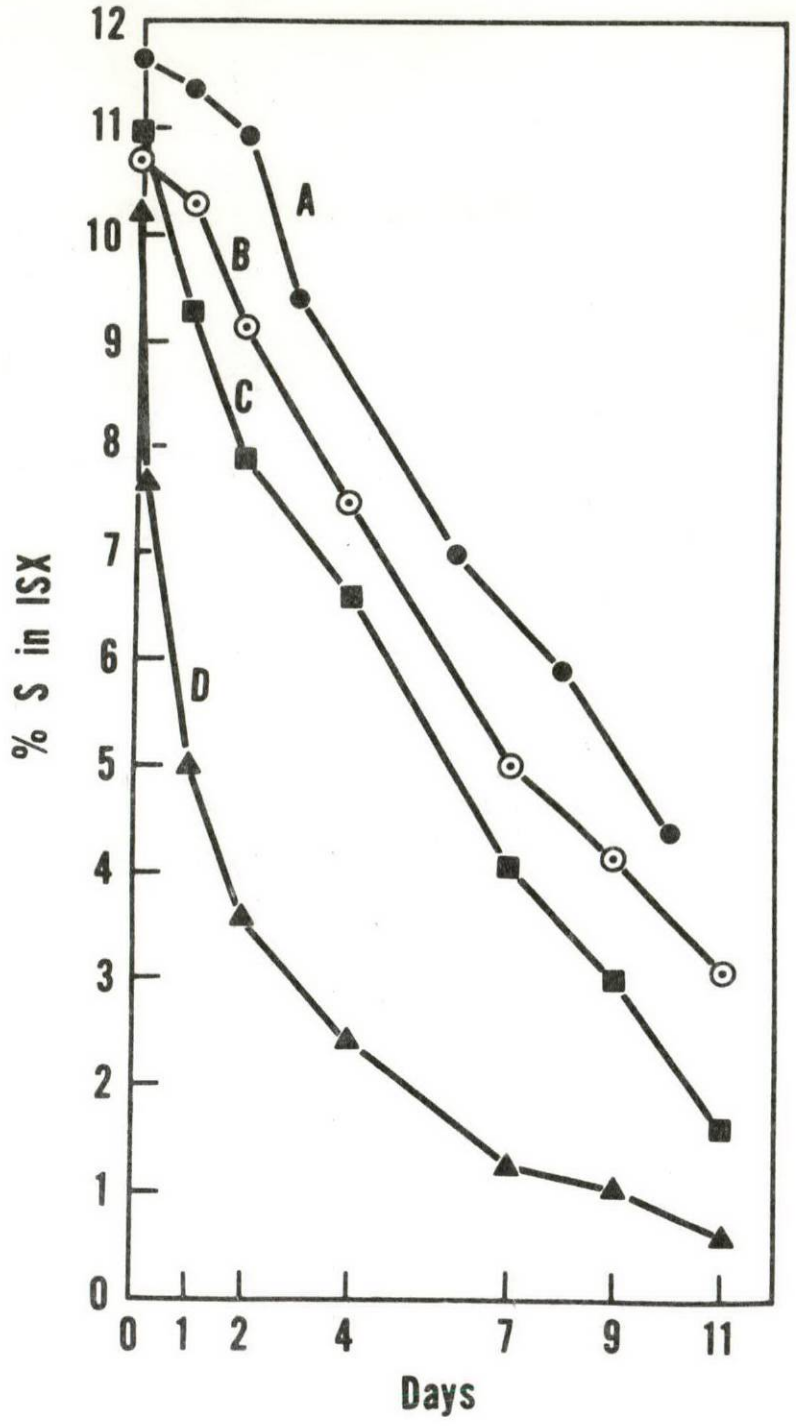


Figure 8. ISX storage stability in solution.

ISX samples were prepared and were stored under the following conditions. Samples were worked-up on the indicated days and the remaining capacity determined (as % S).

A. Reaction mixture as is.

B. Reaction mixture diluted with water.

C. Reaction mixture diluted with water and magnesium sulfate.

D. Isolated ISX reslurried.

TABLE 3. COPPER REMOVAL FROM COPPER-EDTA COMPLEX

Initial* copper conc., mg/l	Calcium salt	Weight of salt, g	Final pH	Polymer mg/l	Residual† copper conc., mg/l
50.0	CaO	0.50	11.6	1.5	0.14
50.0	$CaCl_2$	0.75	11.6	1.5	0.20
50.0	$CaSO_4$	0.92	11.7	1.5	0.44
50.0	$Ca(OH)_2$	0.50	11.7	1.5	0.09
5	$Ca(OH)_2$	0.50	11.7	1.5	0.10
100	$Ca(OH)_2$	1.00	11.6	1.5	0.06
1,910‡	$Ca(OH)_2$	1.29	12.0	2.0	3.40

* Solutions (1,000 ml) of the indicated copper conc. were treated with the solid calcium compound. After stirring 5 min, the solutions were flocculated with polymer (anionic) and were filtered after 15 min settling.

† Determined using a Varian Techtron AA 120 spectrophotometer.

‡ Stock solution (250 ml).

TABLE 4. COPPER REMOVAL FROM OTHER COPPER-COMPLEXES

Complex*	Initial† copper conc., mg/l	Calcium hydroxide, g	Final pH	Residual‡ copper conc., mg/l
NTA	50	0.50	11.7	0.06
HEDTA	50	0.50	11.8	1.73
NDA	50	0.50	11.7	2.86
Tartrate	50	0.50	12.3	13.48
Citrate	50	0.50	12.1	9.01
Gluconate	50	0.50	11.8	23.88
A	50	0.46	11.7	0.32
B	50	0.48	11.7	12.03

* NTA = Nitrilotriacetic acid; HEDTA = N-Hydroxyethylethylenediaminetriacetic acid; NDA = Nitrilodiacetic acid; A = MacDermid sample; B = Shipley sample.

† Solutions (1,000 ml) were treated with solid calcium hydroxide. After stirring 5 min, the solutions were flocculated with polymer (anionic, 1.5 mg/l) and were filtered after 15 min settling.

‡ Determined using a Varian Techtron AA 120 spectrophotometer.

(b) Treatment is effective over the temperature range of 20-60°C.

(c) Treatment is effective on concentrated baths as well as rinse solutions; however, it is ineffective on copper-Quadrol rinses.

(d) Use of an anionic polyelectrolyte (1.5 mg/liter) aids in copper removal by promoting rapid settling of the copper hydroxide.

(e) Analysis of the sludge shows it to be mainly copper hydroxide, except in the case of the tartrate rinse (calcium tartrate has limited solublility).

(f) Copper hydroxide sludge could be reprocessed to help defray cost of treatment.

(g) Treatment can be conducted batchwise and probably could be operated continuously.

(h) Chemical cost of treatment for a 50 mg/liter copper-EDTA rinse with lime and polymer would be about $0.07/3,785 liters.

The supernatant after treatment would still contain a calcium complex that should have a much lower toxicity and could be biodegradable. If desired, the residual Ca^{2+} in the treated rinse could be removed by carbonation with carbon dioxide, which would also give a concomitant lowering of pH to make the effluent more acceptable for discharge. Care should be taken in discharge of the calcium complex effluent, since the complexing agent will combine with other heavy metal ions if the pH is lowered when these segregated streams are treated further (i.e., in a clarifier with other process waters) or are discharged to streams or sewers. Oxidants, i.e., ozone-UV, could be used in decomposing the organic chelants to prevent recomplexation with other heavy metals. However, several recent reports (81-84) show that copper in a complexed form, i.e., with EDTA, NTA, or pyrophosphate, is significantly less toxic than free copper ion.

Formate, a byproduct of formaldehyde catalyzed electroless copper baths, does not interfere with copper removal in this treatment and would remain soluble as calcium formate. The addition of small amounts of ISX (24), sulfide ion (60), dithiocarbamates (85), or mercaptobenzothiazole (86) after the lime treatment results in further copper removal.

High pH-Lime Treatment Case History Report

Recently, an electroless copper plating rinse from a large company was evaluated which contained copper (173 mg/liter) and nickel (51.9 mg/lite as the tartrate complex. After treatment with high pH-lime, the residual copper was 0.3 mg/liter and the nickel was 0.1 mg/liter. These results were unexpected, since treatment of standard copper tartrate complexes only resulted in 60-80% copper removal.

The company made the decision to install hardware for the high pH-lime treatment process (January 1977 start-up). At considerable expense, they had evaluated reverse osmosis (RO), electrochemical, low pH-lime, sodium borohydride, and other techniques. They were using sodium borohydride reduction until the more economical and more effective high pH-lime treatment was installed. They now use a premixed lime-calcium chloride slurry to have a higher calcium ion concentration, and they modify the mixture daily depending on the copper-nickel concentrations. Their electroless copper rinse water (40,000 liters/day) initially contains copper (50-300 mg/liter) and nickel (0-150 mg/liter); after the high pH-lime-polymer treatment to pH 11.5-12.0, the residual concentrations are 0.04-0.3 mg/liter copper and 0.03-1.0 mg/liter nickel, which satisfies the river discharge limit of 1.0 mg/liter for each metal. The sludge is hauled away to an approved landfill.

Another company, using EDTA solutions to periodically backflush RO membranes after copper tartrate rinse water purification reports excellent copper removal using the high pH-lime treatment. Initial copper concentrations (50-200 mg/liter) are adjusted to pH 10-11.5 with caustic, lime is added to pH 12.3, and after anionic polyelectrolyte flocculation the residual copper concentration is <0.1 mg/liter.

Ferrous Sulfate Treatment of Electroless Copper Rinse Waters

Since several electroless copper rinse waters from commercial baths (Quadrol-type) were untreatable by the high pH-lime method, investigations were made to develop an effective treatment process for all types of electroless copper rinses (87). It was found that if the pH of the rinse was lowered to where the complex dissociates, ferrous sulfate was added and the solution was neutralized to a pH greater than 9, effective copper removal was obtained (Table 5). This treatment is effective because the ferrous ion reduces Cu^{+2} to Cu^{+1} and when the pH is raised the copper won't recomplex. Acidification assists in weakening or dissociating the bonds in the copper complex; this is evidenced sometimes by a color change in the rinse from pale blue to colorless. The color change is a useful guide to the amount of acid required for the pH adjustment; if companies have rinses that turn colorless, acid would have to be added only to that pH. Several rinses have been treated effectively without prior acidification.

As the copper concentration of the rinse increases (10 mg/liter to 1,000 mg/liter), the Fe^{+2}/Cu^{+2} ratio can be lowered from 8.0 to 1.0 for effective treatment. This fact is especially important from an economic point of view. Since several companies are going more to counter flow rinsing techniques for water use reduction, the copper complex concentration

TABLE 5. COPPER REMOVAL FROM COPPER-QUADROL COMPLEX--DETERMINATION OF AMOUNT OF FERROUS SULFATE REQUIRED AND EFFECT OF BASE*

Copper conc., mg/l	Adjusted pH	$FeSO_4 \cdot 7H_2O$, g	Fe^{2+}/Cu^{2+}	Base	Residual copper conc.,† mg/l	Residual iron conc.,† mg/l
50	2.7	0.3	1.2	$Ca(OH)_2$	33.0	4.74
50	2.7	0.4	1.6	$Ca(OH)_2$	15.5	8.70
50	2.7	0.5	2.0	$Ca(OH)_2$	0.58	9.46
50	2.7	0.75	3.0	$Ca(OH)_2$	0.16	5.68
50	2.7	1.0	4.0	$Ca(OH)_2$	0.01	2.68
50	2.7	0.5	2.0	NaOH	1.25	8.42
50	2.7	0.75	3.0	NaOH	0.22	4.54
50	2.7	1.0	4.0	NaOH	0.05	5.16
50	9.5‡	0.5	2.0	$Ca(OH)_2$	0.44	6.38
50	7.8	0.75	3.0	$Ca(OH)_2$	0.01	6.70
50	7.2	1.00	4.0	$Ca(OH)_2$	0.01	7.41
50	7.2§	1.00	4.0	$Ca(OH)_2$	0.09	3.06
10	2.7	0.20	4.0	$Ca(OH)_2$	6.60	0.49
10	2.7	0.30	6.0	$Ca(OH)_2$	1.42	1.52
10	2.7	0.40	8.0	$Ca(OH)_2$	0.07	1.00
10	5.4‡	0.20	4.0	$Ca(OH)_2$	1.00	1.48
1000	2.7	3.0	0.6	$Ca(OH)_2$	421.0	27.5
1000	2.7	4.0	0.8	$Ca(OH)_2$	147.0	85.0
1000	2.7	5.0	1.0	$Ca(OH)_2$	0.36	12.5

* Copper-Quadrol solutions (1,000 ml) containing the indicated copper concentration at pH 10.6-11.9 were acidified with 1N H_2SO_4 to pH 2.7. Ferrous sulfate was added as a solid and after 5 min, the pH was raised to 11.2 with the base listed. Nalcolyte 676 (2.5 mg/l) anionic polyelectrolyte was added and the solutions were allowed to settle 5 min before filtering.

† Determined using a Varian Techtron AA 120 spectrophotometer.

‡ No acid added, pH lowering due to ferrous sulfate addition.

§ Solution lowered to pH 2.7 after ferrous sulfate addition.

will increase in these rinses, and more effective utilization of ferrous sulfate will be realized. Lime or sodium hydroxide as neutralization agents (Table 5) were equally effective in copper and iron removal; however, the use of sodium hydroxide gave lower dissolved solids and less sludge. A 5-minute ferrous sulfate contact time was usually sufficient for good copper removal. As long as the pH was raised above 9.0 (Table 6), copper removal was excellent; however, to lower the residual iron to low values the pH had to be raised to 11.7.

The ferrous sulfate treatment was evaluated on solutions containing different synthetic copper complexes (Table 7) and several commercial rinses (Table 8) with excellent copper removal. The use of anionic polyelectrolytes (1.0-2.5 mg/liter) was very effective in the flocculation and settling of the sludge. Even though only batch treatment was evaluated, the method could be operated continuously. The chemical cost of treatment for a 50 mg/liter copper-Quadrol type rinse with sulfuric acid, ferrous sulfate, lime, and polymer would be about $0.36/3,785 liters.

Ferrous Sulfate Treatment Case History Report

Two printed circuit (PC) shops are presently using this method for treating electroless copper and alkaline etch rinses. A large West Coast PC manufacturer batch treats 1,200 liters/day of a MacDermid C rinse and also floor spills from electroless plating and alkaline etchant baths with 5-20 g/liter ferrous sulfate to pH 10.8. After polymer flocculation (3.0 mg/liter), the residual copper concentration averages 0.1 mg/liter, whereas the residual iron concentration is below 1.0 mg/liter. This company is presently installing a continuous flow ferrous sulfate treatment for their more dilute electroless copper rinses.

An East Coast PC manufacturer treats six electroless copper rinses and one alkaline etchant rinse with ferrous sulfate in a continuous flow system. The 100 liters/minute flow of 20-30 mg copper/liter consistently averages less than 1 mg copper/liter after treatment.

Both companies report less volume of sludge than with the previous treatments they were using.

Spent Pickle Liquor Treatment of Copper Complexes

Recently (88) it was found that spent pickle liquor gave excellent copper removal when substituted for ferrous sulfate in the previous treatment. The "pickling" process is the removal of oxide scale from steel products by immersion in hot acid solution. Spent liquor from batch steel processing contains between 0.5-2% by weight free acid and 5-8% by weight ferrous ion, while liquor from continuous steel processing

TABLE 6. EFFECT OF FINAL pH* ON COPPER REMOVAL FROM COPPER-QUADROL COMPLEX

Adjusted pH	Final pH	Residual copper conc.,† mg/l	Residual iron conc.,† mg/l
2.7	7.0	0.24	25.4
2.7	9.0	0.17	10.5
2.7	11.0	0.14	4.5
2.7	11.7	0.05	0.31
6.4‡	7.0	1.34	48.6
6.4‡	9.0	0.01	13.8
6.4‡	11.0	0.01	1.4
6.4‡	11.7	0.01	0.23
9.0§	9.0	0.01	14.1
9.0§	11.0	0.01	1.9
9.0§	11.7	0.01	0.17

* Dilute 39.0 ml copper-Quadrol stock solution to 1 l (50 mg Cu/l) and then adjust the solutions to the desired pH with 1N H_2SO_4. Treat solutions with ferrous sulfate ($FeSO_4 \cdot 7H_2O$, 1.0 g) for 5 min, add calcium hydroxide to the indicated pH and add Nalcolyte 676 (2.5 mg/l) for flocculation. After settling 5 min, an aliquot (10 ml) was filtered through Whatman 54 filter paper for analysis.

† Copper and iron concentrations were determined using a Varian Techtron AA 120 spectrophotometer.

‡ Adjusted to pH 7.0 with acid, then to pH 6.4 with ferrous sulfate.

§ Adjusted to pH 9.0 with ferrous sulfate.

TABLE 7. COPPER REMOVAL FROM SYNTHETIC COPPER COMPLEXES WITH FERROUS SULFATE TREATMENT*

Complex	Initial copper conc., mg/l	2N H_2SO_4, ml	pH for colorless† solution	$FeSO_4 \cdot 7H_2O$, g	$Ca(OH)_2$, g	Residual copper conc., mg/l	Residual iron conc., mg/l
EDTA	50	3.8		1.0	1.16	0.23	0.12
	10	0.8		0.4	0.94	0.28	0.10
NTA	50	2.2		1.0	1.26	0.29	0.11
	10	0.7		0.4	0.44	0.09	0.11
Tartrate	50	8.0	4.5-4.8	1.0	1.54	0.75	0.21
	10	2.0		0.4	0.64	0.35	0.29
Gluconate	50	2.5	4.5-4.7	1.0	0.88	0.82	32.70
	10	0.7		0.4	0.53	0.09	6.20
Citrate	50	4.8	4.0	1.0	0.76	0.01	0.28
	10	1.8		0.4	0.45	0.02	0.18
Triethanol	50	6.0	5.5	1.0	1.04	0.11	24.48
Amine	10	1.5		0.4	0.64	0.53	8.33
Quadrol	50	5.9	3.0	1.0	0.73	0.01	2.68
	10	1.3		0.4	0.51	0.07	1.00

* Solutions (1,000 ml) containing the copper complexes at the indicated concentrations were acidified with 2N H_2SO_4 to pH 2.7. The indicated amount of ferrous sulfate was added and the solution was stirred for 5 min. Calcium hydroxide was added to raise the pH to 11.7 and the solutions were flocculated with Nalcolyte 676 (2.5 mg/l) anionic polymer. After settling, the solutions were filtered for analysis.

† pH values listed is where copper complex dissociates. When no value is listed, the blue complex does not dissociate above pH 1.8.

TABLE 8. COPPER REMOVAL FROM COMMERCIAL COPPER COMPLEXES WITH FERROUS SULFATE TREATMENT*

Bath	Initial copper conc., mg/l	$2NH_2SO_4$, ml	pH for colorless† solution	$FeSO_4 \cdot 7H_2O$, g	$Ca(OH)_2$, g	Residual copper conc., mg/l	Residual iron conc., mg/l	Dissolved‡ solids, mg/l
MacDermid								
A	50	---		1.0	1.42	0.02	7.1	---
A	10	---		0.4	0.46	0.02	2.3	---
B	50	15.0	2.7-3.0	1.0	1.69	0.17	17.8	---
B	10	4.7		0.4	0.50	0.08	6.3	---
C	50	19.0		1.0	2.18	0.09	21.0	---
C	10	6.0		0.4	0.60	0.03	5.9	---
Shipley								
A	50	4.0	4.8	1.0	0.56	0.33	0.53	---
A	10	1.6		0.4	0.27	0.21	0.47	---
B	50	4.5	2.8	1.0	0.61	0.27	24.86	---
B	10	1.1		0.4	0.26	0.31	2.78	---
C	50	8.2	3.9	1.0	0.94	0.20	14.17	---
C	10	1.8		0.4	0.27	0.11	2.72	---
D	50	3.5	3.8	1.0	0.51	0.12	6.94	1,750
D	10	1.7		0.4	0.34	0.20	1.47	720
D	50	---		---	---	---	---	817
D	50	3.5		1.0	0.92	0.08	6.85	2,320
D	50	3.5		1.0	20.5 ml§	0.16	8.88	2,064

* Solutions (1,000 ml) containing the copper complexes at the indicated concentrations were acidified with 2N H_2SO_4 to pH 2.7. The indicated amount of ferrous sulfate was added and the solution was stirred for 5 min. Calcium hydroxide was added to raise the pH to 11.7 and the solutions were flocculated with Nalcolyte 676 (2.5 mg/l) anionic polymer. After settling, the solutions were filtered for analysis.

† pH values listed is where copper complex dissociates. When no value is listed, the blue complex does not dissociate above pH 1.8.

‡ Filtered samples were evaporated to dryness, oven dried at 125°C, cooled, and weighed.

§ Sodium hydroxide (1N).

contains between 4-7% by weight free acid and 5.1-5.9% by weight ferrous ion. Since spent pickle liquor has little commercial value, this process would give a possible advantageous use for some of the 2-4 billion liters of spent pickle liquor produced annually. Tables 9-10 show the effectiveness of spent pickle liquor on a copper-Quadrol and a copper-ammonia etchant rinse. Approximately 11 liters of spent pickle liquor (6.6% by weight ferrous ion) would be required to treat 3,785 liters of a 50 mg/liter copper-Quadrol or copper-ammonia rinse.

Treatment of Electroless Nickel Rinse Waters

The electroless deposition of nickel is commercially the most widely used of the electroless processes. Numerous articles (52,89-100) are available which describe the chemistry and operating conditions of this controlled autocatalytic reduction of nickel. Both acidic (pH 4-6) and alkaline (pH 8-10) formulations are used containing nickel salt ($NiSO_4$ or $NiCl_2$), reducing agent (NaH_2PO_2 or $NaBH_4$), chelating agent (citrate or glycolate) and pH control agent (H_2SO_4-NH_4Cl or NH_4OH-NH_4Cl). Several commercial baths were evaluated.

Very little has been published (101-107) on the treatment of electroless nickel process waters. Preliminary evaluations to see what effect caustic and lime treatments have on rinse waters revealed that electroless nickel rinse waters could be treated this way. Tables 11-12 show that low residual nickel concentrations can be attained with either a caustic or lime treatment at high pH and at various nickel concentrations. Even though the volume of sludge is greater with the lime treatment, the polymer-treated floc settles faster and is more easily removed than when caustic is used. Another apparent advantage of using lime is the removal of some of the decomposition product of the reducing agents used in the plating. Hypophosphite and borohydride decompose according to the following equations to yield orthophosphite and metaborate which

$$Ni^{2+} + H_2O + H_2PO_2^- \longrightarrow H_2PO_3^- + 2H^+ + Ni^\circ$$

$$4Ni^{2+} + 8OH^- + BH_4^- \longrightarrow BO_2^- + 6H_2O + 4Ni^\circ$$

form only slightly soluble calcium salts, allowing them to be precipitated.

It was found (107) in the treatment of some of the formulations that a longer contact time at high pH gave lower residual nickel values. Acid baths contain compositions having less buffering action (NH_4^+/NH_3),

TABLE 9. SPENT PICKLE LIQUOR TREATMENT OF QUADROL-BASED ELECTROLESS COPPER PLATING RINSE WATERS*

Initial copper conc., mg/l	Initial pH	Pickle liquor, ml	Neutralization agent	Final pH	Residual copper conc., mg/l
50	11.2	10.6	NaOH	11.4	0.05
50	11.2	10.6	$Ca(OH)_2$	11.3	0.04
500	11.6	32.0	NaOH	11.4	0.44
500	11.6	32.0	$Ca(OH)_2$	11.2	0.21
1000	12.0	53.0	NaOH	11.4	0.50
1000	12.0	53.0	$Ca(OH)_2$	11.4	0.31

* Solutions (1000 ml, 50-1000 Cu/l) were treated with the indicated amounts of pickle liquor (18.8 g/l ferrous ion) at pH 2.5 for 15 minutes. The solutions were neutralized with sodium hydroxide (5N) and/or lime (solid) to the indicated pH and then flocculated with anionic polymer (2.5-5.0 mg/l). The samples were filtered through filter paper for analysis, using atomic absorption spectrometry.

TABLE 10. SPENT PICKLE LIQUOR TREATMENT OF COPPER-AMMONIA ETCHANT RINSE WATERS*

Initial copper conc., mg/l	Pickle liquor, ml	Final pH	Residual copper conc., mg/l
50	2.65	11.7	15.66
50	5.30	11.7	27.21
50	7.45	11.7	0.65
50	10.6	11.7	0.37
50	10.6	9.4	3.88
50	10.6	10.0	0.57
50	10.6	11.0	0.41
50	10.6	11.3	0.15

* Solutions (1000 ml, 50 mg Cu/l) were treated with the indicated amount of pickle liquor (18.8 g/l ferrous ion) at pH 9.4 for 15 minutes. The solutions were neutralized with sodium hydroxide (5N) to the indicated and then flocculated with anionic polymer (2.5 mg/l). The samples were filtered through filter paper for analysis, using atomic absorption spectrometry.

TABLE 11. EVALUATION OF $Ca(OH)_2$ AND NaOH FOR NICKEL REMOVAL FROM MACDERMID A ELECTROLESS NICKEL RINSE WATERS*

Initial nickel conc., mg/l	$Ca(OH)_2$ added, g	Final pH	Residual nickel conc., mg/l	NaOH(5N), ml	Residual nickel conc., mg/l
10	0.04	10	10.00	---	---
10	0.11	11	10.00	0.6	6.38
10	0.35	12	0.25	2.4	1.76
10	1.60	12.5	0.20	10.4	0.18
50	0.17	10	25.00	---	---
50	0.59	11	6.87	1.0	26.92
50	0.85	12	1.88	3.8	4.50
50	2.49	12.5	0.61	14.2	0.23
500	1.33	11	39.20	8.0	81.24
500	2.73	12	30.20	20.0	42.85
500	4.93	12.5	27.75	35.0	21.53

* Solutions (1,000 ml) containing the indicated nickel concentrations from a MacDermid A electroless nickel plating bath at pH 8.6 were treated with the indicated amounts of $Ca(OH)_2$ or NaOH(5N). After a 30 minute contact time, the solutions were flocculated with Nalcolyte 676 (2.5 mg/l) and then analyzed for residual nickel.

TABLE 12. EVALUATION OF $Ca(OH)_2$ AND NaOH FOR NICKEL REMOVAL FROM MACDERMID B ELECTROLESS NICKEL RINSE WATERS*

Initial nickel conc., mg/l	$Ca(OH)_2$ added, g	Final pH	Residual nickel conc., mg/l	NaOH(1N), ml	Residual nickel conc., mg/l
10	0.01	9	5.68	0.4	4.50
10	0.03	10	1.59	0.7	1.10
10	0.04	11	0.51	2.5	0.05
10	0.18	12	0.49	3.8	0.05
50	0.08	9	0.49	2.6	2.53
50	0.13	10	0.44	3.9	0.19
50	0.16	11	0.05	6.4	0.21
50	0.32	12	0.02	24.4	0.12
500	0.82	9	2.27	37	6.57
500	0.97	10	0.69	45	2.47
500	1.12	11	0.30	54	2.80
500	1.56	12	0.29	81	1.41

* Solutions (1,000 ml) containing the indicated nickel concentrations from a MacDermid B electroless nickel bath at pH 4.7 were treated with the indicated amounts of $Ca(OH)_2$ or NaOH(1N). After a 30 minute contact time, the solutions were flocculated with Nalcolyte 676 (2.5 mg/l) and then analyzed for residual nickel.

and considerably less base is needed to adjust the pH. Also, the acid bath rinse waters for the most part allowed better nickel removal at a lower pH (11 vs 12.5) and gave a faster settling sludge. However, preliminary results in treating rinse waters from an acidic (pH 5.4) Shipley bath showed the best results at high pH (12.5) with long contact times (2-16 h).

Electroless Nickel Case History Report

A large Midwestern company using an OMI-Udylite A electroless nickel plating bath containing Ni^{2+}, hypophosphite, citrate, and ammonia for plating on plastics has installed the previously described high pH-lime-caustic treatment. A previous treatment tried by the company using phosphoric acid and then caustic was unsuccessful because some of the nickel-ammonia complex was not destroyed. The company treats 30,000 liters/day (85-140 mg/liter nickel) of a dragout rinse (pH 8.6) with lime (45.4 kg) to pH 9.5-10.0 for 1 hour with agitation. Caustic (22.7 kg as pellets) is added to adjust the pH to 12.0-12.5. A 1% solution of a Benchmark Separaid-10 anionic polymer (12.5 mg/liter) is added for flocculation. The sludge is settled for 2-3 hours and the supernatant (less than 0.5 mg/liter residual nickel) is pumped off and discharged. The sludge is removed weekly from the pit and filter pressed. This treatment has allowed this company to lower their nickel discharge to a zero flow receiving stream, from 3.2 kg/day to 0.014 kg/day. Eventually, they would like to install carbon and ion exchange columns for further effluent treatment and complete water reuse. Even though laboratory treatments on OMI-Udylite A (new bath) rinse waters were only 95-98% effective, the on-site treatment by this company has always proved to be 96-99% effective and sometimes 100% effective on spent rinse waters.

Treatment Process for Copper Pyrophosphate Electroplating Rinse Waters

Copper plating in alkaline media with the copper pyrophosphate complex anion has been known for over 125 years; however, it only gained commercial importance about 35 years ago (108-109). Numerous articles have appeared disclosing bath formulations, operating conditions, and applications (110-114); however, very little information is available on the treatment of copper pyrophosphate rinse waters (115-122).

After the articles are plated, they go into a dragout or stagnant rinse tank, then through a series of flowing rinses. The dragout rinse usually is added back to the plating bath for makeup water. The flowing rinse water, containing $Cu(P_2O_7)_2^{6-}$, $P_2O_7^{4-}$, and HPO_4^{2-} has to be treated before discharge to meet the ever more stringent standards.

Preliminary experiments showed that good copper hydroxide removal (50 mg/liter copper lowered to 0.44 mg/liter) was obtained by adjusting copper pyrophosphate rinse waters to pH 12.2 with caustic; however, no pyrophosphate ($P_2O_7^{4-}$) or orthophosphate (HPO_4^{2-}) removal was observed. Since strict phosphorus discharge standards have to be met, an alternate treatment was sought. It is well known that cations such as Ca^{2+}, Mg^{2+}, Zn^{2+}, Al^{3+}, and Fe^{3+} form insoluble precipitates with HPO_4^{2-} and $P_2O_7^{4-}$ when an excess of cation is present (123-131). Since calcium hydroxide, lime, and calcium chloride are economical sources of Ca^{2+}, they were chosen for this study. As the Ca^{2+} is added to the rinse, it complexes with the HPO_4^{2-} and excess $P_2O_7^{4-}$ and precipitates them as their insoluble calcium salts. When the excess $P_2O_7^{4-}$ is removed, the copper probably precipitates as $Cu_2P_2O_7$.

The copper pyrophosphate baths and rinses evaluated (117) were from the printed circuit industry which uses these baths for through-hole-plating of printed circuit boards. Since occasional analysis (132-133) for copper, pyrophosphate, orthophosphate, and ammonia is required for control purposes to keep the bath in good operating condition, the plater knows the relative concentrations of pyrophosphate and orthophosphate in his rinses. Using this analysis information, a treatment process has been designed to lower copper and phosphorous concentrations of synthetic and actual rinse waters. The treatment process can be modified as the orthophosphate concentration builds up. New baths will contain very little orthophosphate, and treatment of these rinses with calcium hydroxide or lime at pH's above 9 will give excellent copper and phosphorous removal. As the orthophosphate concentration builds up to greater than 90 g/liter, the substitution of some calcium chloride for lime will be required to get more Ca^{2+} into solution for excellent precipitation.

Some experimental results for this treatment are shown in Tables 13 and 14. Some general observations and comments about this treatment process are:

(a) Good removal is obtained at pH 9.0-11.5 in the presence of excess calcium ion.

(b) Lowering of the copper concentration to less than 0.02 mg/liter and phosphorous concentration to less than 1 mg/liter, 3.0 mmoles Ca^{2+} is required for each mmole of $P_2O_7^{4-}$, and 2.0 mmoles Ca^{2+} is required for each mmole of HPO_4^{2-}.

(c) Rinses containing high orthophosphate concentrations should be treated with higher proportions of calcium chloride for greater Ca^{2+} solubility.

(d) Use of an anionic polyelectrolyte (3-5 mg/liter) aids sludge settling.

TABLE 13. $Ca(OH)_2$ TREATMENT OF ACTUAL COPPER PYROPHOSPHATE ELECTROPLATING RINSES*

Rinse	Initial Cu conc., mg/l	Initial pH	Initial $P_2O_7^{4-}$ conc., mg/l	Initial HPO_4^{2-} conc., mg/l	$Ca(OH)_2$, mg	Residual Cu conc., mg/l	Residual P conc., mg/l	Residual Ca conc., mg/l	Final pH
A	67.36	8.9	728.7	45.0	992	0.02	0.2	30.2	11.4
B	74.50	8.1	686.7	347.8	1,387	0.04	0.6	14.3	11.5
C	70.84	7.7	893.6	668.7	2,124	2.54	3.1	3.6	11.4
A	50	8.6	539	33.4	734	0.02	0.2	27.4	11.1
B	50	8.0	460	233	929	0.01	0.2	19.7	11.2
C	50	7.7	625	468	1,487	0.02	0.2	44.7	11.3
A	10	8.4	108	6.7	147	0.01	0.2	---	10.6
B	10	8.1	92	47	186	0.01	0.2	---	10.8
A	100	8.7	1,078	67	1,470	0.02	0.2	---	11.6
B	100	8.1	920	466	1,860	0.02	0.2	---	11.6
A	50	8.6	539	33.4	550 (as lime)	0.01	0.2	---	11.1

* Copper pyrophosphate rinse solutions (1,000 ml) containing the indicated concentration were treated with calcium hydroxide. After stirring for 5 min, anionic polyelectrolyte (Dow A-23, 5 mg/l) was added and residual copper, calcium, and phosphorous were determined after filtration.

TABLE 14. $Ca(OH)_2$-$CaCl_2$ TREATMENT OF ACTUAL COPPER PYROPHOSPHATE ELECTROPLATING RINSES*

Rinse	Initial Cu conc., mg/1	Initial pH	Initial $P_2O_7^{4-}$ conc., mg/1	Initial HPO_4^{2-} conc., mg/1	$Ca(OH)_2$, mg	$CaCl_2$ mg	Residual Cu conc., mg/1	Residual P conc., mg/1	Residual Ca conc., mg/1	Final pH
A	67.36	8.9	728.7	45.0	925	97	0.02	0.3	25.4	11.4
B	74.50	8.1	686.7	347.8	872	751	0.01	0.2	10.2	11.4
C	70.84	7.7	893.6	668.7	1,135	1,444	0.01	0.2	37.2	11.1
A	50	8.6	539	33.4	685	72	0.02	0.2	16.1	11.2
B	50	8.0	460	233	584	503	0.01	0.2	16.7	11.1
C	50	7.7	625	468	794	1,011	0.02	0.2	31.5	11.1

* Copper pyrophosphate rinse solutions (1,000 ml) containing the indicated concentration were treated with calcium hydroxide and calcium chloride. After stirring for 5 min, anionic polyelectrolyte (Dow A-23, 5 mg/1) was added and residual copper, calcium, and phosphorous were determined after filtration.

(e) Treatment can be conducted batchwise and probably could be operated continuously.

(f) Chemical cost of treatment using lime and polymer for a copper pyrophosphate rinse containing Cu^{2+} (54 mg/liter), $P_2O_7^{4-}$ (500 mg/liter), and HPO_4^{2-} (250 mg/liter) would be about $0.16/3,785 liters.

Copper Pyrophosphate Case History Report

A large tool manufacturer in the Southwest uses copper pyrophosphate baths for carburizing parts. The rinse waters (40-50 mg/liter copper, 40 liters/minute) until a few months ago were not segregated and were treated with other process waters. This company now segregates the rinse waters for treatment with caustic at pH 12.2. This practice enables them to meet their copper discharge limits and, since they discharge to a sewer, their phosphorus level is below discharge limits. However, they are having problems filtering the copper hydroxide floc and will have to meet stricter phosphorous limits; therefore, they are evaluating the lime treatment.

The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

SUMMARY

The selection of the most effective treatment for any given wastewater containing a combination of pollutants requires a review of the chemistry of the compounds followed by bench scale tests to determine the most effective chemical usage, treatment procedures, and attainable concentrations. It is also necessary to consider economics, ease and safety of handling chemicals, disposal of sludge, process reliability, and degree of automation required. Finally, the planned approach should lend itself to upgrading in the future as further reductions in effluent concentration may be required by regulatory or business decisions. Installation of a wastewater treatment plant is frequently and erroneously considered the final step in the resolution of a pollution problem. Actually, it is the first step in a continuous program that most plants will have to live with for a considerable number of years.

References

1. C. L. Swanson, R. E. Wing, W. M. Doane, and C. R. Russell, Environ. Sci. Technol., 7(7), 614 (1973).
2. R. E. Wing, C. L. Swanson, W. M. Doane, and C. R. Russell, J. Water Pollut. Control Fed., 46(8), 2043 (1974).
3. C. L. Swanson, R. E. Wing, and W. M. Doane, U.S. Patent 3,947,354 (1976).
4. R. E. Wing, W. M. Doane, and C. R. Russell, J. Appl. Polym. Sci., 19(3), 847 (1975).
5. R. E. Wing, Ind. Wastes, 21(1), 26 (1975).
6. R. E. Wing and W. M. Doane, U.S. Patent 3,979,286 (1976); 4,051,316 (1977); 4,083,783 (1978).
7. R. E. Wing, Circuits Manuf., 16(12), 10 (1976).
8. R. E. Wing, B. K. Jasberg, and L. L. Navickis, Staerke, 30(5), 163 (1978).
9. R. E. Wing, L. L. Navickis, B. K. Jasberg, and W. E. Rayford, EPA-600/2-78-085 (May 1978).
10. R. E. Wing, Ind. Finish. 54(10), 38 (1978).
11. R. E. Wing, W. E. Rayford, and W. M. Doane, Plat. Surf. Finish. 65(12), 52 (1978).
12. W. E. Rayford, R. E. Wing, and W. M. Doane, J. Appl. Polym. Sci. (in press).
13. R. E. Wing, W. E. Rayford, W. M. Doane, and C. R. Russell, J. Appl. Polym. Sci. 22(5), 1405 (1978).
14. ALK-ETCH, Technical Bulletin, No. 18, Philip A. Hunt Chemical Corp., Palisades Park, NJ.
15. S. Ikeda and S. Mizugami, Japanese Patent 75 102,572 (1975).
16. S. S. Sorokin and V. V. Titarenko, U.S.S.R. Patent 472,108 (1975).
17. R. Haas and G. Wartenberg, German Patent 2,310,679 (1974).
18. K. J. Radimer, F. E. Caropreso, D. Goldstein, G. W. Siwinski, and B. J. Hogya, Plating, (East Orange, NJ), 53(12), 1445 (1966).
19. F. E. Caropreso, K. J. Radimer, and B. J. Hogya, U.S. Patent 3,399,090 (1968).
20. T. Yamaguchi, K. Hatanaka, and S. Ikebe, Japanese Patent 76 140,360 (1976).
21. C. H. Roy, U.S. Patent 3,816,306 (1974).
22. G. Lordi, L. A. Greenberg, and J. Shorr, Proceedings AES Second Pollution Abatement Seminar, Chicago, IL, October 15-17, 1975, pp. 137-148.
23. R. E. Wing, Fall I.P.C. Meeting, San Francisco, CA, September 27-30, 1976.
24. R. E. Wing, 6th Annual Merrimack Valley Branch, A.E.S. Workshop, Danvers, MA, March 9-10, 1977.
25. M. Tanaka, Japanese Patent 76 28,350 (1976).
26. T. Senda and T. Umehara, Japanese Patent 76 11,091 (1976).
27. L. E. Lancy, U.S. Patent 3,218,254 (1965).
28. P. R. Ammann, G. M. Cook, and C. Portal, U.S. Patent 4,028,202 (1977).
29. A. S. Rappas and J. P. Pemsler, U.S. Patent 4,047,940 (1977).
30. W. Gottfried and E. Mack, German Patent 2,524,546 (1976).

31. C. P. Pesek, German Patent 2,651,675 (1977).
32. M. Tanaka, Japanese Patent 77 71,375 (1977).
33. T. Katsura, PPM, 7(9), 24 (1976).
34. N. Tanaka, Japanese Patent 76 71,270 (1976).
35. T. Senda and T. Umehara, Japanese Patent 76 11,092 (1976).
36. M. Tanaka and M. Yoshida, Japanese Patent 75 131,697 (1975).
37. E. H. Newton, J. M. Ketteringham, J. L. Iienczyk, and C. M. Isaacson, U.S. Patent 3,783,113 (1974).
38. K. C. Leimkuehler, Ind. Wastes, 21(5), 38 (1975).
39. G. B. Hill, Plating, (East Orange, N.J.), 56, 172 (1969).
40. J. F. Zievers and C. J. Novotny, U.S. Patent 3,681,210 (1972).
41. J. A. Landy, J. Water Pollut. Control Fed., 43, 2242 (1971).
42. E. I. Onstott, W. S. Gregory, and E. F. Thode, Environ. Sci. Technol., 7, 333 (1973).
43. S. Rothstein, Plating, (East Orange, N.J.), 45, 835 (1958).
44. T. V. Arden and M. Giddings, J. Appl. Chem., 11, 229 (1961).
45. A. W. Oberhofer, U.S. Patent 3,414,510 (1968); 3,223,620 (1965).
46. A. J. Saraceno, R. H. Walters, D. B. Jones, and W. E. Wiehle, U.S. Patent 3,664,950 (1972).
47. L. Sloan, N. J. Nitti, and J. B. Pratt, U.S. Patent 3,306,859 (1967).
48. J. F. Zievers, C. W. Riley, and R. W. Crain, U.S. Patent 3,658,470 (1972).
49. K. D. Linstedt, C. P. Houck, and J. T. O'Conner, J. Water Pollut. Control Fed., 43, 1507 (1971).
50. L. L. Navickis, R. E. Wing, and E. B. Bagley, Ind. Wastes (in press).
51. W. Goldie, "Metallic Coating of Plastics," Vol. 1, Ch. 6, Electrochemi Publications Limited, Middlesex, England (1968), pp. 59-73.
52. L. N. Schoenberg, J. Electrochem. Soc., 118, 1571 (1971).
53. E. B. Saubestre, Met. Finish., 60(6), 67; 60(7), 49; 60(8), 45; 60(9); 59 (1962).
54. R. M. Lukes, Plating, (East Orange, NJ), 51, 1066 (1964).
55. P. Fintschenko and E. C. Groshart, Met. Finish., 68, 85 (1970).
56. E. B. Saubestre, U.S. Patent 3,666,447 (1972).
57. R. E. Wing, W. E. Rayford, and W. M. Doane, Plat. Surf. Finish., 64(6), 57 (1977).
58. R. E. Wing and W. E. Rayford, 31st Industrial Waste Conference, Purdue University, West LaFayette, IN, May 4-6, 1976, pp. 1068-1079.
59. K. Nagai, Japanese Patent 75 17,778 (1975).
60. A. Abrao, Publ. IEA #311, 6 pp. (1973); C.A. 84: 20673 (1976).
61. M. Tanaka and Y. Komatsu, Japanese Patent 76 10,176 (1976).
62. M. Tanaka, K. Koike, and W. Tani, Japanese Patent 76 02,251 (1976).
63. I. Takahashi, K. Hashimoto, and T. Sato, Japanese Patent 75 85,569 (1975).
64. C. Abels and A. Voigt, German Patent 2,446,117 (1976).
65. K. Imai, Y. Ago, and T. Wakayama, Japanese Patent 76 63,555 (1976)
66. Z. S. Stepanova, G. V. Kupinskaya, A. Y. Krol, and L. V. Kuzmichev Russian Patent 525,627 (1976).
67. T. Senda and A. Kitamura, Japanese Patent 76 139,167 (1976).
68. H. Honma, H. Mitsui, and H. Kohara, Kinzoku Hyomen Gijutsu, 27(4), 195 (1976).

69. M. Tanaka, Japanese Patent 76 83,068 (1976).
70. M. Tanaka, Japanese Patent 76 85,266 (1976).
71. I. Takahashi, K. Hashimoto, and T. Sado, Japanese Patent 76 02,253 (1976).
72. M. Tanaka, Japanese Patent 76 93,549 (1976).
73. J. Sakagami, H. Ichino, and T. Matsuoka, Japanese Patent 76 107,660 (1976).
74. W. Schaefer-Burkhard, German Patent 2,628,649 (1977).
75. M. Hirai, T. Ishibashi, and Y. Fujuwara, Japanese Patent 77 23,863 (1977).
76. H. Sato and N. Nishida, Japanese Patent 77 04,644 (1977).
77. Z. Hagiwara and H. Sato, Japanese Patent 76 102,355 (1976).
78. K. Kariyone, K. Abe, and K. Sato, Japanese Patent 76 49,564 (1976).
79. K. Kariyone, K. Abe, and H. Shibatani, Japanese Patent 77 65,974 (1977).
80. Y. Sadahiro, K. Sakamoto, T. Koike, and T. Kato, Japanese Patent 77 17,366 (1977).
81. R. W. Andrew, "Toxicity to Biota of Metal Forms in Natural Water," Proceeding of a Workshop, Duluth, MN, October 7-8, 1975, R. W. Andrew et al. (editors), pp. 127-144.
82. R. W. Andrew, K. E. Biesinger, and G. E. Glass, Water Res. 11(3), 309 (1977).
83. Y. K. Chau, J. Chromatogr. Sci., 11, 579 (1973).
84. J. B. Sprague, Nature, 220, 1345 (1968).
85. K. Fukunaga, Japanese Patent 75 136,280 (1975).
86. M. Ichiki, N. Ogawa, and M. Ishii, Japanese Patent 76 00,764 (1976).
87. R. E. Wing, W. E. Rayford, and W. M. Doane, Plat. Surf Finish., 64(10), 39 (1977).
88. R. E. Wing and W. E. Rayford, Met. Finish. 76(3), 31 (1978).
89. W. Goldie, "Metallic Coating of Plastics," Vol. 1, Ch. 7, Electrochemical Publications Limited, Middlesex, England (1968), pp. 74-98.
90. A. Brenner and G. E. Riddell, J. Res. N.B.S., 37(7), 31 (1946).
91. A. Brenner and G. Riddell, J. Res. N.B.S., 39(11), 385 (1947).
92. J. D. MacLean and S. M. Karten, Plating, 41(11), 1284 (1954).
93. A. Brenner, Met. Finish., 52(12), 61 (1954).
94. C. H. DeMinjer and A. Brenner, Plating, 44(12), 1297 (1957).
95. A. W. Godenstein, W. Rostoker, F. Schossberger, and G. Gutzeit, J. Electrochem. Soc., 104(2), 104 (1957).
96. G. Gutzeit, Plating (East Orange, NJ), 46(10), 1158 (1959).
97. S. Wein, Glass Ind., 40(12), 532 (1959).
98. D. G. McBride and G. P. Vlasak, J. Electrochem. Soc., 118(12), 2055 (1971).
99. N. Feldstein and T. S. Lancsek, J. Electrochem. Soc., 118(6), 869 (1971).
00. M. Lelental, J. Electrochem. Soc., 122(4), 486 (1975).
01. H. Ohguro and K. Okada, Japanese Patent 75 103,471 (1975).

102. T. Hayashi and Y. Asano, Japanese Patent 76 77,121 (1976).
103. L. Gianelos, Plat. Surf. Finish., 64(10), 22 (1977).
104. T. Kasuya, H. Yoshizawa, and Y. Tashiro, Japanese Patent 76 138,518 (1976).
105. K. Tsukamoto, Japanese Patent 76 59,454 (1976).
106. A. Miyazaki, Japanese Patent 75 161,056 (1975).
107. R. E. Wing, W. E. Rayford, and W. M. Doane, Met. Finish., 76(1), 54 (1978).
108. J. E. Stareck, U.S. Patent 2,081,121 (1937); 2,250,556 (1941); 2,437,865 (1948); 2,493,092 (1950).
109. T. G. Coyle, Proc. Am. Electroplat. Soc., 29, 113 (1941).
110. F. Passal, Plating, (East Orange, NJ), 46, 628 (1959).
111. R. W. Couch and J. E. Stareck, "Pyrophosphate Copper," Modern Electroplating, F. A. Lowenheim, Ed., 2nd ed., John Wiley and Sons, New York, pp. 200-206 (1963).
112. J. W. Dini, Plating (East Orange, NJ), 51, 119 (1964).
113. C. J. Owen, H. Jackson, and E. R. York, Plating, (East Orange, NJ), 54, 821 (1967).
114. J. W. Dini, H. R. Johnson, and J. R. Helms, Plating, (East Orange, NJ), 54, 1337 (1967).
115. W. A. Parsons and W. Rudlofs, Sewage Ind. Wastes Eng., 22, 313 (1951).
116. H. Yamada and H. Kojima, Japanese Patent 73 00,295 (1973).
117. R. E. Wing, W. E. Rayford, and W. M. Doane, Met. Finish., 75(5), 101 (1977).
118. T. Ishibashi, Y. Fujiwara, S. Muranishi, and T. Ohtsuki, Japanese Patent 77 49,652 (1977).
119. S. Mizukami, K. Akatsuka, T. Miyamatsu, Y. Tsutsui, and H. Harada, Japanese Patent 77 23,861 (1977).
120. M. Hirai, T. Ishibashi, and T. Kudo, Japanese Patent 77 30,059 (1977).
121. K. Hirose, Japanese Patent 76 55,775 (1976).
122. D. Gleisberg, Galvanotechnik, 67(5), 346 (1976).
123. J. F. Ferguson, D. Jenkins, and J. Eastman, J. Water Pollut. Control Fed., 45(4), 620 (1973).
124. D. F. Bishop and J. B. Stamberg, U.S. Patent 3,617,540 (1971).
125. R. A. Boehler and M. R. Purvis, Jr., U.S. Patent 3,617,542 (1971).
126. S. L. Daniels and D. G. Parker, U.S. Patent 3,617,569 (1971).
127. J. R. VanWazer and C. T. Callis, Chem. Rev., 58, 1011 (1958).
128. J. I. Watters and A. Aaron, J. Am. Chem. Soc., 75, 611 (1953).
129. M. Bobtelsky and S. Kertes, J. Appl. Chem., 4, 419 (1954).
130. L. B. Rogers and C. A. Reynolds, J. Am. Chem. Soc., 71, 2081 (1949).
131. M. J. Hammer, Water and Waste-Water Technology, John Wiley and Sons, Inc., New York, pp. 452-455 (1975).
132. S. Konishi, Met. Finish., 63, 58 (1965).
133. The Meaker Company, Nutley, New Jersey, Technical Bulletin MC-01-111, Ready-to-Plate Copper Pyrophosphate Process, July 1968.

S-4

Environmental II
Session S

Advances in the Commercialization Of Electrodialysis for the Control And Recovery of Electroplating Solutions

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"ADVANCES IN THE COMMERCIALIZATION OF ELECTRODIALYIS FOR THE CONTROL AND RECOVERY OF ELECTROPLATING SOLUTIONS"

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Electrodialysis is now commercial. The electrochemical cell utilizing permselective membranes is no longer a laboratory curiosity. It is a practical commercial tool useful not only for the recovery of chemicals lost through rinse water dragout in metal finishing operations, but is now finding use in the control and maintenance of many different types of solutions used in the finishing industry. These electrochemical cells which use ion exchange permselective membranes to provide isolation between two fluids are unique because of the qualities of these membranes. These membranes do not function as the membranes do in reverse osmosis. In reverse osmosis, the membranes merely act as a barrier essentially for all dissolved species indiscriminately. The membranes used in electrodialysis are specific for ionic charges and sometimes even for specific ions. This ion selective property along with the ability to operate in extremely corrosive solutions over a wide pH range sets electrodialysis apart and makes it a highly sophisticated tool capable of performing many functions useful in the finishing industry.

Commercialization of electrodialysis has probably progressed furthest in the recovery of rinse waters. In this particular process, the electrodialysis cell functions merely as a concentrator extracting ions from rinse water concentrating them and returning them to the plating bath. This process differs from both reverse osmosis and evaporation in that, rather than removing the water from the contaminated rinse water the ions themselves are extracted from the rinse water. The ions pass through the membranes into the concentrate or plating bath. Rather than expend a great deal of energy for the removal of a large amount of water from a small amount of dissolved solids, electrodialysis extracts the dissolved solids from the large volume of water.

In a comparison with evaporation, evaporation in one stage generally can concentrate by a factor of ten; that is, the rinse water can be maintained at a concentration approximately 10% of that in the plating bath. To operate over greater concentration ranges, multiple effects must be used, adding greatly to the cost of the equipment and the complexity of its operation. The expenditure of a great deal of energy for the evaporation of extremely large volumes of water would make the process extremely unattractive from an economic as well as a mechanical standpoint. In electrodialysis, concentrations as high as 100 times can be achieved in a single cell. It is true that the more dilute the solution the higher the power consumption. The efficiency, of the operation, however, does not fall off measurably. In this manner rinse waters of a much greater dilution can be used and recovered. Thus recoveries of a higher percentage in a single stage are possible with this technique.

A comparison with construction of the equipment shows that evaporators require expensive materials of construction to cope with the corrosive solutions being dealt with. This is particularly true of heat transfer surfaces. In addition, construction must be rugged as the equipment must deal with vacuums at elevated temperatures. ED Cells are constructed almost entirely of polymeric materials with the exception of the electrodes. The pumps, piping, and even the membranes themselves are constructed of polymeric materials. In addition, the cells operate at essentially the temperature of the rinse water. Except in extreme cases the materials of construction are from commonly available polymeric materials; such as, PVC, CPVC, and Polyproplyene.

In the case of energy consumption and the auxiliaries required, evaporators utilize steam which requires the use of the auxiliaries of a boiler fired by one of the many fuels, the supply of which is threatened. Additionally, a vacuum pump and a great deal of cooling water are required. The cooling water either results in a large expenditure for water or requires the auxiliary of a cooling tower. In contrast electrodialysis utilizes electricity which though not inexpensive is readily available and utilizes the electrical energy very efficiently; at a much greater efficiency than steam is utilized in evaporation. No vacuum pumps are required and cooling water is only required when the equipment is utilized with baths that must be kept at a low temperature. In many cases the cooling water required can be the rinse water used subsequent to the process.

A comparison between two evaporation and electrodialysis processes is now presented: The first, a standard watts nickel plating operation, and second a cadmium cyanide plating bath. In these comparisons, a dragout rate was set that would most ideally suit the evaporator. In both cases a dragout rate of 7.5 gallons per hour of plating solution. In the case of the evaporator this would require an evaporator with a 75 gallon per hour boil off rate. The following table shows a comparison between the equipment costs and operating costs of both systems operating on both baths

WATTS NICKEL

Operation: 3 Shifts Per Day - 5 Days Per Week
Dragout Losses: 7.5 Gallons Per Hour
Bath Composition: $NiSO_46H_20$ 44 oz/gal
$NiCl_2$ 6 oz/gal
H_3BO_3 5 oz/gal
Losses Per Month: 3780 Gallons Sol Approx. $9,300/mo

	EVAPORATOR	ELECTRODIALYSIS
First Cost	$42,500 Does Not Include Cost of Boiler or Cooling Tower	$45,300
P Pumps	(Cooling Tower & Boiler 2 Pumps Not Included)	7
ooling Water $0.50/1000 gal.	51 gal/min 25° Rise 26 gal/min 50° Rise 786000 gal/mo $393	None
eam $3.50/1000#	750#/hr 378000# $1323/mo	None
ectrical Power $0.04/KWH		32 KW 16128/mo $645
	30 PSIG	None
ual Costs (7 yrs) Maint rane Replacement rve	$20,592 6,071 1,200	$7,741 6,471 1,200 2,500
l	$27,863	$17,912

CADMIUM CYANIDE

Operation: 2 Shifts Per Day - 5 Days Per Week
Dragout Loss: 7.5 Gallons Per Hour
Bath Composition: Cd 2.66 oz/gal
NaCN 13.3 oz/gal
NaOH 1.9 oz/gal
Losses: 2520 gal/mo Approx. $2,200
Cyanide Destruction @ $2.00# 4,200
$6,400

	EVAPORATOR	ELECTRODIALYSIS
First Cost	$62,200 Does Not Include Boiler or Cooling Tower	$45,300
HP Pumps	3 (Boiler & Cooling Pumps & Blowers not included)	7
Cooling Water @ $0.50/1000 gal	85 gal/min 15° Rise 51 gal/min 25° Rise 1,028 160 gal $514/mo	8 gal/min 20° Rise 161280 gal $8
Steam @ $3.50/1000#	252000# $882/mo 750#/hr	None
Electrical Power @ $0.04/KWH		32 KW 10752 $43
Air	30 PSIG	None
Annual Cost	$16,752	$6,132
Dep. (7 yrs)	8,886	6,471
Est. Maint	1,200	1,200
Membrane Replacement Reserve		2,500
Total	$26,838	$16,303

From the above tables it is obvious that recovery in either case is a good idea. However, the annual operating costs of the electrodialysis system are far better than that of the evaporative system. In fairness to evaporation at this point it must be stated that the water recovery from the evaporative system is very pure water and can be returned to the rinse tanks for reuse. The water recovered in electrodialysis is not pure as it must be electrically conductive in order for electrodialysis to work. However, the water contains only those chemical compounds which are already present in the rinse water and in actual fact the quality of the water is quite adequate to use for rinsing.

Whereas evaporation and reverse osmosis can only be used for concentration, electrodialysis can perform other functions and does so on a commercial scale. An example of this is the reoxidation of plastic etching solutions. In this process trivalent chromium is reoxidized to hexavalent chromium. The solutions used are a highly corrosive mixture of chromic acid and sulphuric acid which are operated hot, these solutions are used to etch ABS Plastics prior to plating. In the process the chrome is reduced to the trivalent state as the surface of the plastic is etched and oxidized. As the trivalent chromium increases in the bath, the etching rate slows down and if not removed the bath would have to be discarded. This process of reoxidation along with simultaneous removal of cationic impurities; such as copper, and nickel has achieved commercial success. The etching bath or dragout rinse water is circulated through the unit and the chrome is oxidized back to the hexavalent state. In the case of rinse water the oxidation unit is coupled with an evaporator for reconcentrating the etch solution back to its normal strength. In this particular installation electrodialysis is unsuitable for the concentration of the chrome solution as it is far too vigorous in its action and tends to destroy the electrodialysis membranes. This process could also be applied to hard chromium plating operations where a removal of cationic impurities and reoxidation is necessary. The use of an evaporator above to recover the water from these installations is insufficient as the build-up of both trivalent chrome and cationic impurities would soon render the bath inoperable. The combination, however, works very well and results in substantial savings in chemical and destruction costs.

Another example of where electrodialysis performs more than one function is the recovery and reconditioning of rinse water from a Halogen tin plating bath. In this process tin is plated from a solution containing a complex sodium tin fluoride compound. Due to oxidation of this fluo stannite complex to the fluo stannate complex as a result of large quantities of air entrainment in continuous strip plating, there is an excess of sodium, which is the reaction product from the oxidation process. If the rinse water were merely concentrated by electrodialysis and returned to the plating bath, there would be a continual increase of sodium ions to the point where the plating bath would have to be discarded. A certain amount of control can be exercised by the addition of acid, however, the total ion concentration would continue to build which would cause other problems. In this particular situation, the rinse water after having been concentrated (the dilute is returned for further rinsing), the concentrate passes through a cell which extracts sodium and replaces it with hydrogen. This sodium depleted stream is then returned to the plating bath for reuse. By this means the pH of the plating bath can be controlled and the total ionic concentration can be retained at the level desired. The sodium which has been removed is removed in the form of sodium hydroxide which is quite pure and usable for other areas in the plant, such as cleaning.

Another process which has received commercial acceptance is high speed alkaline tin plating utilizing insoluable stainless steel anodes in place of tin anodes. In this process the use of the stainless steel anodes allow large increases in plating speed and is accompanied with an almost total elimination of rejects because of stannite plating. The use of potassium stannate as a source of tin rather than tin anodes is more than economically feasible. This is particularly true if complex shapes are being plated. In this process, when tin is plated from potassium stannate solution there is a generation of free potassium hydroxide. This potassium hydroxide must be neutralized or the bath would have to be discarded in time. One means of accomplishing this, is through the use of expensive tin oxide sols. Another is the use of electrodialysis. In this patented process the plating bath is circulated through an electrochemical cell and the exce potassium ions are extracted in the form of potassium hydroxide which can be used elsewhere in the plant while the reconditione plating bath is continuously returned to the plating operation.

As a final example of other processes of interest to the finishing industry is a new process for which patents have been applied for the regeneration and reconditioning of electroless copper plating solutions. This process, which shows great commercial promise, is currently in the process of being piloted. In this process electroless copper plating solution is continuously circulated through the electrochemical cell and the reaction products are removed leaving behind the unreacted compounds to which only need be added additional copper, sulfate, and formaldehyde to bring the bath up to correct strength. This process shows the ability to be operated automatically and maintain the plating bath at any desired plating rate. In the past, many thousands of gallons of solution which contain many valuable chemicals were discarded and destroyed. In this manner these solutions can be used over and over again both eliminating a serious pollution control problem and with a savings of many thousands of dollars.

There are many other processes which are being investigated on a laboratory and pilot scale which would be of interest to the industry. There are many advances yet to come before electrodialysis realizes its potential in the market place. Some of these are more than already on the horizon. Methods of reducing power consumption by as much as 35% from that which is presently required, better membranes, and new techniques for the utilization of these cells to solve problems which today may be considered unsolvable.

Electrodialysis is still in its infancy but it is growing rapidly and its here commercially. With the steadily increasing cost of power and the steadily increasing value of the various chemical compounds used in the finishing industry the loss or destruction of these compounds is economically unacceptable this equipment provides an economical solution for many these problems. The equipment is not a panacea but it a tremendous potential for the finishing industry in particular.