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General Interest Session A

Application of CVS to the Analysis of Organic Additives in Nickel Plating Baths

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APPLICATION OF CVS TO THE ANALYSIS OF ORGANIC ADDITIVES IN NICKEL PLATING BATHS

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Abstract

The Cyclic Voltammetric Stripping (CVS) technique was evaluated for the monitoring of organic additives in bright and semi-bright nickel plating solutions. Results are presented, which indicate that the organic additives used in nickel plating cause changes in the structure of the nickel coating, and/or changes in the polarization during plating onto a platinum working electrode. Analytical procedures based on CVS have been developed to monitor the effective additive concentration levels in the plating bath, utilizing these polarization and structure changes. In this study, class I and class II additives were evaluated individually and in various combinations. A comparison of CVS and Hull cell techniques was performed and results are discussed.

Introduction

Quality, cost savings and control are the key ingredients in any modern, successful plating shop. The search for these pillars of success has been a driving force in the rapid advances seen in the electronics and the metal finishing industries. The application of the Cyclic Voltammetric Stripping (CVS) to plating bath analysis represents one such advance. The CVS technique [1] has emerged as one of the most promising analytical tools to aid platers in achieving these goals.

Since its introduction in 1977, CVS has been routinely used for control of copper pyrophosphate and acid copper sulfate plating solutions, providing scores of platers with the quantitative analytical technique they have been looking for. Over the years, work at Rockwell, UPA, as well as a number of

other companies, has led to about 40 articles* and written procedures for analysis of various additives and their components in copper pyrophosphate and acid copper sulfate plating baths [2]. Application of CVS within the copper-plating community has helped a number of platers to re-discover some basic rules of electroplating: cleanliness, regular maintanance of the bath including proper analysis, and timely and appropriate additions of bath components. Rediscovering these basics, which are often forgotten, coupled with tight control over all of the bath parameters, led to considerable improvements of yields, quality, as well as decreased reject rates, decreased usage of additives, and more effective carbon treatments generally at less frequent intervals; all leading to substantial monetary savings.

Recently, the CVS method has been extended to the analysis of nickel plating baths [2,3]. Nickel plating is presently one of the most important and wide-spread plating processes. Nickel plating is used primarily for corrosion protection and/or diffusion barrier layer. A host of additives have been employed in nickel plating baths and classified as class I or class II brighteners [4]. Usage of most additives leads to codeposition of sulfur or carbonaceous material into the plate, affecting the brightness, stress and corrosion resistance of the plating.

This paper will concentrate on expanding the preliminary results reported earlier. The effect of the class I and class II brighteners on nickel voltammograms will be discussed and linked to structural changes in the nickel deposit. Also discussed will be approaches to the analysis of these brighteners in the nickel plating solutions.

Principles of CVS Analysis

The Cyclic Voltammetric Stripping (CVS) analysis of organic additives is based on the effect these compounds exert on electrodeposition of the metal, i.e. Cu or Ni. The voltammetric cycle consists of varying the potential of a rotating platinum electrode between negative and positive potential limits, alternately plating and stripping the small quantities of metal to and from the platinum electrode. The total charge required to dissolve the metal back into the solution is automatically measured by integrating the stripping peak (see Figure 1). The charge (A_R) can then be related to the concentration of the additive in the plating bath. Techniques used for the analysis of various copper plating

* Actual up-to-date bibliography can be obtained from UPA Technology, Inc.

additives were reviewed recently in a separate paper [2]. The research and analytical procedures for nickel bath additives described here are based partly on the experience gained working with additives used in copper plating solutions.

Experimental Procedure

All of the voltammetric experiments described were performed using a commercially available computerized voltammetric analyzer*, employing a 3-electrode cell. The electrodes were: rotating platinum disc electrode (A = 0.125cm^2) used at 2500RPM, platinum wire auxiliary electrode and saturated calomel reference electrode (SCE). The working and auxiliary electrodes were cleaned with 50% v/v HNO_3 and conditioned before each experiment by cycling between -1.45 and +1.75V vs the SCE in virgin nickel plating solution** for a few minutes, or until consistant stripping charge was obtained. The chemicals used were all of analytical reagent grade.

The additives tested included Electrobrite^{TM} 711 and P-730 manufactured by the Electrochemicals Corporation, bright nickel process 794 from OMI/Udylite and Lectro-nic^{TM} 10-03 from OMI/Sel-Rex Corporation. All of the solutions and additives were prepared and used according to manufacturers' specifications. The Hull-cell experiments were performed in a heated (60°C) 267ml cell with mechanical agitation, using brass plates with 3A current applied for a period of 6 minutes. The plates were electrocleaned in detergent solution and activated with 5% v/v HCl. Any additional parameters used are specified with experiments.

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* Qualiderm Q-1000, manufactured by UPA Technology, Inc.

** Virgin nickel solution was prepared by dissolving $NiSO_4 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and H_3BO_3 as recommended by given manufacturer in distilled water. No additive was used to prepare virgin solution, not even surfactant.

Results and Discussion

A. Class I Brighteners

A number of proprietary additives used for electrodeposition of bright nickel contain saccharin, a class I brightener [4]. Figure 2 shows a voltammogram obtained for a Watt's nickel virgin solution without any additive. A number of small peaks are present on the voltammogram. The predominant one, however, appears at about 1.1V vs SCE. This peak corresponds to the dissolution of the majority of nickel from the rotating platinum electrode (RPE). The peak is often broad and not well defined, overlapping the background signal. Visual inspection of the RPE, when removed from solution at the positive potential limit of 1.75V, confirms complete dissolution of nickel.

Addition of saccharin or a saccharin containing additive to the virgin nickel plating solution causes drastic alternation in the shape of the voltammogram (see Figure 3). The stripping peak is shifted from 1.1V to about 0.3V when a small amount of saccharin is added. After the peak is completely shifted to the lower potential, further additions of saccharin or saccharin containing additives produce no visible change in voltammogram, even with amounts well beyond manufacturer's recommendation. For the given additive, the shift of peak was completed with about 5% of the recommended amount of additive.

This shift of the stripping peak to a lower potential indicates that lower energy is needed to dissolve nickel plated from a solution containing saccharin. This conclusion is consistent with the observations that sulfur is codeposited along with nickel, when bright nickel is plated from saccharin containing Watt's bath. In addition, the change in the voltammogram agrees well with the studies indicating that sulfur containing bright nickel provides lower corrosion protection than the sulfur-free semibright nickel.

In addition to sodium saccharin and proprietary additives known to contain saccharin, several other compounds, classified as class I brighteners, such as di- and tri-naphthalene sulfonic acids and sodium allyl sulfonate, and some non-saccharin proprietary additives were tested as well. All of the compounds tested (except sodium allyl sulfonate, which will be mentioned later) behave in the same manner as saccharin, and can therefore be determined using the procedure presented in this paper.

This shift of the stripping potential peak can be used for quantitative determination of all class I additives in Watt's nickel baths. To analyze a solution, one would measure the

total charge, A_R, needed to strip the nickel at the lower potential (integrating the stripping current up to 0.5V vs. SCE), and plot the value of A_R as a function of the concentration of saccharin or class I additive. Figure 4 shows A_R values measured when a synthetic Watt's nickel solution with 20ml/l of saccharin containing additive is added to a virgin Watt's solution. The total amount of nickel plated onto the electrode, as monitored by measuring stripping charge up to a potential of 1.25V, is virtually unaffected by the addition of saccharin containing additive component.

Based on the curve shown in Figure 4, we have developed an analytical procedure for determination of the effective concentration of class I brighteners in Watt's nickel production solutions. The technique is similiar to the previously introduced dilution titration method, used for analysis of "suppressors" (wetters and carriers) in acid copper sulfate plating baths, with slightly modified end-point detection. This technique can be used because drastic changes in stripping charge are observed at solution concentrations considerably lower than manufacturers' recommended levels.

To perform the analysis, one starts with known volume of virgin Watt's nickel electrolyte in the cell (concentration of $NiSO_4$, $NiCl_2$ and H_3BO_3 should be close to those used in production solution). After conditioning the system to stability, the electrode potential is continuously cycled at 200mV/s between the limits of -1.30V and +1.75V. Small volumes of the production solution (generally 2-5 ml additions to 200ml of virgin solution) are then added after every second cycle, and A_R values, obtained by integration of stripping current up to 0.5V, are recorded. The curve resulting by plotting these A_R values as a function of added volume of the production solution (see Figure 5) is then used to calculate effective concentration of class I additive in the production solution, using the equation:

$$\text{conc. of additive} = \frac{Z_p\,(V_{soln} + V_{end})}{V_{end}} \qquad (1)$$

where:
- V_{soln} = volume of virgin solution used
- V_{end} = volume of production solution needed to reach endpoint
- Z_p = concentration of saccharin or class I additive at the endpoint, as determined from calibration curve.

Two very important concepts need to be clarified at this time: endpoint and its determination, and calibration curve.

The term "endpoint" is used rather arbitrarily in this case, as is the method for its selection. What we actually need, is a reference point on the curve, that can be used for calibration purposes. One of the most convenient points is the increase of A_R to 50% of its final value. Since the slope of the curve is rather steep at this point, choosing the endpoint between 50-70% of the final value (wherever it might be) changes the concentration of additive by only few percent. Other points that could be used for reference purposes are the intercepts of vertical and horizontal lines at the beginning or the end of the transition phase of the curve. 50% point, however, was found to give more reproducible additive concentrations. Curves and 50% points corresponding to four determinations of the same solution, on two consecutive days, are shown in Figure 6.

The Z_p-value, which signifies the concentration of saccharin or class I additive at the endpoint, is determined during the calibration procedure. The calibration procedure is identical to the determination of production solutions, however, a solution with known concentration of saccharin or class I additive is used in place of production solution. The Z_p-value is then calculated from the equation:

$$Zp = \frac{C_{cal} \cdot V_{end}}{V_{soln} + V_{end}} \qquad (2)$$

where: V_{soln} and V_{end} have the same meaning as in equation (1), and C_{cal} is the concentration of saccharin or the additive being determined (this concentration is usually 10ml/l or concentration recommended by manufacturer of the additive). In the determination shown in Figure 5, 1% solution of the proprietary additive was used for calibration purposes (curve 5a), and the z-value was calculated from equation (2):

$$Zp = \frac{C_{cal} \cdot V_{end}}{V_{soln} + V_{end}} = \frac{1\% \times 9.2ml}{50ml + 9.2ml} = 0.155\%$$

The concentration in production solution, depicted by curve 5b, was calculated from the equation (1):

$$\text{conc. of additive} = \frac{Zp\ (V_{soln} + V_{end})}{V_{end}} = \frac{0.155\%\ (50 + 5.6)ml}{5.6\ ml} =$$

$$= 1.55\% = 15.5\ ml/l$$

The production solution was actually a test solution containing 1.5% of additive. Tests with actual production solutions are presently under way.

B. Class II Brighteners

The secondary brighteners, added in most bright nickel systems to attain levels of luster not achievable by primary (class I) brighteners, introduce carbonaceous material into the deposit and have been classified as class II brighteners [4]. The CVS behaviour of these compounds is completely different than that exhibited by class I brighteners. Figures 7 and 8 show the effect of secondary brightener additions on the voltammogram of nickel in Watt's baths with and without class I brightener present. The class II brighteners (primarily unsaturated organic compounds) increase the polarization of nickel plating, thus decreasing the amount of nickel plated as their concentration increases. This increase in polarization was observed regardless of the presence or absence of class I brightener, as can be seen from Figures 7 and 8. A plot of A_R vs concentration of class II brightener, in solution containing 20ml/l of class I brightener is shown in Figure 9. As can be seen from this curve, decrease in A_R eventually saturates, at concentrations beyond the manufacturer's recommended levels (in this case recommended concenteration is 1.25-3 ml/l).

The effective concentration of the class II brightener can be determined directly fom a calibration curve (such as shown in Figure 9), or by adding known amounts of the brightener directly to the production solution until the saturation is reached.

The determination of the effective concentration of the class II brighteners by the latter procedure is similar to the dilution titration technique used to determine class I brighteners. Here, however, small amounts of class II brightener are added directly to the production solution (instead of adding production solution to the virgin make-up), until further additions do not change the A_R value. The end-point, V_s, is the intercept of the vertical and horizontal segments of the curve, rather than 50% of the final A_R value. The concentration of the class II brightener in the production solution can then be calculated from the equation:

$$\text{conc. of class II brightener} = Z_s - \frac{V_s}{V_{soln} + V_s} \qquad (3)$$

where Z_s: is the concentration of class II brightener at saturation

V_{soln}: is the initial volume of production solution used

V_s: is the volume of class II brightener added to the production solution to reach saturation.

The concentration of the class II brightener at the saturation, Z_s, is determined by adding known amount of brightener to the virgin bath (calibration) and calculating Z_s from the equation (4):

$$Z_s = \frac{1000ml/l.V_{end}}{V_{soln} + V_{end}} \qquad (4)$$

where: V_{soln} = volume of virgin make-up used

V_{end} = volume of brightener needed to reach endpoint.

The endpoint used in this case is the saturation value, described above.

At the present time, experiments are being carried out to test this technique with different production solutions and to determine the effect of varying bath composition. Some effects from differing nickel and chloride concentrations are expected. The magnitude of these effects, however, has not yet been established.

Sodium Allyl Sulfonate

As mentioned earlier, sodium allyl sulfonate was tested together with other class I brighteners, but was found to behave differently than the rest of the class I brighteners tested. Since sodium allyl sulfonate contains a sulfonate group with C = C bond attached to it, it is classified as a class I brightener. Sodium allyl sulphonate, same as other unsaturated aliphatic sulfonic acids [4], give brighter plates, under the same conditions than benzene and naphthalene sulfonic acids do, because it introduces to the nickel deposit carbonaceous materials in addition to sulfur.

Voltammetrically, sodium allyl sulfonate is expected to exhibit the behaviour of both - class I and class II brighteners. As can be seen from Figure 10, this has been confirmed. Sodium allyl solfonate increases the polarization of the nickel deposit the same way class II brighteners do, and at the same time, changes the structure of nickel deposit through codeposition of sulfur as class I brighteners do.

Comparison of CVS and Hull Cell Studies

The power of the CVS predictive capabilities with respect to additive concentration determination, was studied by analyzing solutions with various amounts of class I brightener (saccharin containing component), and comparing them to a qualitative evaluation of plating tests performed in Hull Cell. A dull plate was obtained from the solution without any additive present, as should be expected. Increased amounts of saccharin containing brightener produced semi-bright plates, with the brightness range and luster increasing with increasing concentration (see Figure 11). This improvement proceeded until about 2.5 ml/l (.25% v/v) of the brightener was added to the solution, at which point the improvement of plating luster ceases. Further increase in the concentration of this additive component, up to 20ml/l (recommended by manufacturer) and beyond led to increased pitting of the plated surface, but no improvement in brightness, or the range of brightness. Saccharin is known to decrease the overpotential of hydrogen reaction, thus promoting pitting [5]. The CVS results indicated that the nickel stripping peak starts shifting to lower potentials at about 0.5ml/l, and the transition is completed when about 2-3 ml/l of the saccharin containing brightener is added. No change is observed beyond this level, even if a large excess of brightener is added. The CVS results thus predict accurately the minimum amount of the class I brightener needed for proper functioning of the bath.

Addition of the recommended amount of the second component (class II brightener with recommended bath concentration of 3ml/l), increased brightness of the Hull cell plate slightly and suppressed the pitting of the nickel surface. Further tests using CVS and Hull cell for comparison purposes will be carried out in the future.

Conclusion

New developments in the monitoring of effective concentration of class I and class II brighteners in Watt's nickel plating solutions were described. The results presented show that the CVS technique can be used successfully to monitor both classes of brighteners by a simple procedure. Comparison between the CVS and Hull cell indicates that CVS was able to predict the minimum concentrations of saccharin containing additive to produce maximum plating quality. The CVS technique can thus be useful for the development of new brighteners for nickel plating solutions. Additional work is presently being carried out to confirm these results obtained on laboratory solutions by checking various used production solutions.

Acknowledgements

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References

1. D. Tench and C. Ogden, "A New Voltammetric Stripping Method Applied to the Determination of the Brightener Concentration in Copper Pyrophosphate Plating Baths", J. Electrochem. Soc., 125, 194 (1978).

2. P. Bratin, "New Developments in the Use of Cyclic Voltammetric Stripping for Analysis of Plating Solutions", Proceedings of AES Analytical Methods Symposium, March 1985, Chicago, IL.

3. D. Cupolo, J. Nadeau, G. Fonseca and P. Bratin, "Applications of CVS to the investigations of Relationships and Effects of Organic Brighteners in Bright Nickel Baths", paper # 425, presented at the meeting of the Electrochemical Society, New Orleans, LA, October 1984.

4. "Modern Electroplating", F.A. Lowenheim, ed., Wiley & Sons, NY, 1974.

5. "Encyclopedia of the Electrochemistry of the Elements", A. Bard and H. Lund, eds., Marcel Dekker, NY 1973-80, V-3.

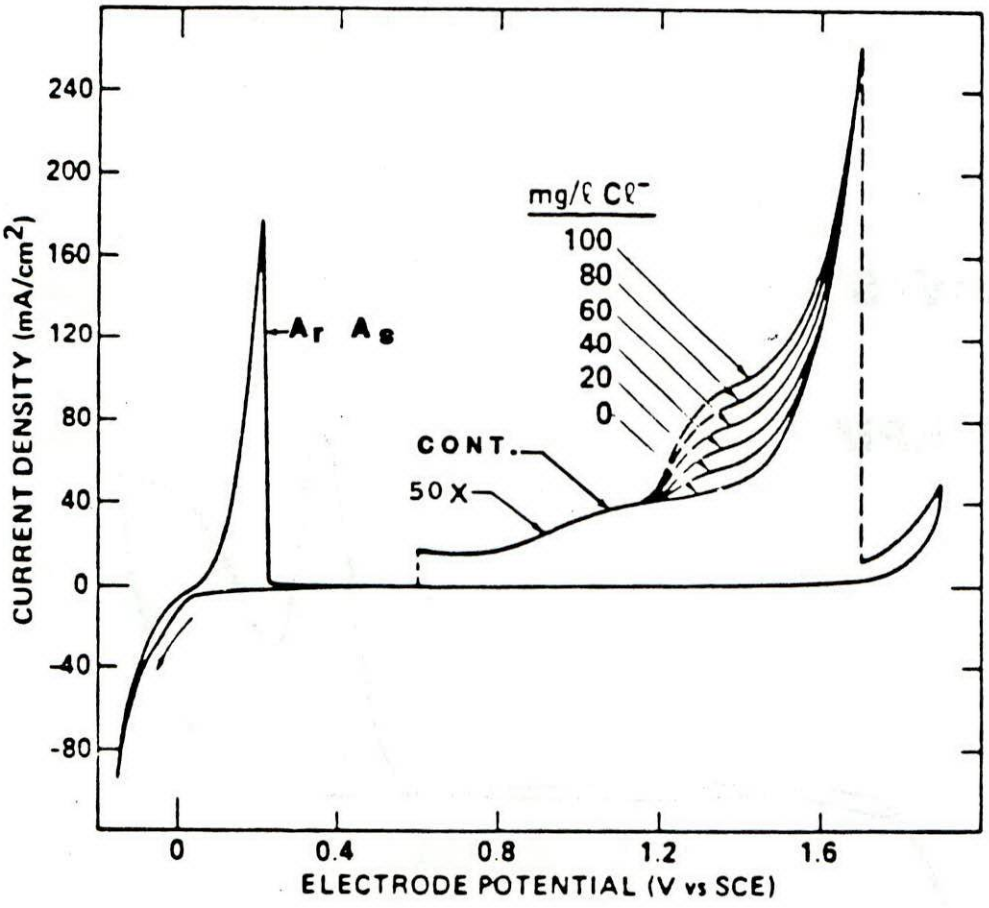

Fig. 1 Typical cyclic voltammograms, obtained in additive containing copper sulfate bath with various chloride concentrations. Note the expanded current scale for part of the anodic sweep (Scan rate = 100mV/S, rotation rate = 2500RPM).

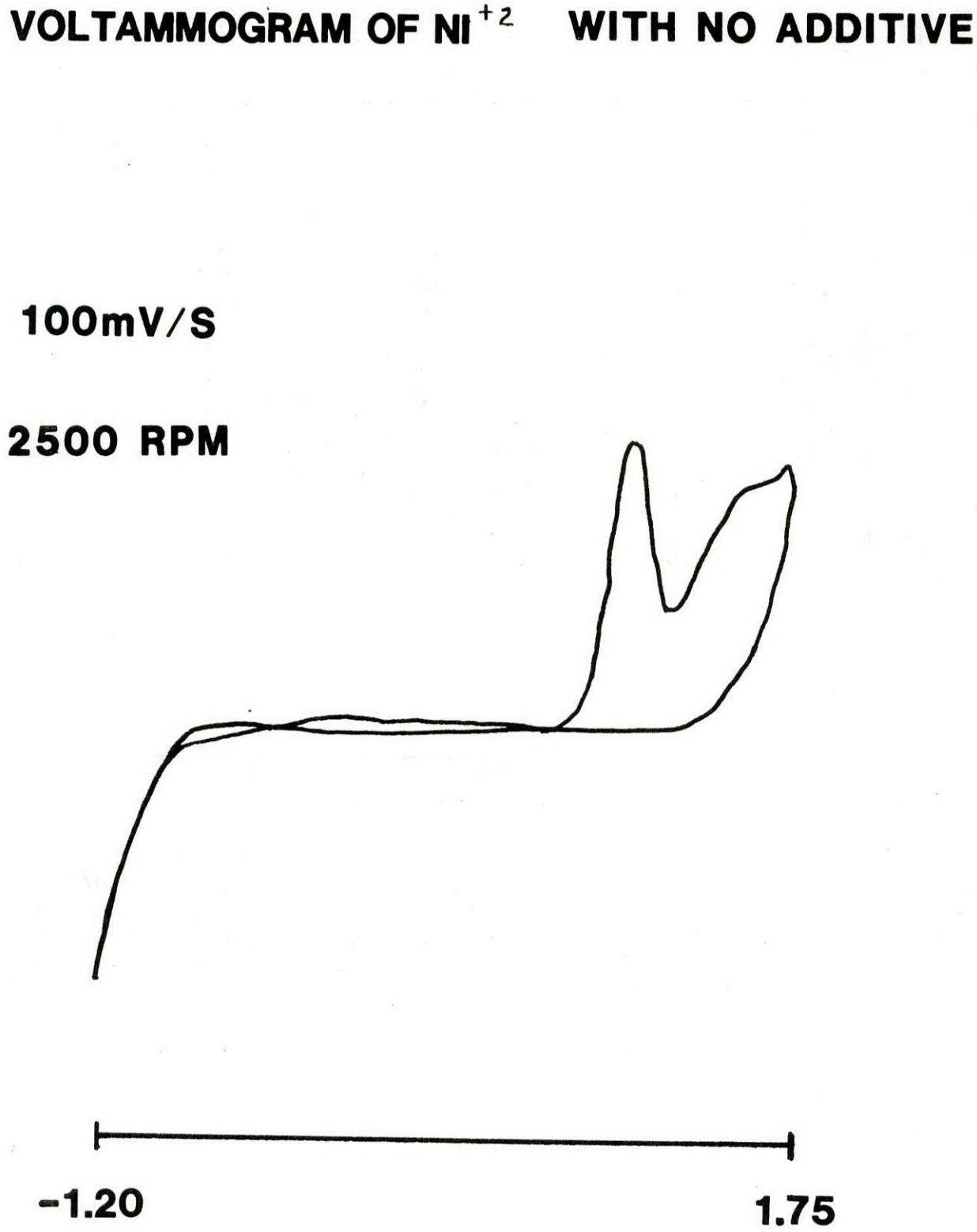

Fig. 2 Voltammogram of additive-free Watt's nickel plating bath (Pt rotating electrode, scan limits = -1.20 to 1.75V vs SCE, scan rate = 100mV/S, rotation rate = 2500RPM).

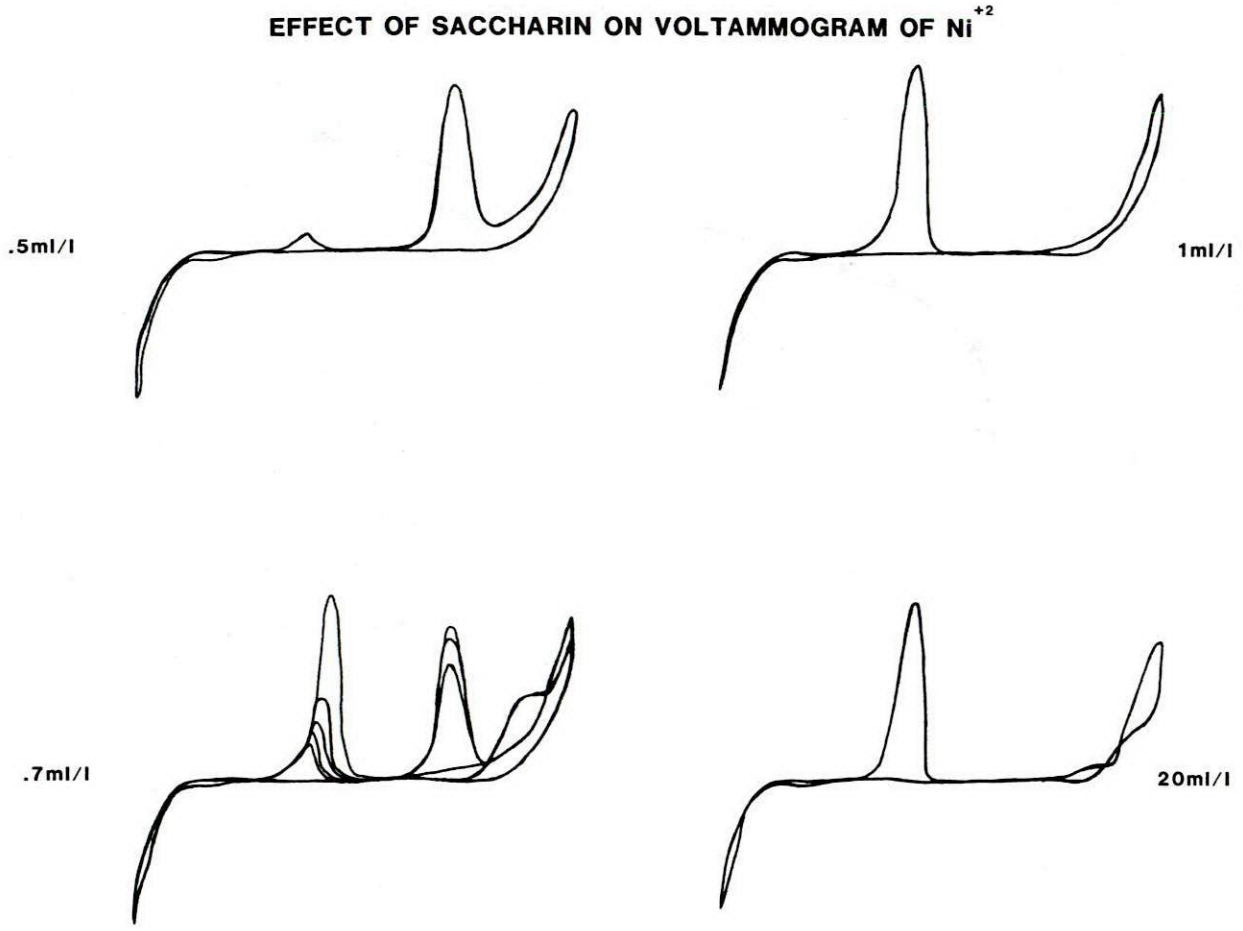

Fig. 3 Effect of saccharin-containing additive on the voltammogram of Watt's nickel plating bath (Pt rotating electrode, scan limits = -1.20 to 1.75V vs SCE, scan rate = 100mV/S, rotation rate = 2500RPM).

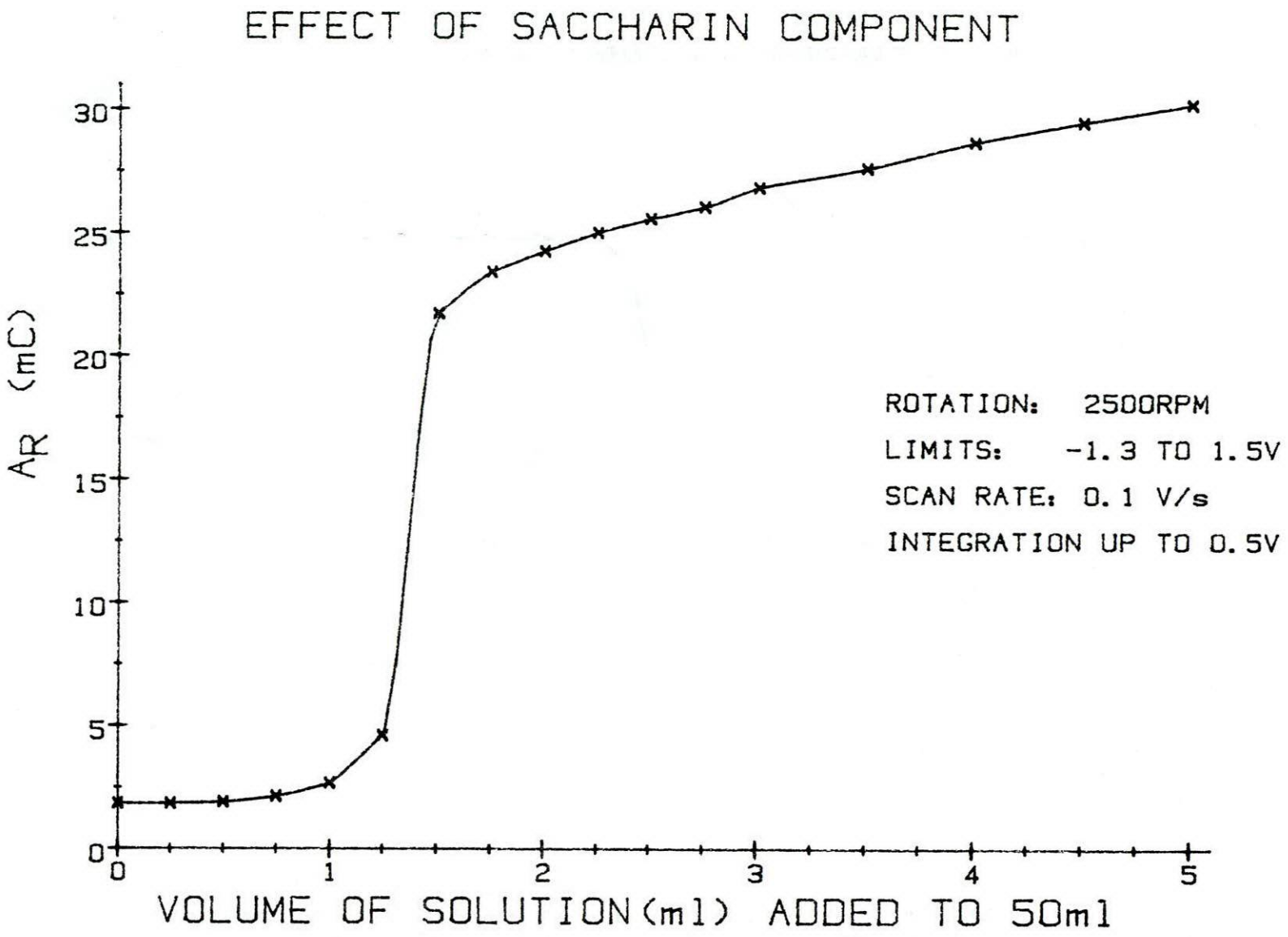

Fig. 4 Calibration curve showing effect of saccharin containing class I brightener on the A_R value of nickel virgin solution.

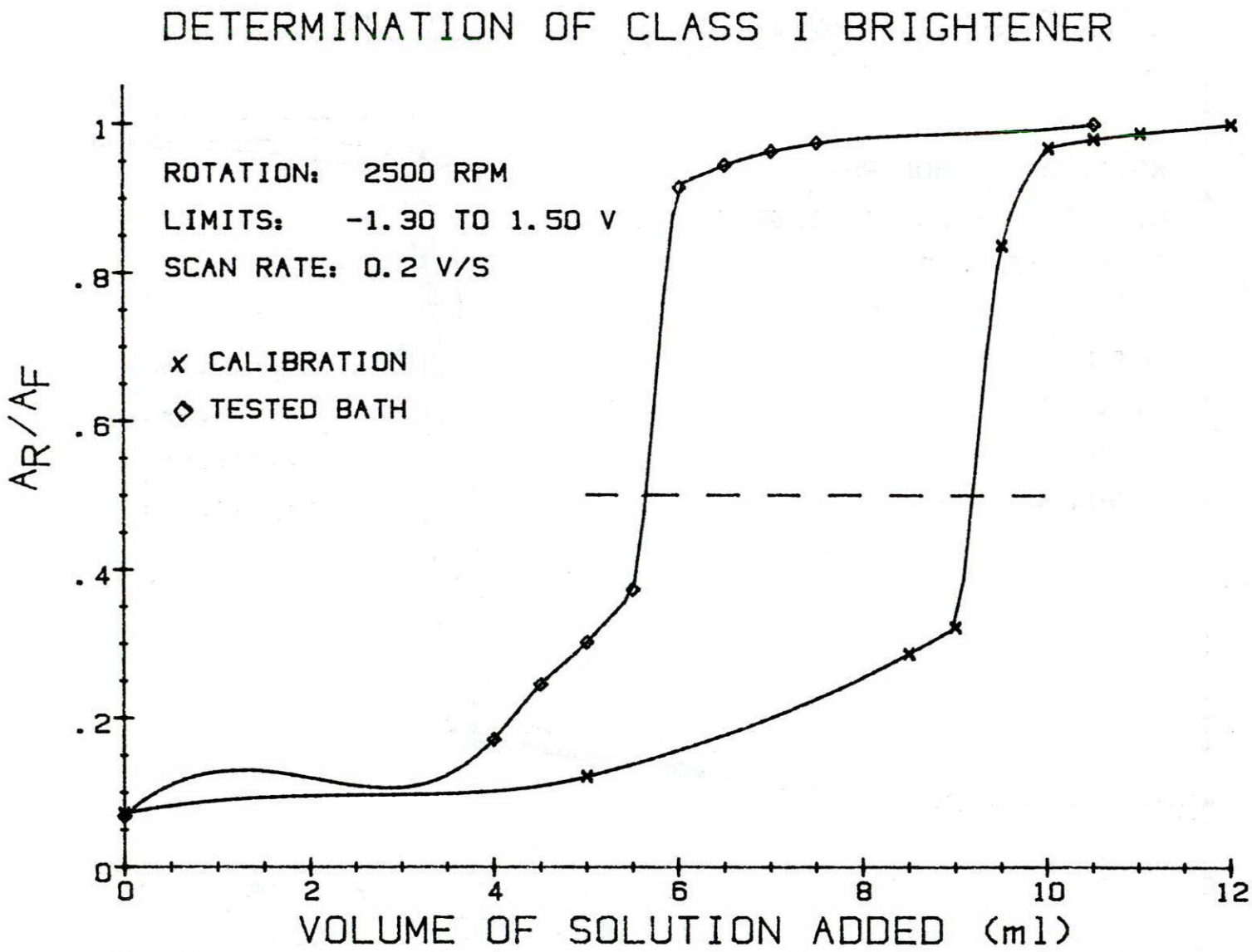

Fig. 5 Determination of effective concentration of saccharin containing class I brightener using the dilution titration technique with endpoint at $A_F/2$.

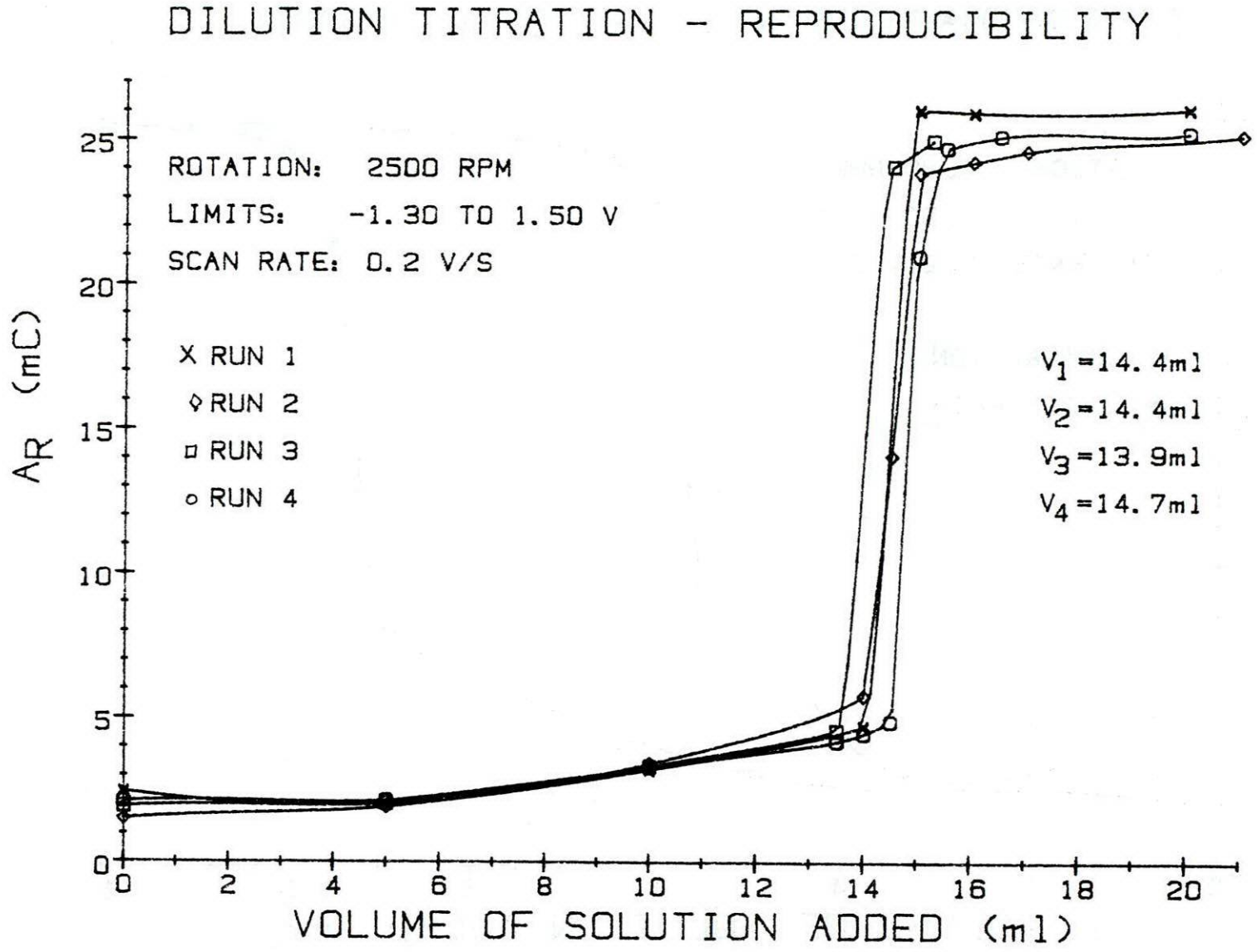

Fig. 6 Repeatability of dilution titration procedure for determination of effective concentration of class I brightener. Runs 1-3 were performed on the first day, run 4 on the following day.

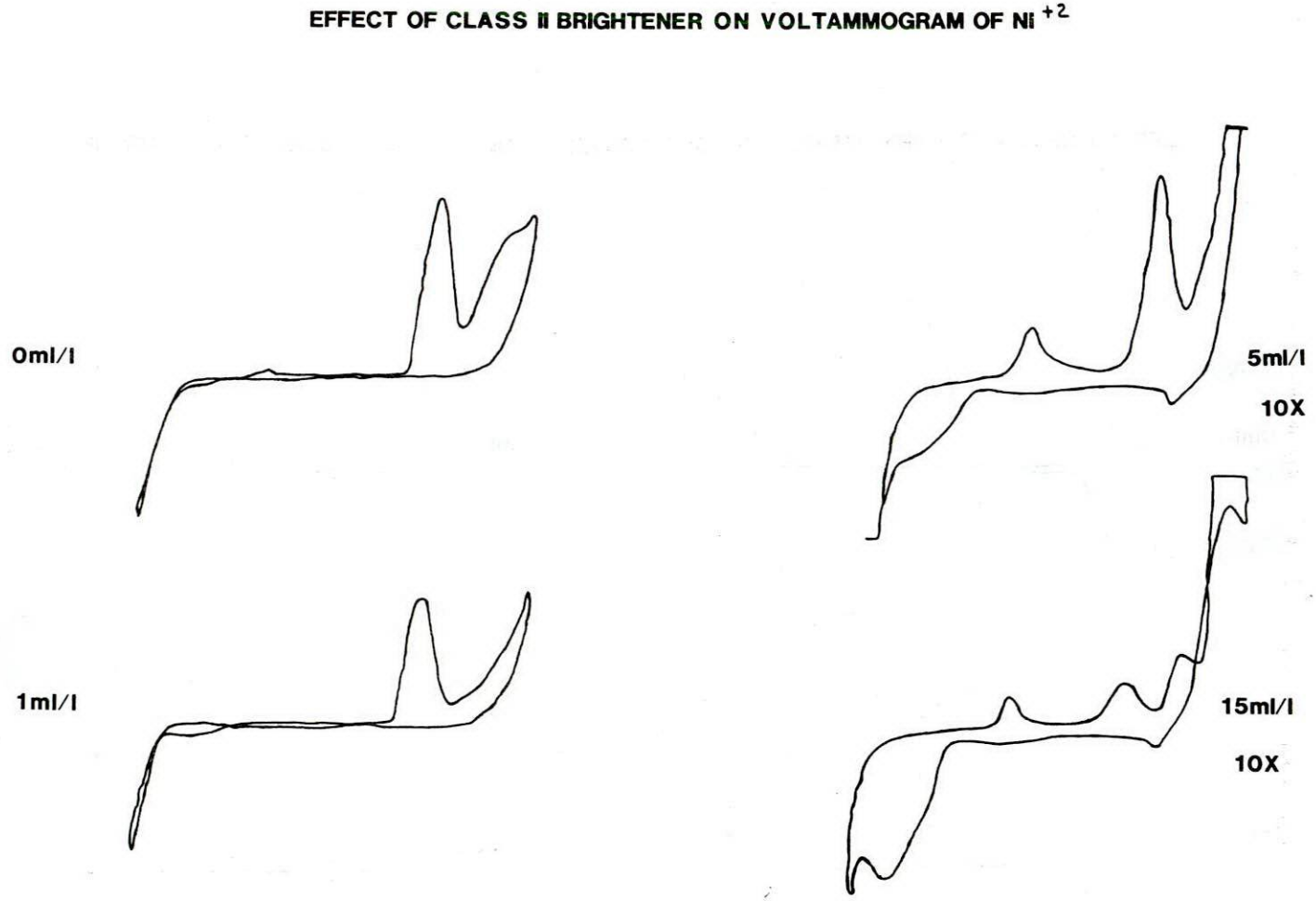

Fig. 7 Effect of class II brightener on the voltammogram of Watt's nickel plating bath (Pt rotating electrode, scan limits = -1.30 to 1.75V vs SCE, scan rate = 200mV/S, rotation rate = 2500RPM).

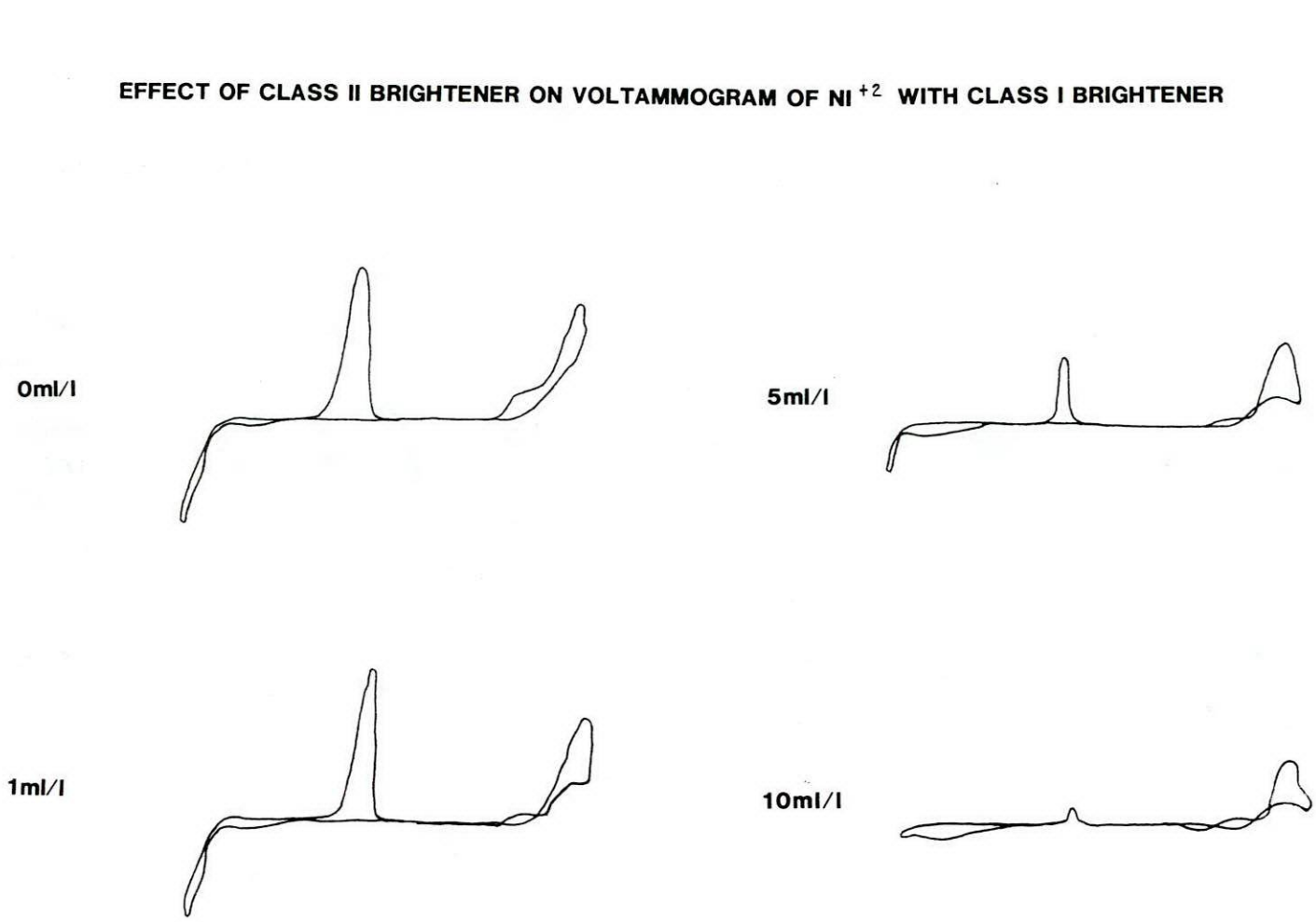

Fig. 8 Effect of class II brightener on the voltammogram of Watt's nickel plating bath containing 20ml/l of class I brightener (Pt rotating electrode, scan limits = -1.30 to 1.75V vs SCE, scan rate = 200mV/S, rotation rate = 2500RPM).

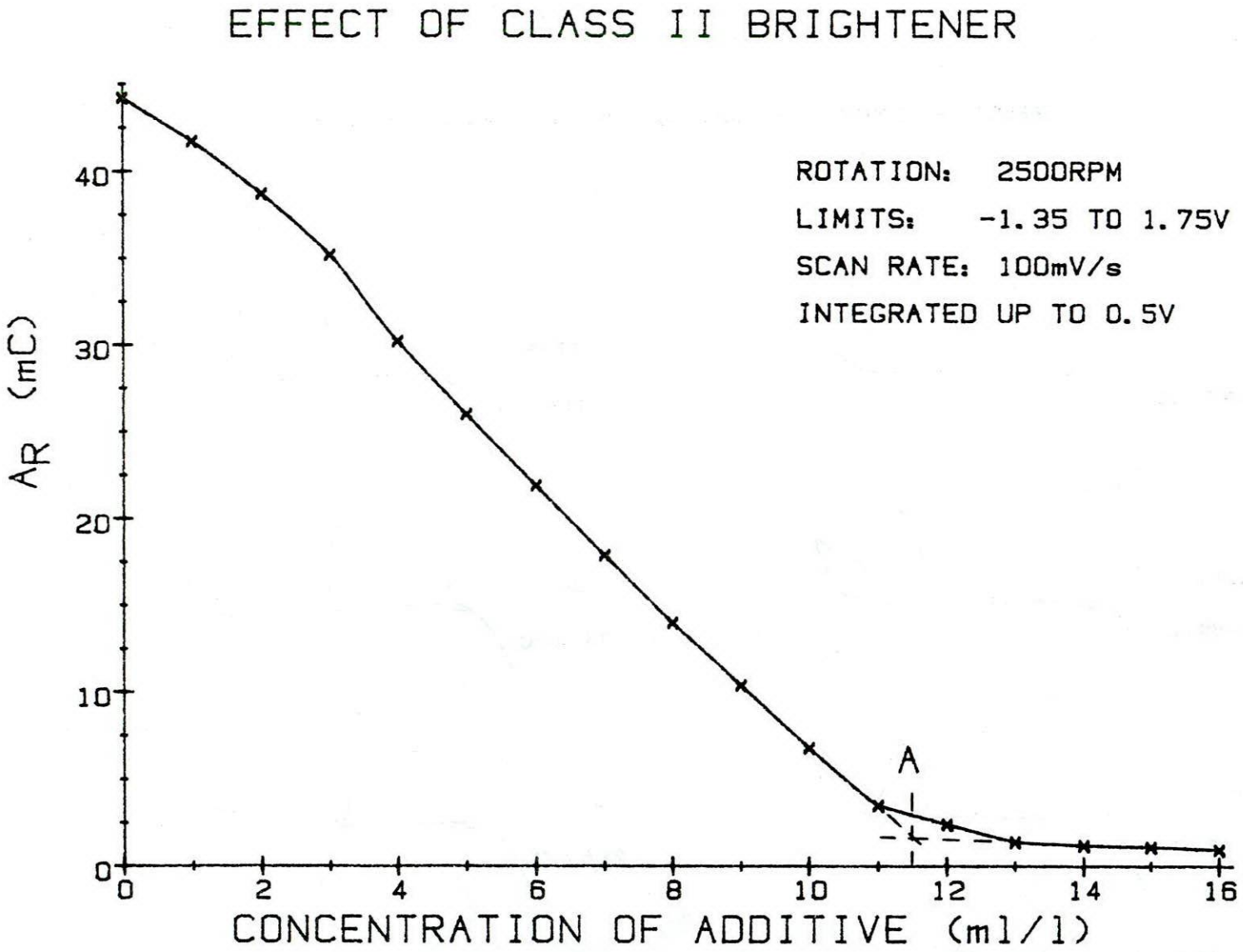

Fig. 9 Calibration curve showing effect of class II brightener on the A_R value of nickel virgin solution containing 1% of class I brightener. Point A denotes recommended endpoint.

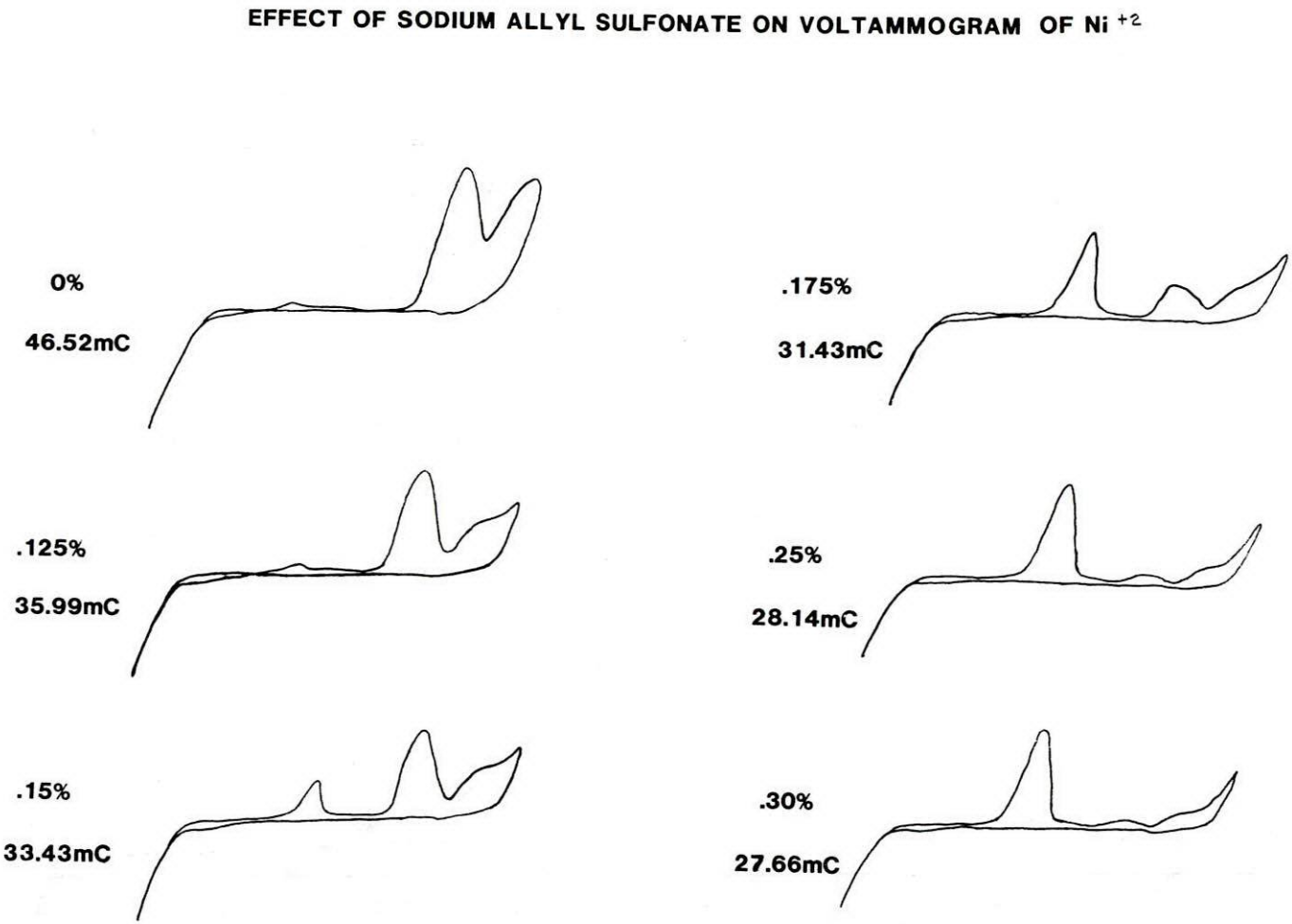

Fig. 10 Effect of sodium allyl sulfonate on the voltammogram of Watt's nickel plating bath (Pt rotating electrode, scan limits = -1.30 to 1.75V vs SCE, scan rate = 200mV/S, rotation rate = 2500RPM).

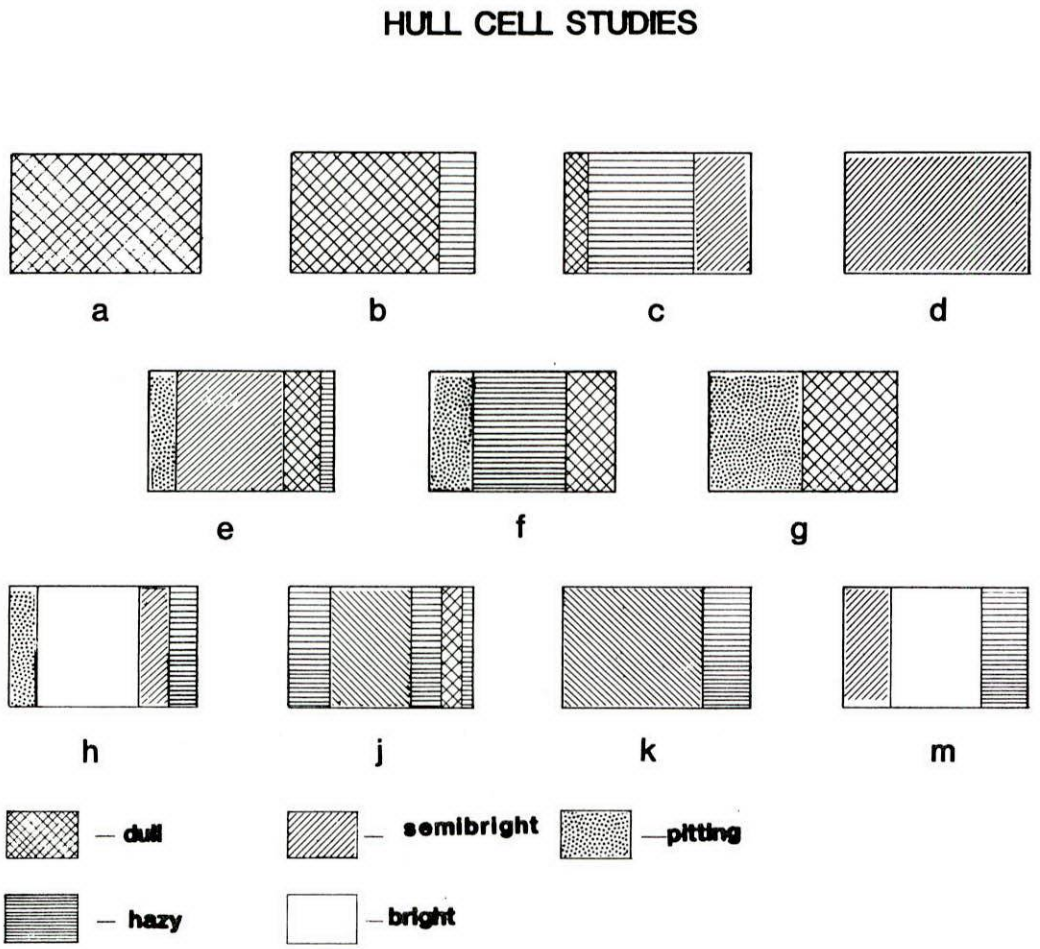

Fig. 11 Hull cell results (267ml cell, 60°C, current = 3A, time = 6 min, mechanical agitation, brass plates) a. no additive, b. 0.5ml/l, c. 1.0ml/l, d. 2.0ml/l, e. 5ml/l, f. 10ml/l, g. 20ml/l of saccharin containing class I brightener; plates h, j, k and m were plated in solution containing 20ml/l of class I brightener plus g. 0.75ml/l, h. 1.25ml/l, j. 3ml/l and m. 5ml/l of class II brightener.

A-2

General Interest Session A

Electrodeposited Aluminium And Its Importance For Surface Technology

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Electrodeposited aluminium and its importance for surface technology

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1. Introduction

Due to its physical, chemical and mechanical properties, aluminium finds a wide variety of applications in aviation, transportation, electrical engineering, optics and in surface finish design.

These properties show that aluminium must also be of considerable interest for surface finishing. This means that it is possible to combine existing properties of the base material to advantage with those of the aluminium coating thereby giving the workpiece a longer life and making it suitable for new applications.
Aluminium is also of interest from economic and ecological aspects. It is physiologically harmless and is available in unlimited quantities.

The aluminium process* developed by Siemens is the only existing process which permits high-purity aluminium to be applied as an electroplated coating on a commercial scale for rack-plating.

The process and plant technology required for its implementation was developed jointly with our Dutch licencee HGA B.V. from the laboratory to the production stage since 1980.

2. Process technology

When comparing aluminizing with conventional aqueous plating processes, the parts to be plated pass through the same process steps in both cases:

- Pretreatment
- Electrodeposition
  and eventually
- Post treatment

* Sigal(R) - process

The parts to be aluminized are pretreated in aqueous solutions.
These are matched to the requirements of an adhering aluminium coating, as well as surface protection of the parts by aluminium which is to be effective under various climatic conditions.

As the aluminizing process must take place in a non-aqueous organic medium for electrochemical reasons, the aqueously pretreated material must be subjected to an additional dewatering step beforehand.

The aluminizing process as such is an absolutely clean, ecologically harmless and reliable process step and is performed in an enclosed electroplating cell which is loaded and unloaded through air-locks. The aluminizing electrolyte must remain enclosed because any contact with atmospheric oxygen and moisture will sooner or later become useless for electroplating purposes.
An eventual post treatment following the electrodeposition of aluminium would again take place in an aqueous medium.

The electrodeposition proper of the aluminum does not take place from an aqueous solution because of the negative deposition potential of E_o = -1.67 V but from an aluminium organic complex salt dissolved in toluene. The electrolyte system has a throwing power comparable with cyanide cadmium electrolytes which can be controlled and even increased considerably by varying the process parameters.

Plate anodes of the Raffinal or Super-Raffinal quality grades are dissolved in the electrolyte when the anode is polarized. The electrolyte transports the "dissolved" aluminium to the products which are polarized as cathode.

During this process an aluminium of higher purity than existing in the anode is deposited on the products.
The anode constituents which are not soluble in the electrolyte are filtered out continuously from the electrolyte.

The aprotic electrolyte system causes no corrosion whatsoever of the plating cell, any more than do the reaction products of the electrolyte with air and moisture.
Due to the chemical nature of the electrolyte it is impossible for hydrogen to be evolved.

3. Plant technology

Fully-automatic aluminizing lines are in operation satisfactorily for applying the galvano-aluminizing process on a commercial scale.

Each of these lines comprises a pretreatment section of conventional design, a dewatering station and the aluminizing section, consisting of the enclosed automatic aluminizing unit with two air-locks and peripheral equipment such as the electrolyte storage tank and filters.
The automatic aluminizing unit is followed by a conventional post treatment section. The aluminizing cell with its electrolyte capacity of 15 m^3 can handle 32 racks 500 x 1000 mm simultaneously for coating products with a surface area up to 48 m^2/h with an aluminium layer of 10-12 µm thickness.

4. Application potential

The galvano-aluminium process can be used in practice in the field of corrosion protection and for special functional surfaces and surface design.

4.1 Corrosion protection for high-tensile steels

Galvano-aluminium coatings are particularly suited for protecting high-tensile steels, such as springs, against corrosion as they are deposited from proton-free solutions and the base material does not suffer from hydrogen embrittlement.

The high-purity, finely crystalline galvano-aluminium layers approximately 8 - 25 µm thick present a particularly effective surface protection when they are yellow chromated, assuming appropriate surface finish quality and pretreatment of the base material. For example, the corrosion resistance in the salt-spray test according to ASTM B-117 is comparable with yellow chromated cadmium layers of similar thickness. Both coating systems withstand this test for 1000 h, while nickel, zinc, tin/zinc and tin coatings corrode.

Galvano-aluminium coatings provide outstanding corrosion protection when in contact with nitrous gases and fluorine. This property is of importance for applications in electrical and nuclear technology.

Galvano-aluminium is very suitable for applications where work pieces are subjected to both mechanical and thermal loading because of the low internal stresses and high ductility of the aluminium coating. The aluminium coating is not liable to crack formation which would propagate corrosion.

Because of its considerably higher melting point as compared to cadmium zinc and tin, galvano aluminium can be used to particular advantage for surface protection in the temperature range between 250° and 500°C.

4.2 Corrosion protection of aluminium and zinc pressure die-castings

In addition to iron and steel components, aluminium and zinc die-castings can also be provided with an adhering corrosion-resistant coating.

4.3 Galvano-aluminium for special functional surfaces

Galvano-aluminium coatings are eminently suitable to provide special functional surfaces. In semiconductor technology, for example, it is possible to produce solid bonds between aluminium connection leads and galvano-aluminized lead-frames. This all-aluminium assembly technique brings economic advantages because of the saving of precious metals, such as silver.

Galvano-aluminium coatings can also be anodized. This means that relatively soft surfaces can be converted into a new, hard material surface, which is at the same time, wear and corrosion-resistant and provides electrical insulation.

This surface is of importance for example, for the optical industry and for electrical engineering. Because of the compatibility of anodized aluminium coatings on, say steel, with human tissue, implants made in this way are suitable for surgical applications.

4.4 Galvano-aluminium for surface design

Like no other metal, galvano-aluminium is attracting increasing attention for surface design applications for a wide range of products, from various branches of industry such as the optical industry and the clock and watch industry.

This application potential is based on the possibility of anodizing galvano-aluminium to form transparent coatings which can also be dyed in various non-fading colours right up to black.

5. Economic aspects

Galvano-aluminium is very favourable in cost when compared to its proven quality.
Economically speaking, it is the equal of say cadmium or copper-nickel coatings with comparable corrosion-resistance.
When considering the increasing restrictions on the use of cadmium and the ever more costly disposal of its highly poisonous waste products, galvano-aluminium is the answer to high-quality corrosion protection for the foreseeable future.

In general galvano-aluminium coatings cannot compete with zinc coatings of comparable thickness in terms of price.
However, when including the greater surface protection effect of galvano-aluminium compared to zinc in the cost balance, galvano-aluminium can certainly be an economic alternative to zinc for some applications.

6. Future aspects

Work is now in progress on increasing the output capacity of the process for rack plating.
The process and plant technology for barrel plating has reached an advanced stage of development.

A-3

General Interest Session A

The Synthetic Assessment of the Engineering Designing of Electroplating Centre

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Beijing, People's Republic of China
Huang Ruiguang

The Synthetic Assessment of the Engineering Designing of Electroplating Centre

China Electronics Engineering Design Institute
Beijing, People's Republic of China
Huang Ruiguang

Many manufacturers require electroplating to enhance the decorative and functional quality of their products. Typically large- scale manufacturers include a captive electroplating shop in their factory. More factories mean more electroplating shops, which creates more environmental problems for the cities. If the individual shops were combined into a single electroplating centre that could service all of the factories, it would be possible to both reduce the environmental problems and reduce costs by taking advantage of volume production benefits, such as automation. Also, the technical personnel could be concentrated into a location and the conbined construction funds could be used to purchase the advanced equipment and instruments needed to develop the technology and processes required for modernization.

Recently the production organization of the electroplating centre pays attention to people more and more in our country. Therefore, the four main components of

engineering design of the electroplating centre are process, environmental protection, economic energy and economic benefit. Each must be synthetically assessed proceeding engineering designing to attain the optimum scheme.

1. The characteristic of the synthetic assessment of the engineering design:

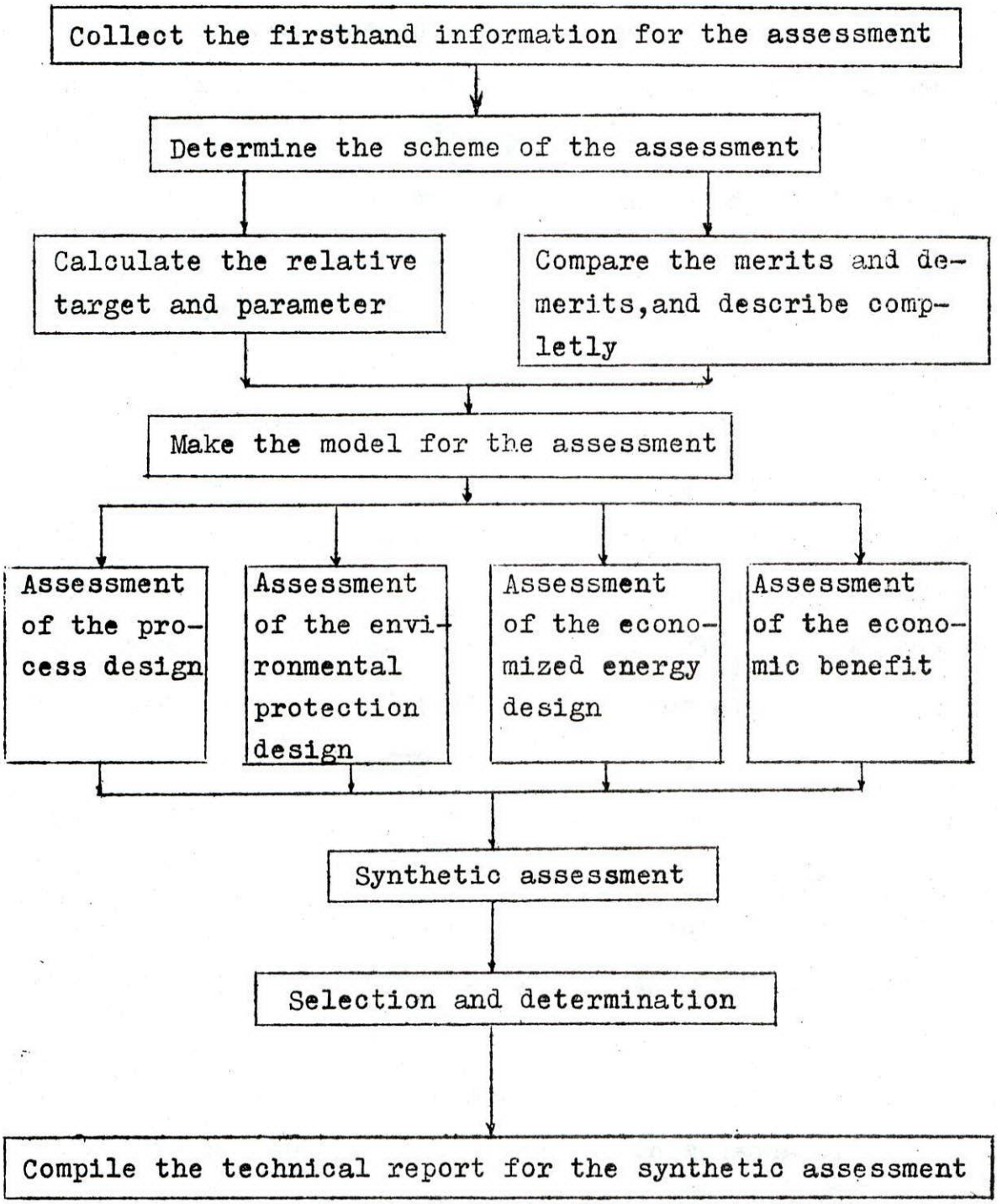
It is difference between the synthetic assessment of the engineering designing and the single assessment of process, environmental protection, economized energy and economic benefit. The single assessment of the process design always describes partially the adoption of the advanced techniques, the advanced equipment and advanced instruments for coming up to the optimum yield index and the optimum quality index of the products. But it doesn't consider the results and the appearence of troubles after it adopts the advanced techniques, etc. Such as: is it better or worse to environment; does it economize energy, is its economic benefit achievable to the optimum level? After construction and production it will appear some troubles or worse results causing the loss of money. In the same reason, it only partially considers to adopt the new technique of the environment or the economy of energy but not economic benefit. After

construction and production, it will get deficit.

The synthetic assessment of the engineering design studies how to adopt the new process, and it also forecasts the organic relationship among the environmental protection, the economy of energy and the economic benefit. It compares objectively the merits and demerits of the various factors from the different schemes. Then the scheme recommended shall be optimum. It shall be afforded to the construction unit refering to self-condition scientifically to choose such scheme. It shall be also afforded to the leading body of our government consulting to ratify rightly the capital construction project. It is quite evident, the synthetic assessment of the engineering design consists not only the investigation and the concrete analysis of the whole engineering technique of the electroplating centre, but also the forecast of the engineering design of the electroplating centre.

2. The procedure and the content of the synthetic assessment of the engineering design of the electroplating centre:

You may see the whole procedure and content of the synthetic assessment of the engineering design of the electroplating centre from the following block drawing:



2.1 Collect firsthand information for the assessment:

2.1.1 Process design:

(1) The yield of the output per year.

(2) The requirement and the standard of the coating quality.

(3) The possibility of adopting the traditional process of the new process.

(4) The possibility of adopting the common equipment and instruments, or the advancing equipment and instruments.

(5) The amount of the workers and staff members from various process schemes.

(6) The possibility of undertaking the cooperation of products for others or entrusting to others.

(7) The possibility of the development scale within 5 or 10 years.

(8) Others

2.1.2 Environmental protection design:

(1) The sources of waste water, the quantity and quality of waste water.

(2) The sources of waste gas, the quantity of waste gas, and the harmful materials and their properties.

(3) The sources of waste residue and sludge, their quantity and quality.

(4) The sources of noise pollution, and the quantity of noise.

(5) The requirement and the target of the environmental protection in the locality.

(6) The law, regulation and standard of the environmental protection from the leading body of the government.

(7) The basic condition for the environmental protection design.

(8) Others.

2.1.3 The economized energy design:

(1) The kinds, quality and quantity of the adopting energy.

(2) The possibility of the economized energy from the adopting various processes or equipment.

(3) The possibility of the economized energy from the different architectural design and the adopting equipment of the environmental protection.

(4) The different indexes of the consuming energy from the different equipment of energy.

(5) Others.

2.1.4 The funds of various items of the construction:

(1) The prices of the equipment and instruments of various processes.

(2) The costs of different architectural schemes.

(3) The funds of the different schemes of the en-

vironmental protection.

(4) The prices of the different power equipment of the consuming energy.

(5) The operation charge and the depreciation charge of the equipment from the different schemes.

(6) The total wages of the workers and the staff members from the different schemes.

(7) The information about other prices and the production cost.

2.2 Determine the scheme of the assessment:

Determine the four single technology - economic targets of process, environmental protection, economized energy and economic benefit recpectively to scheme 1, scheme 2, scheme 3, ... scheme n for assessment.

2.3 Calculate relative target and parameter:

Calculate the relative targets and parameters from firsthand information of the different schemes.

2.4 Compare the merits and demerits and describe completely:

Compare the merits and demerits completely about the techniques, the economy and the administration for the different schemes, and describe fully and clearly in a general table.

2.5 Make the model for the assessment:

According to the contents of the assessment with

the relative targets and parameters, make the model for assessment. Determine the unity of standards and calculation.

2.6 The assessment of the process design:

Put forward the technology - economy targets, the relative targets and the parameters from the various schemes of the process design in following table (1). Describe the merits and demerits fully and clearly.

Table (1) Assessment of the process design

no	Item \ Scheme	1	2	3	n	Remarks
1	Technological process					
2	Choose the types of equipment					
3	Choose the types of instruments					
4	Area of construction					
5	Consumed energy					
6	Amount of workers and staff members					
7	Area electroplating centre					
8	Others					
	Result of the single assessment					

* In the table: Max. value is 5, min. value is 0.

(also in later table).

2.7 The assessment of the environmental protection design:

Under the condition of the requirement from the process design to fulfil the task of the products, assess the technicality of the waste gas, the waste water, the sludge and the noise pollution in the treatment design. Emphasis must be placed on the effect of the treatment according to the national standard. On the other hand, the problem of the material recovery and the repollution needs to be solved. They are in following table (2).

Table (2) The assessment of the environmental protection design

no	Item \ Scheme	1	2	3	n	Remarks
1	Process of treatment					
2	Equipment for treatment					
3	Instruments for control and inspection					
4	Effect of treatment					
5	Material recovery					
6	Treatment for repollution					
7	Others					
	Result of the single assessment					

2.8 The assessment of the economized energy design:

Energy design refers to every item of the overall engineering design of electroplating centre. The electroplating process with low temperature, the general layout handled properly, the energy adopted measure for economy and workshops handled rational plan, have directive influence on the energy to be consumed. They are in following table (3).

Table (3) The assessment of the economized energy design

no	Item \ Scheme	1	2	3	n	Remarks
1	Process design					
2	Architectural design					
3	General layout and outdoor pipeline					
4	Types of power equipment					
5	Measure for economized energy					
6	Rate of utilized energy					
7	Others					
	Result of the single assessment					

2.9 Assessment of the economic benefit:

The economic benefit of the engineering design of the electroplating centre is to spend the minimum fund for the capital construction. And the process design, the environmental protection design, the economized energy design and other special engineering design shall be ensured with the rational scheme. The economic benefit also refers to the price of the original material and the electroplating products. But the contents of assessment do not consist with them. The contents of assessment are in following table (4).

Table (4) The assessment of the economic benefit

no	Item \ Scheme	1	2	3	n	Remarks
1	Yield of the output per year per member					
2	Value of the output per year per member					
3	Fund for the process design					
4	Fund for the environmental protection					
5	Fund for the economized energy					
6	Fund for the architecture					
7	Total fund for the electroplating centre					
8	Total wages for workers and staff members					

9	Total value of the output					
10	Total net profit per year					
11	Time of the repaying loans for the bank					
12	Others					
	Result of the single assessment					

2.10 The synthetic assessment:

We have got the four assessing results; the process design, the environmental protection design, the economized energy design, and the economic benefit of the various schemes from above four tables. Then the assessing results with "index" form of the multiplication and the addition for the selected scheme n shall obtain the total benefit index (TBI) by means of the calculation of the linear equation.

The method of the calculation is showed in following equation:

$$TBI_b = f(X_{ab}) = \sum_{b-1}^{4} K_b \cdot X_{ab}$$

It means $a = 1 \ldots\ldots n$

X_{ab} ..... the index mumber of the b item with a scheme.

K_b ..... the authority of the assessing factor to be distributed to b.

$b = 1 \ldots\ldots 4$

By means of the calculation, we shall get the decision that the max. value of TBI_b in the n items is the optimum item.

The value K of the assessing factor may be ordered by the opinions from the technical experts according to the different conditions and the different situations of every item. Then the authorized value shall be decided. The authorized value is max. While the content of the item signs the most important in all. While the content of the item is not important, the authorized value is min.. So the value K_b of the assessing factor shall be decided in order of importance.

By means of the mathematical matrix arrangement and calculation, the result is signed to the optimum scheme.

The method of the calculation is showed in following equation:

$$\begin{bmatrix} TBI \end{bmatrix} = \begin{bmatrix} X_{ab} \end{bmatrix} \begin{bmatrix} K \end{bmatrix}$$

In equation: $\begin{bmatrix} X_{ab} \end{bmatrix}$ ..... is matrix of n lines 4 rows.

K ..... in the vector of the benefit authority (4x1 steps matrix).

$\therefore \begin{bmatrix} TBI \end{bmatrix}$ ..... n x 1 step matrix.

Order: $\sum K_b = 1$ $\therefore \begin{bmatrix} TBI_a \end{bmatrix}$ max. value is equal to 1.

no	Item / Scheme	Process design	Environmental protection design	Economized energy design	Economic benefit
1	1	X_{11}	X_{12}	X_{13}	X_{14}
2	2	X_{21}	"	"	X_{24}
3	3	X_{31}	"	"	X_{34}
.	.	.	.	.	.
.	.	.	.	.	.
.	.	.	.	.	.
n	n	X_{n1}	X_{n2}	X_{n3}	X_{n4}

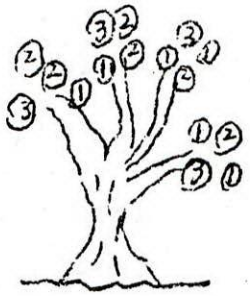
$$\text{Vector of authority} = \left| \begin{array}{l} \text{Process design} \\ \text{Environmental protection design} \\ \text{Economized energy design} \\ \text{Economic benefit} \end{array} \right|$$

$$\text{Total benefit index} = \left| \begin{array}{l} TBI_1 \\ TBI_2 \\ \vdots \\ TBI_4 \end{array} \right|$$

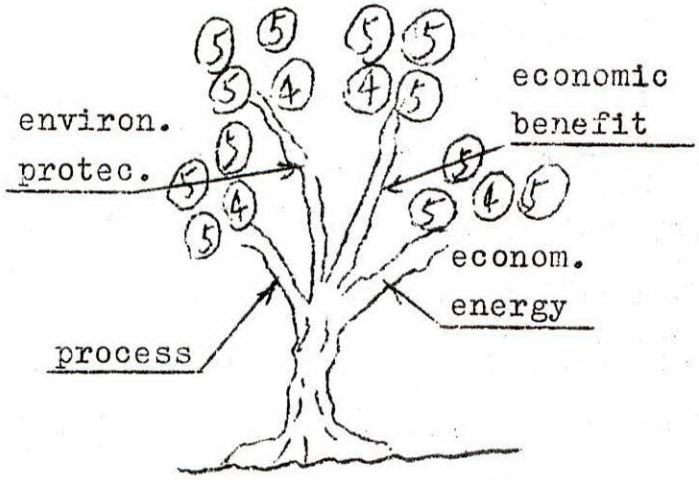
The max. total benefit index is signed to max.$\left[TBI_a\right]$. The max. value of $\left[TBI\right]$ in the calculating result is signed to the optimum scheme of the assessing result of the electroplating centre engineering design.

If we create the image for every scheme of the as-

sessment result, we may draw the assessment trees. The branch of tree is signed the item for the assessment; and the leaves are signed to the value. Every tree is signed to every scheme. The more leaves are luxuriant; the more value is great; the tree is larger. The largest tree is signed to the optimum scheme of the engineering design of the electroplating centre. Such as



Scheme $-n_1-$ bad



Scheme $-n_2-$ good

2.11 Selection and determination

The result by means of the synthetic assessment is recommended as an optimum scheme for the engineering design of the electroplating centre. It is the scientific conclusion. Therefore, the synthetic assessment of the engineering design of the electroplating centre reaches a conclusion on a case.

2.12 Compile the technical report for the synthetic assessment:

Compile "The Report of the Synthetic Assessment of the Engineering Design of the Electroplating Centre" with the proceedure, the content and the result of the synthetic assessment. Give the report to the construction unit, the higher authorities and the leading body of the government consulting to ratify rightly the project.

3. Conclusion

It is necessity and possibility to do the synthetic assessment for the engineering design of the electroplating centre. The technical benefit of the engineering design will be united with the economic benefit by means of the synthetic assessment. Provide the scientific foundation for the construction unit and the leading body. At present, the new process, the new environmental protection technology, the new measure for the economized energy appear countinuously. We adopt the optimum design scheme effectively be means of the synthetic assessment to compare the merits or demerits of the various technology. This is to promote quickly the realization of the electroplating modernization.

B-1

Plating on Plastics
Session B

Vacuum Preplate Process for Plating on ABS (Acrylonitrile-Butadiene-Styrene)

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VACUUM PREPLATE PROCESS FOR PLATING ON ABS (ACRYLONITRILE-BUTADIENE-STYRENE)

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INTRODUCTION

In recent years, changes in automotive manufacturing methods, for cost and vehicle weight reduction, have resulted in an increased use of plated plastics. Acryonitrile-butadiene-styrene is the most commonly used plastic substrate for electroplated decorative parts. Many chemical preplate processes are available which allow the application of an adherent, conductive metal layer on the plastic substrate. The results meet all durability requirements and such technology has gained wide industrial acceptance.

Nevertheless, there is a price to pay in terms of dollar cost, process complexity, chemical control and environmental concerns. Accordingly, we began efforts to develop an alternative method which offered equivalent performance and showed potential in alleviating the concerns involved with chemical solution pretreatment. The result is a preplate process using vacuum technology which has the potential for reduced cost, is relatively simple, eliminates solution processing and has virtually no environmental considerations.

Our vacuum preplate alternative involves three steps: 1) a glow discharge oxygen plasma treatment to condition the surface, 2) an active metal bonding layer, preferably nickel, to bond to the conditioned surface and 3) a copper conductance layer to provide enough electrical conductivity for subsequent conventional electroplating.

This paper will consider the process concept, our sample preparation and testing procedures and the results in terms of bonding layers, plasma parameters, performance and adaptation to production.

PROCESS CONCEPT

On first analysis, it is easy to believe that metal-plastic bonding in chemically preplated ABS is purely mechanical. The electroless preplate is anchored in pits produced by etching butadiene particles in the ABS surface by chromic acid solution (1). However, there have been a number of studies which indicate that chemical bonding is also significant (2,3,4). With this in mind, we sought to use a chemical bonding approach which would create a number of active functional groups on the plastic surface which could in turn bond to a subsequently deposited metal film. This led us to the use of a glow discharge plasma.

A plasma can be considered to be a mixture of ionized and/or excited gases (5), which can be quite reactive. Such a condition can be achieved in a vacuum chamber by applying a DC voltage across two electrodes in a low pressure gas. This in another form is the essence of sputtering. A plasma can also be created by subjecting a low pressure gas to a radio frequency (RF) field. In either case, gas molecules can be excited, dissociated or ionized, depending on the energies applied.

Exposure of polymers to such environments has been shown to result in chemical changes at the surface. With either helium or oxygen plasmas, Hansen and Schonhorn produced an insoluble, cross-linked surface on polyethylene (6,7). Burkstrand, in preliminary work with us on ABS, showed, by electron spectroscopy (ESCA), that DC oxygen plasma exposure produced a significant increase in single and double carbon-oxygen bonds (8).

If a metal with an affinity for oxygen, (e.g., Ni, Cr or Ti) were vacuum deposited on such an oxygen-enriched surface, a metal-oxygen-polymer bond could be established. Since such metals would passivate on exposure to air and since the deposit would not be sufficiently conductive for subsequent electroplating, a layer of vacuum-deposited copper would be necessary to overcome those obstacles.

It was with these concepts that we undertook to develop the vacuum preplate process. The results of this work were quite successful.

EXPERIMENTAL PROCEDURE

Because of the simpler operation involved with DC glow discharge plasmas, we elected to work with them first. Much of the information to follow was based on using DC plasmas. As will be discussed later, when applied to production moldings containing some degree of molding stress conditions, RF plasmas were found to be more appropriate.

Plaques of injection-molded ABS (7.6 x 12.7 cm) were treated in a DC or RF plasma of oxygen, vacuum-metallized by electron-beam evaporation and electroplated for adhesion and durability testing. In the case of DC plasmas, both plasma treatment and vacuum metallization were carried out in the same vacuum chamber, as shown in Fig. 1. The fixturing allowed both processes to be carried out in a single pumpdown cycle. The electron-beam crucibles, hidden behind a shield in the figure, were positioned at the bottom of the plasma ring and shielded to minimize deposition on the bell jar. The negative plasma electrode, a 23 cm diameter ring made from 0.64 cm diameter 316 stainless steel tubing was located above the electron beam gun. All other fixturing was grounded. The ABS plaques were mounted on a sample platen, face-downward, as shown. Provision for varying the substrate-to-electrode distance was available. Irregularly shaped production moldings were processed by use of a rotating device (not shown), positioned at the height of the sample platen.

The chamber was rough pumped to a pressure of 10-15 Pa and backfilled with oxygen to the operating pressure under study and maintained by an automatic pressure controller. After waiting 5 min to flush out most of the residual air from the chamber, plasma treatment was carried out as in Fig. 2. Variations in time, voltage, pressure and substrate-to-electrode distance were studied.

Prior to metallization, the vacuum chamber was flushed with argon to minimize oxide formation during vacuum deposition. The chamber was then pumped to 1-2 MPa of pressure. The e-beam metallization of the bonding layer and the copper layer were carried out as in Fig. 3. All layers were 100 nm in thickness. Besides nickel, which turned out to be the metal of choice, several other metals were studied for use as the bonding layer. The chamber was then filled to atmosphere and the samples were ready for electroplating.

Samples treated with RF plasma were processed in a separate RF plasma reactor consisting of an evacuated chamber (11 cm dia x 21 cm long) surrounded by external RF electrodes. The RF plasma treated samples were then transferred to the chamber described earlier for metallization. Preliminary tests showed that the intermediate exposure to atmosphere caused no significant loss in adhesion.

Adhesion Testing

Adhesion of vacuum-preplated copper-plated ABS samples was determined by the Jacquet peel adhesion test (3,9). The plaques were plated in an acid copper plating solution (225 g/L $CuSO_4 \cdot 5\ H_2O$, 75 /mL/L H_2SO_4) at 4.0 A/dm^2 to a thickness of 50 µm. Two 2.54 cm wide strips were peeled from each plaque.

Edge Adhesion Testing

The line-of-sight character of vacuum evaporation allows for selective plating, with appropriate masking. A V-pattern plating test was used to determine metal-to-plastic adhesion loss at exposed deposit edges during electroplating. The plaques were masked with a metal shield to expose a triangular area on the surface and were vacuum preplated as described earlier. This pattern was electroplated with bright acid copper and bright acid nickel from commercial solutions. If edge adhesion loss occurred, it appeared as an undercutting inward from the exposed edge and was readily seen after peeling back the deposit.

Durability Testing

Production moldings for durability tests were vacuum-preplated and taken to a production plating facility, where they were electroplated in regular production on the plating racks designed for the parts. They were plated according to the following minimum thicknesses specified for significant surfaces:

Acid Copper Plate	30	µm
Semi-Bright Nickel Plate	14	µm
Bright Nickel Plate	6	µm
Chromium	0.25	µm

The plated moldings were subjected to a 22 h copper-acetic acid salt spray (CASS) test or a 22 h ambient temperature water soak (where corrosion resistance information was not desired). They were then thermal cycle tested as follows: 1) 1.0 h at -30°C, 2) 15 min at 25°C, 3) 1.0 h at 82°C and 4) 15 min at 25°C. The cycle was repeated four times, unless failure occurred earlier.

As a comparison, samples of the same production moldings, which had been conventionally preplated, and production plated on the same unit, were obtained for durability testing.

BONDING LAYER STUDIES

The peel adhesion test results for the various bonding metals studied are shown in Fig. 4. The values represent a plasma treatment of 3 min at 700 V DC in 40 Pa of oxygen. In general, the best adhesion was obtained where a metal with a high affinity for oxygen was used. Nickel, chromium and titanium showed good adhesion. Aluminum, molybdenum and silicon showed good initial adhesion, but it was significantly reduced after 48 h, primarily through passivation effects, either via the exposure of the interface at the plaque edges or through the grain boundaries of the copper deposit. The more "noble" metals, such as copper and gold, showed lower adhesion. Silver, with high adhesion, was an anomaly. Other metals were tested but showed no significant bonding due to inherent difficulties in their evaporation.

The V-pattern tests showed that the more active metals were resistant to edge adhesion loss. In Fig. 5A, no undercutting was evident for nickel, chromium, or titanium after copper and nickel plating. The whitened area within the triangle outlining the original deposit area indicates complete cohesive failure within the peeled substrate. The same was true for aluminum, molybdenum and silicon, in Fig. 5B, but passivation at the interface led to separation between the vacuum deposited bonding and copper layers. Edge adhesion loss, penetrating inward, did occur in nickel plating, but not in copper plating for the more "noble" copper, gold and silver, as in Fig. 5C. Here, metal-plastic separation is seen to penetrate inward from the original deposit pattern. The grey color matches that in the unplated area. This effect is related to electroplating potential (10).

Under the conditions studied, nickel, chromium and titanium best met the requirements of producing a chemical bond between metal and oxygen DC plasma-treated ABS. Nickel was considered to be the metal of choice because of its ease of evaporation in the electron-beam system. A brief study into other techniques showed that similar results were obtained by nickel and copper sputtering. Chromium sublimes from the solid state and is difficult to handle. Titanium appears to work well, but it is more expensive. We regret to conclude that copper exhibited lower adhesion and no resistance to edge adhesion loss. A single metal deposition would have been very desirable.

Having established the nickel-copper metallization system, the next phase was to optimize the operation of the oxygen plasma.

DC PLASMA OPTIMIZATION STUDIES

Using a 100 nm nickel and 100 nm copper metallization system, the following DC plasma operating variables were studied and the resultant peel strengths were determined.

Plasma Gas:	oxygen, air
Time:	1, 3, 5, 10 min.
Voltage:	400, 600, 800, 1000, 1200, 1600, 2000V
Pressure:	15, 27, 40 Pa
Substrate-Electrode Distance:	10, 15, 20 cm

Plasma Gas

While most of this work dealt with an oxygen plasma, a cursory study was made of other plasma media, namely air. Peel strengths for samples plasma treated for 3 min at 700 V in a 40 Pa air plasma averaged 10.7 N/cm, versus 10.6 N/cm for oxygen under like conditions. This finding can favorably effect the economy of operating the process.

Plasma Time

The chemical surface changes which lead to metal-plastic bonding are established within 1.0 min of plasma exposure. The results of time variations for several voltages are shown in Fig. 6. With no plasma (zero time) a minimal adhesion was observed. The adhesion generally increased to a maximum value with 1.0 min of plasma time and remained at that level with further treatment. This effect was quite reproducible at 1000 V where the highest adhesion was obtained. For purposes of practicality a 3 min time is recommended.

Plasma Voltage

Next to the choice of bonding material, plasma voltage was the most important variable effecting adhesion. As shown in Fig. 7, for the conditions indicated, a small increase in adhesion occurred up to 600 V. We observed little or no visible glow discharge up to this point. At 800 V, adhesion increased rapidly, reaching a maximum above 1200 V, and remained at that level to 2000 V. The values were equal to those obtained by conventional chemical preplating (17.5 N/cm and above). A slight decrease at 2000 V, suggested a heat softening of the ABS. The practical operating voltage is recommended at 1000 V.

The results of the bonding layer studies, discussed earlier, reflect adhesion obtained at 700 V, which turned out to be below the optimum level.

Plasma Pressure

At 1000 V, variation of oxygen pressure from 15 to 40 Pa had little effect on adhesion, as shown in the response surface of Fig. 8. Consequently there is a large latitude in controlling oxygen pressure. The pressure variation had a larger effect at 800 V. Here, the adhesion decreased at 15 Pa, owing to a reduction in the plasma density as the mean free path increased. The decrease in adhesion as the pressure was raised to 40 Pa resulted from a decrease in the mean free path and the resultant contraction of the plasma away from the substrate surface. This contraction was readily observed. These effects were sensitive at 800 V. At 1000 V, however, there was a large latitude in selecting an operating pressure.

Substrate-to-Electrode Distance

At 1000 V, a wide latitude in substrate-to-electrode distance was observed with respect to adhesion, as shown in Fig. 9. This is particularly important where irregularly shaped parts are considered. At higher voltages, short separation became a problem, with the adhesion weakening because of heating effects, such as is shown at 1200 V. At lower voltages, the plasma was weaker, and adhesion was again reduced, as at 800 V.

Plasma Optimization

Under the conditions and system geometry studied, a 3 min, 1000 V DC oxygen plasma, with nickel-copper metallization, provided metal-to-plastic adhesion comparable to that obtained conventionally. There was a wide range of oxygen pressures and substrate-to-electrode distances over which this condition obtained, as shown in Fig. 10.

PERFORMANCE WITH PRODUCTION MOLDINGS-DC PLASMA

Up to this point, our tests dealt entirely with well-molded ABS plaques containing a minimum of flow anomalies or molding stress. Production moldings, on the other hand, are irregularly shaped and perfect surface conditions are difficult, if not impossible, to achieve over the entire surface of the part. Accordingly, the usefulness of the process could only be shown by durability testing of vacuum preplated production moldings.

A series of small production moldings were obtained and vacuum preplated under the optimum conditions determined above: 1) time = 3 min, 2) voltage = 1000 V, 3) pressure = 27 Pa and 4) substrate (centerline of rotation)-to-electrode distance = 15 cm. They were then production plated and tested along with a group processed conventionally in regular production. The parts selected were normally used in interior applications and certain deep recesses were exempted from evaluation in the CASS test.

All conventionally processed parts endured 22 h of CASS exposure and four thermal cycles on significant surfaces with no evidence of corrosion or blistering. Unfortunately, the vacuum preplated parts did not perform as well. Prior to testing, we observed certain areas, at corners or on radii, where small blisters had occurred, as in Fig. 11. The CASS exposure and three thermal cycles produced no enlarging of the blisters or new blisters. However, on the fourth thermal cycle, two of the six parts tested showed new minor blisters on significant surfaces.

The chemical bond obtained with DC oxygen plasma was felt to be sensitive to the variety of surface stress conditions encountered in production moldings. As seen in Fig. 12A, DC plasma resulted in no physical etching. Our approach was to augment the chemical bonding with mechanical bonding achieved through a surface etch. Such an etch was produced in an RF oxygen plasma, as seen in Fig. 12B.

PERFORMANCE WITH PRODUCTION MOLDINGS - RF PLASMA

The plasma induced by an external RF field is more energetic and efficient. The percentage of excited or dissociated molecules is higher owing to the oscillation of electrons in the field (11). Further, the RF field effects the wall potential of the non-conductive ABS, resulting in some species bombardment; this is similar to effects in RF sputtering (11).

A series of tests was run on ABS plaques using RF oxygen plasma treatment. At the pressures used with DC plasma, control was difficult. Power requirements were less owing to the energy of the RF plasma. The curve in Fig. 13 represents the peel strength versus time curve for an RF plasma operating at 35W forward power (reflected power < 0.2 W) in 175 Pa of oxygen. An optimum processing time of 10 min was indicated. Lower power levels required additional time, while higher powers (e.g., 50 W) led to overheating and softening of the plastic. Again, adhesion values reached those produced with conventional processing. The effects of the various bonding metal layers were virtually the same as for DC plasma.

With this, a second series of the same production moldings was RF-plasma treated, vacuum metallized with the nickel and copper preplate layers and production plated. These samples showed no evidence of blistering after electroplating. After 22 h of CASS exposure and four thermal cycles, there was no evidence of metal-plastic adhesion failure. It appears that the mechanical interlocking afforded by the RF plasma etching was sufficient to augment the chemical bond and thereby produced good durability performance.

Our experience with the production parts indicated that one small variation was required in the electroplating process. The first 5-10 min of acid copper strike plate should be done at a low current density (1.0 A/dm^2) to build up the copper coating and to avoid contact burnoff.

PREPLATE STABILITY

The oxygen-plasma treated surface is stable. Delays of up to 72 h at atmospheric pressure prior to metallization have resulted in no reduction in metal-to-plastic adhesion. The process could thus be done in two separate steps. However, there are inherent productivity advantages in designing the chamber to accommodate both steps in one vacuum pumpdown cycle.

The metal-to-plastic bond is stable. Electroplated samples aged at room temperature for up to 7 years have shown no loss in peel strength. This applies to both DC and RF-plasma-treated samples.

ACKNOWLEDGMENT

The authors gratefully acknowledge the assistance of J. M. Burkstrand, formerly of the Physics Department, for his efforts in surface analysis by ESCA. We are particularly grateful to G. Carlson and his staff at Fisher Body-Elyria for providing their facilities and talents in the production plating of the injection moldings. Through their efforts, we were able to demonstrate the workability of the process in a manufacturing environment.

REFERENCES

1. R. G. Wedel, Int. Met. Rev. 22, 97(1977).

2. G. R. Logis and A. Rantell, Trans. Inst. Metal Finishing, 46, 91(1968).

3. E. B. Saubestre, et al. Plating, 52, 982(1965).

4. R. G. Wedel, Plating, 62, 235(1975).

5. L. B. Loeb, "Electrical Coronas-Their Basic Physical Mechanisms," University of California Press, Los Angeles (1965).

6. H. Schonhorn and R. H. Hansen, J. Appl. Poly. Sci., 11, 146(1967).

7. Ibid, 134, 203(1966).

8. J. M. Burkstrand, J. Vac. Sci. Technol., 15, 223(1978).

9. American Society of Electroplated Plastics," Standards and Guidelines-Electroplated Plastics," ASEP, Washington, DC(1979).

10. J. H. Lindsay, unpublished results.

11. L. I. Maissel and R. Glang, "Handbook of Thin Film Technology," McGraw-Hill, New York (1970).

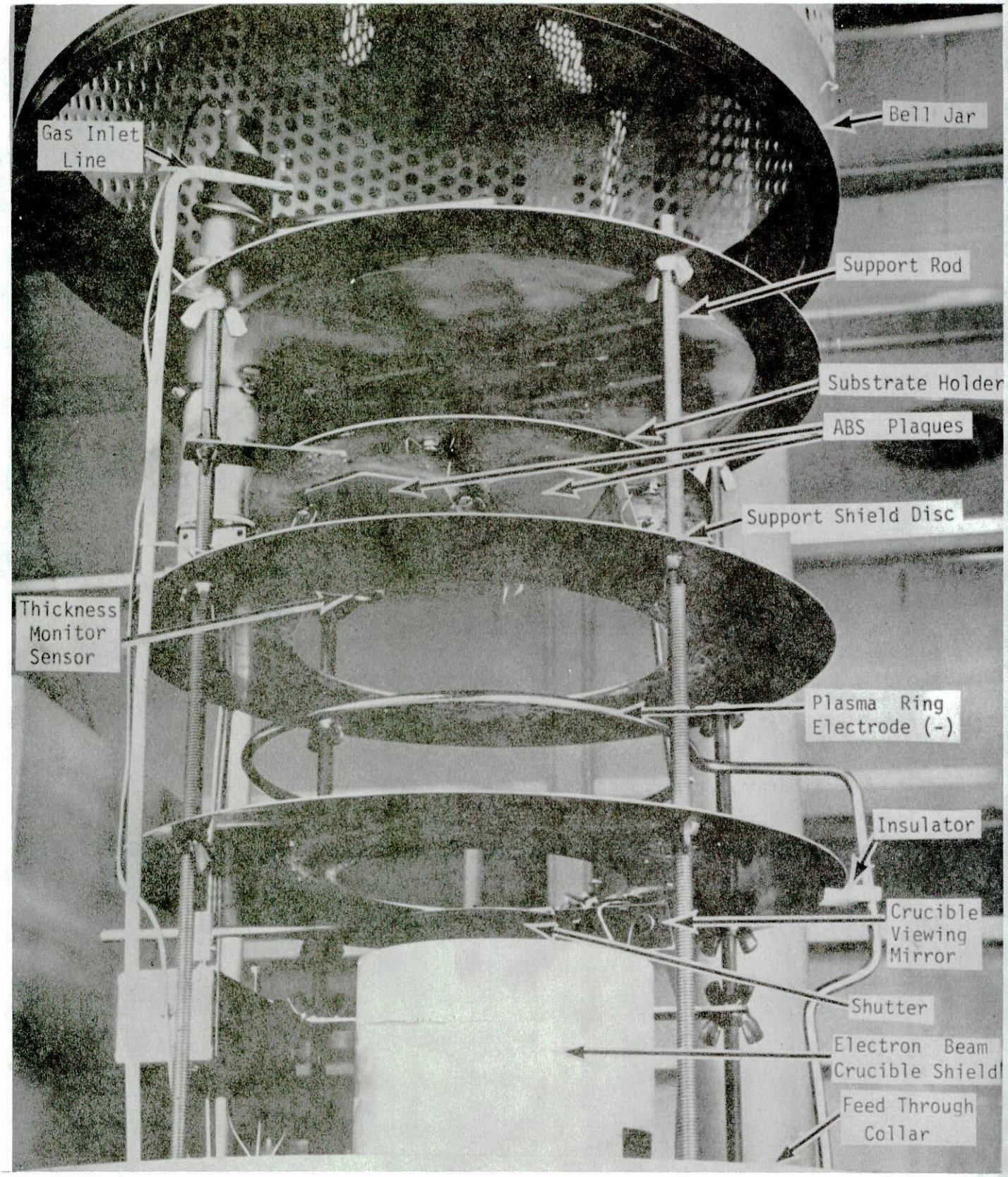


Fig. 1. Apparatus for plasma-vacuum metallizing pretreatment.

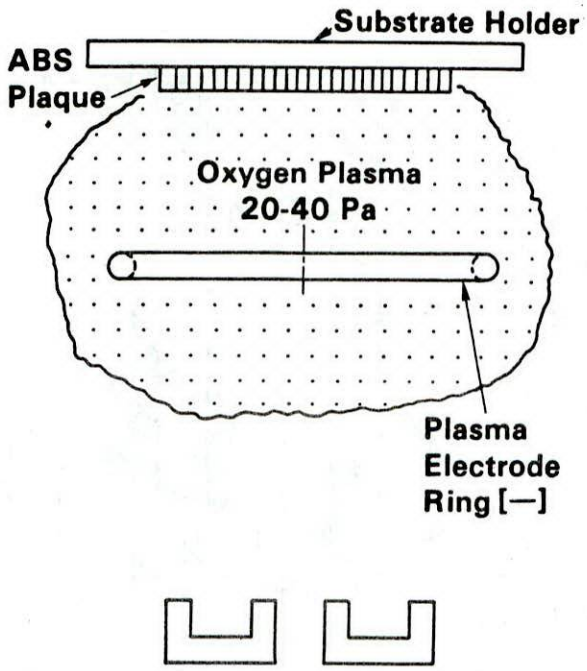


Fig. 2. DC plasma treatment step.

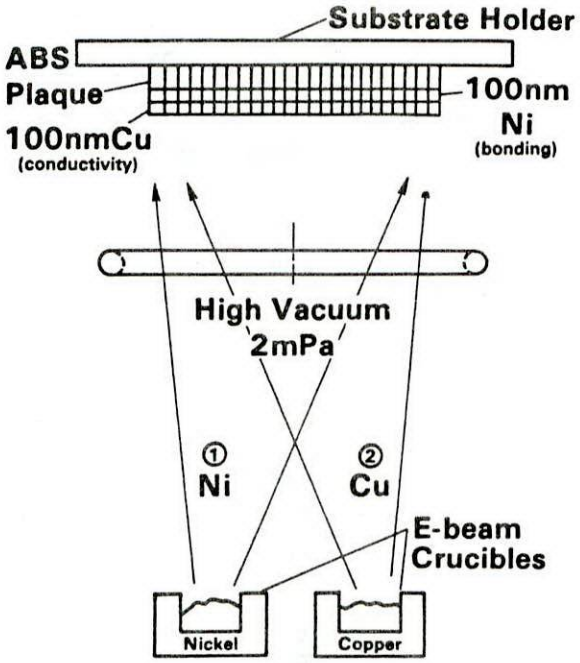


Fig. 3. Ni/Cu metallizing steps.

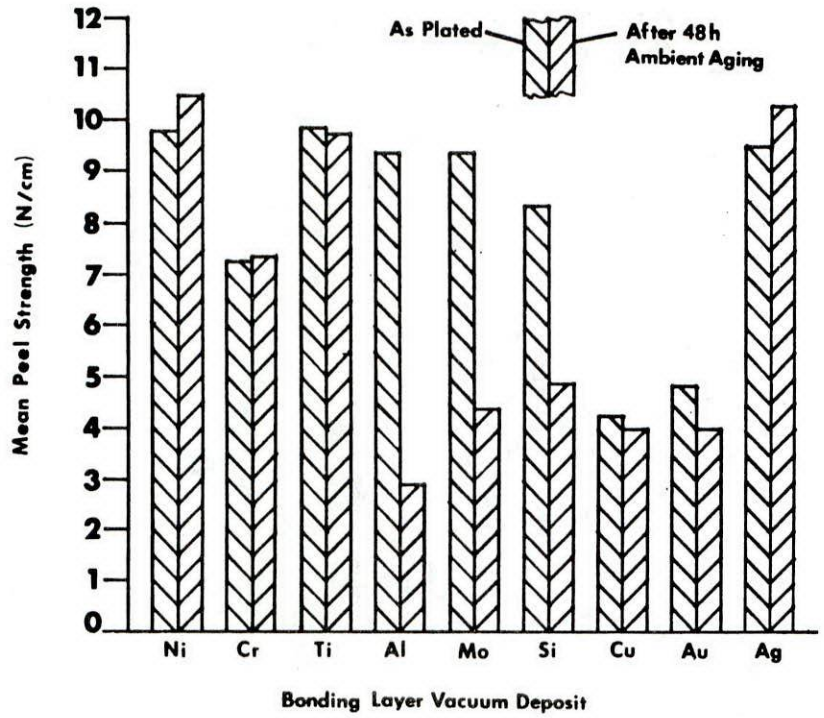
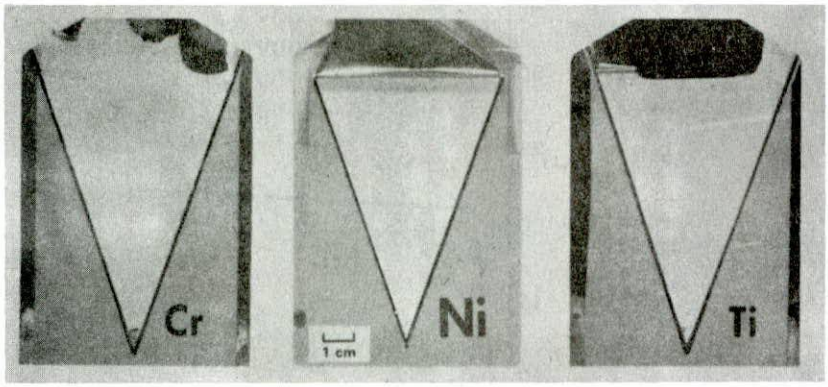
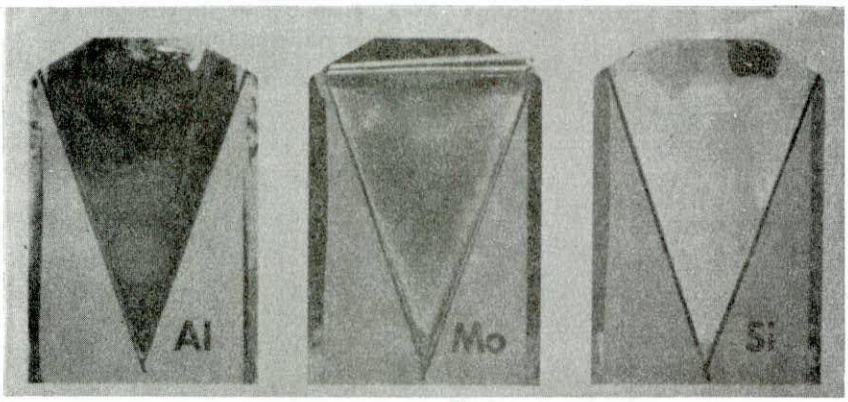


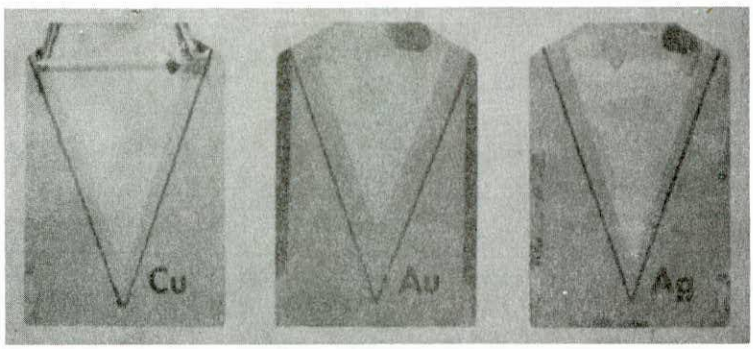
Fig. 4. Results from Jacquet peel adhesion test (mean peel strength)



A. Active metals: Cr, Ni, Ti
Good adhesion properties.



B. Active metals: Al, Mo, Si
Passivation effects.



C. Noble metals: Cu, Au, Ag
Edge adhesion loss.

Fig. 5 - V-pattern edge adhesion test results.

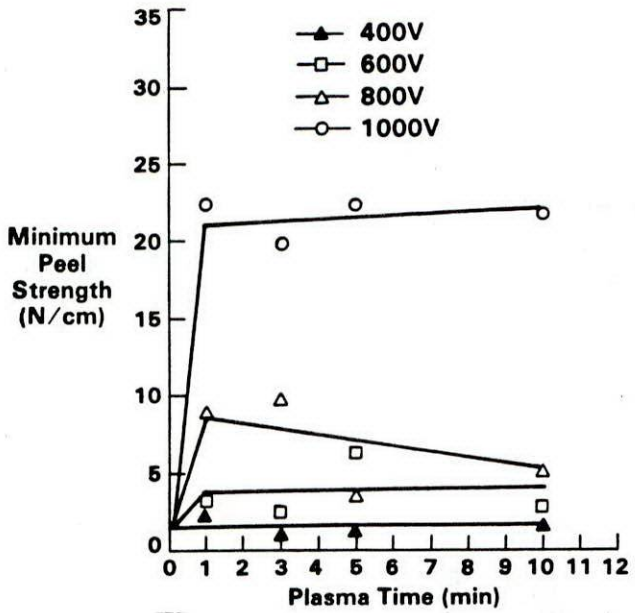


Fig. 6. Peel strength vs. dc plasma time.

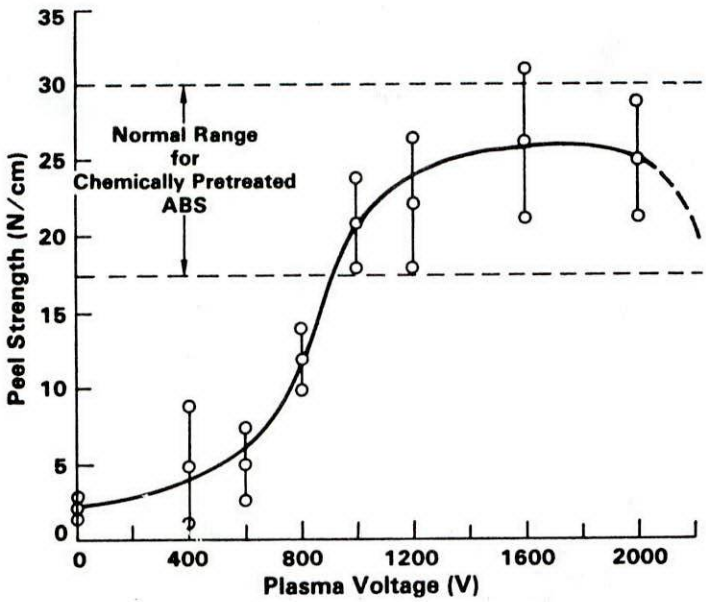


Fig. 7. Peel strength vs. dc plasma voltage.

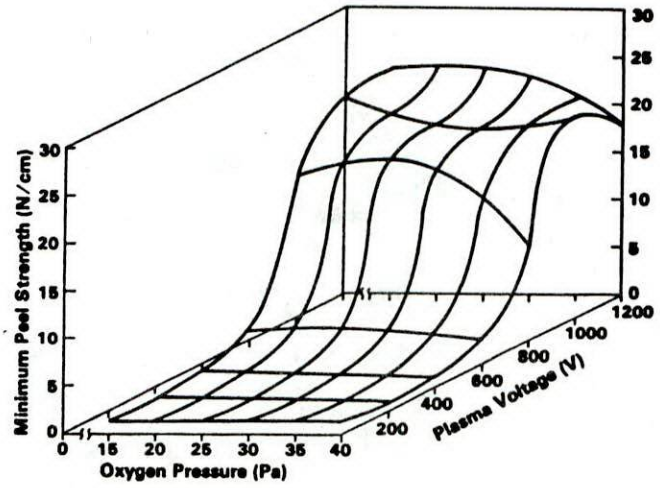


Fig. 8. Peel strength vs. dc plasma voltage and O2 pressure.

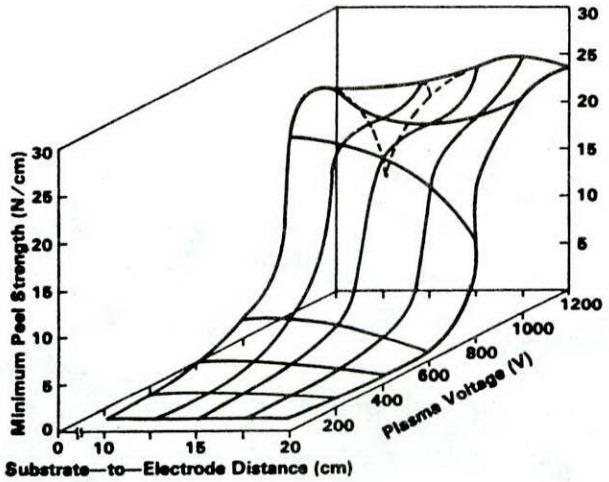


Fig. 9. Peel strength vs. dc plasma voltage and substrate-to-electrode distance.

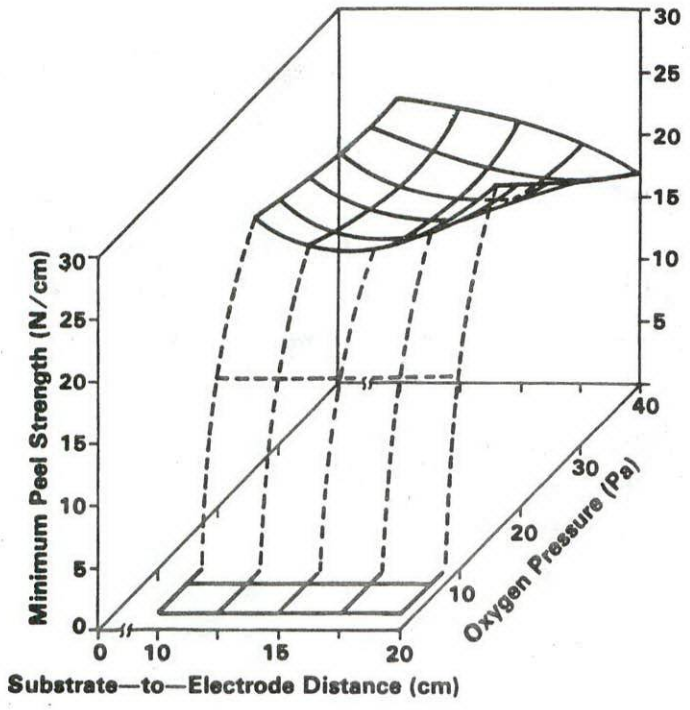


Fig. 10 - Peel strength (N/cm) vs. O_2 pressure (Pa) and substrate-to-electrode distance (cm).

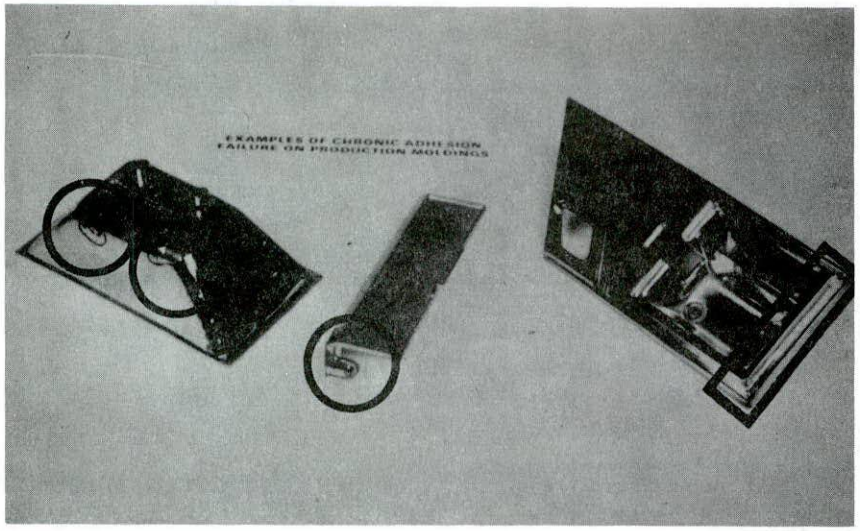
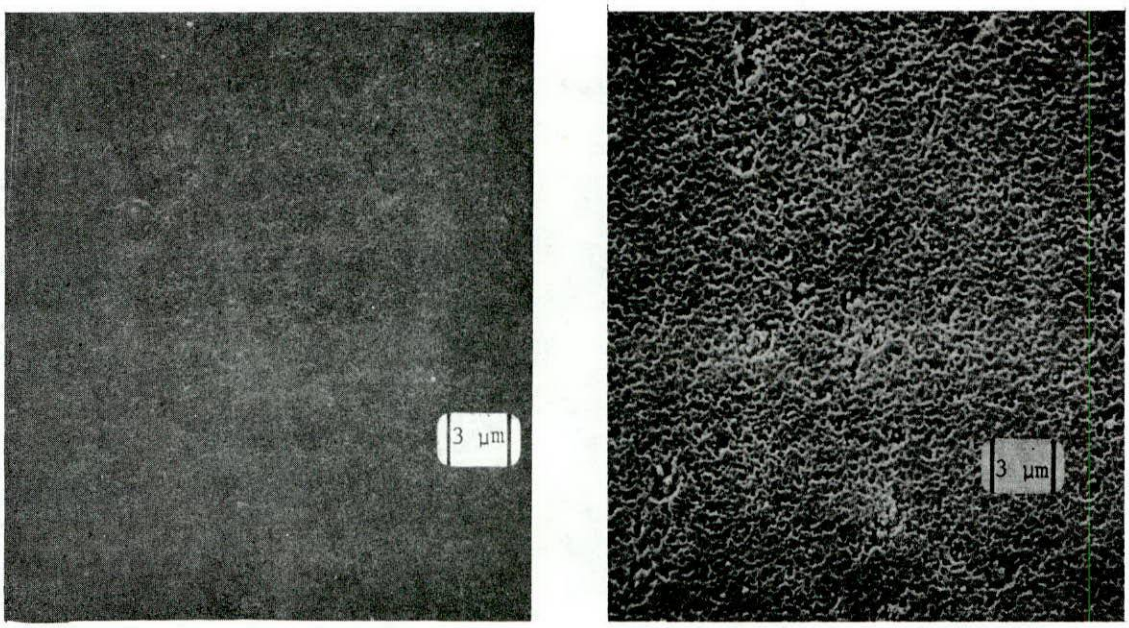


Fig. 11 - As-plated blisters on ABS production moldings.



A. DC plasma (10 min)

B. RF plasma (12 min)

Fig. 12 - Surface character of plasma-treated ABS (SEM: 3000X @ 30°).

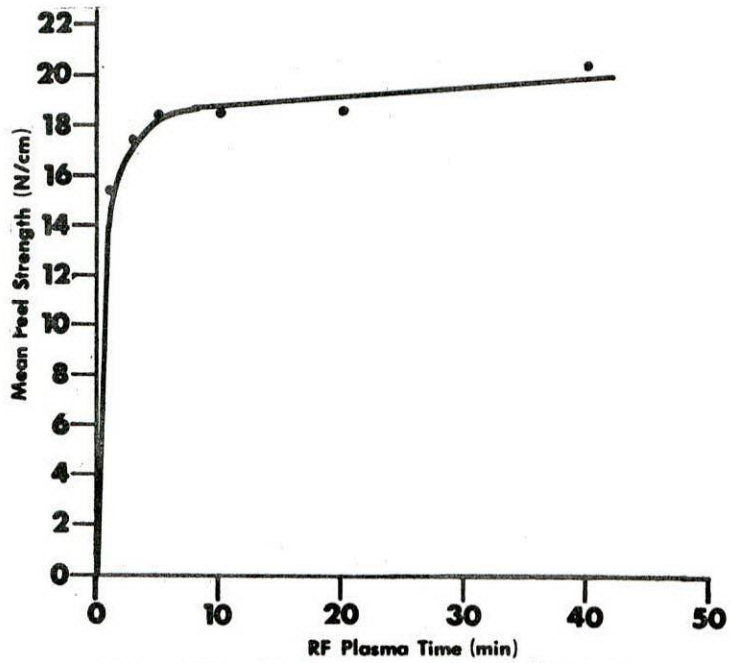


Fig. 13 - Peel strength (N/cm) vs. RF plasma time (min); Power = 35W.

B-2

Plating On Plastics
Session B

Selective Plating On Non-Conductive Substrates

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SELECTIVE PLATING ON NON-CONDUCTIVE SUBSTRATES

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Abstract
A review of methods for Selective Plating on plastics will be presented. Major emphasis will be on recent methods utilizing plateable coatings and strippable resist coatings. These methods have the advantage that unplated areas retain their as-is or as-molded appearance. Applications for these methods such as EMI/RFI shielding of computer enclosures will be discussed.

Introduction

Various selective plating techniques on non-conductive substrates (mainly plastics) have been utilized for many years in decorative plating on plastics and for printed circuit applications. New demands in the marketplace, have stirred new interest in old techniques, and the development of new techniques, for selective plating. A review of the most popular methods follows:

Basic plating on Plastic Steps (Preplating)

In order to understand selective plating techniques, one must understand the basic steps for plating on plastics.

Etching: The plastic part is roughened through mechnical or chemical attack. In addition this step creates a hydrophyllic or water loving surface. Etching is necessary to create bonding sites and to allow the surface to wet out during subsequent processing steps.

Neutralizing/Sensitizing: Residual chemical etchants are removed or neutralized since they can interfere with subsequent process steps. For certain plastics sensitizing agents are added to promote subsequent catalyst pickup.

Catalizing: In this step catalytic material traditionally consisting of palladium chloride/stannous chloride is deposited onto the surface of the part.

Accelerating: Some of the stannous chloride is removed exposing active catalytic sites.

Electroless plating: Electroless copper or nickel plating is initiated by the palladium, and then continues via auto-catalytic means. The part is now electrically conductive and can be electroplated or used as is where decorative plating is not desired.

Resist Coatings

To date most selective plating on plastics has been done by using resist coatings. These coatings are applied to the area of the part which is not to be plated. Through various methods, these coatings resist being plated through standard processing steps thereby yielding a selectively plated part.

Advantages are:

1. Reduced electroplating costs since only desired areas are plated.
2. Tried and proven technology.

Disadvantages are:

1. Does not yield as molded appearance in non-plated area and sometimes requires painting to improve appearance.
2. Generally works only on plastics which are plateable by traditional methods.
3. Scrap parts cannot be stripped, reground and fed back into the process.

Strippable Resist Coatings:

These coatings operate by the same mechanisms as regular coatings, however, they are removed from the finished part. This can be done chemically as a step in the plating process, or for certain materials the coating is either physically or chemically stripped from the finished part.

Advantages are:

1. Reduced electroplating costs.
2. As molded appearance and color of non-plated areas.
3. Scrap parts can be stripped and either replated or reground.

Disadvantages are:

1. Physically stripping the coating is labor intensive and costly.
2. In process chemical stripping can lead to contamination of subsequent plating baths causing quality and reject problems.
3. Generally works only on plastics which are plateable by traditional methods.

Plateable Coatings

There are three types of coatings which are plateable and can be used in selective plating applications.

The first is silver filled paint which is highly conductive and can be directly electroplated.

The second type is coatings which are filled with metals such as copper or nickel. These coatings can be acid activated and then electrolessly plated to form a continuous highly conductive metal layer.

The third is coatings which will directly absorb electroless plating catalysts without etching. These coatings can then be used for selective plating by utilizing the final three steps of plastic preplating.

Advantages are:

1. Non plated areas retain as molded appearance and color.
2. Will work on many plastics.
3. Since it is the coating that plates, the plating process cycle remains the same for all substrates.

Disadvantages are:

1. Silver paints are prohibitively expensive.
2. Appearance can be a problem for decorative applications.

Applications for Selective Plating Systems

There are many existing and potential applications for selective plating techniques. Following are some applications which are currently receiving interest:

EMI/RFI shielding - A plastic computer housing is electrolessly plated on the inside leaving the exterior as molded.

Decorative - A plastic automobile tail lamp lens is selectively electroplated, thereby combining a plated bezel and lens assembly into a single part.

Printed Circuit - The inside of a plastic housing is selectively plated with a circuit pattern thereby eliminating the need for a separate circuit board.

Summary

The most popular methods and applications for selective plating on non-conductive substrates have been discussed. There are many other specialized techniques and applications available. For specific information on processes available, it is suggested that discussions be held with platers, plating chemical suppliers, plastic resin manufacturers, and coating suppliers.

C-1

Mechanical Finishing
Session C

Mechanical Surface Preparation of Printed Circuit Boards, Flat Sheets and Coils Utilizing Non-Woven Abrasives

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MECHANICAL SURFACE PREPARATION OF PRINTED CIRCUIT BOARDS, FLAT SHEETS AND COILS UTILIZING NON-WOVEN ABRASIVES

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A successful printed circuit board producer regards surface finishing operations vital both as isolated processes and in their inter-relationship to the overall board. Surface preparation operations are required during the entry, middle and end phases of P.C.B. manufacture. Mechanical deburring and scrubbing utilizing cylindrical abrasive brushes are the primary methods for achieving these finishes. Correct abrasive media selection is the single most important factor controlling the performance of these operations. This paper examines each surface finishing component and makes recommendations which, if followed, will lead to higher quality boards with improvements in yield.

Deburring

The drilling of P.C.B. laminate produces copper burrs on both top and bottom sides of the laminate. Burr heights are determined by factors including laminate copper foil thickness, drill quality and the back-up and entry material used. Burr heights range from .0002" - .008". A properly deburred surface will aid the subsequent electroless copper deposition process and, later, ease component placement by automatic insertion equipment.

The deburring machine is typical of the construction used in all types of mechanical P.C.B. finishing equipment. Conveyor rolls drive the horizontal panels to the brushing chamber where they are thoroughly wetted and processed by abrasive brushes, top and bottom, rotating at 1800-2000 R.P.M. The panels immediately pass through a forced air dryer and then exit the machine ready for the next process. Deburring brush outside diameters are 5-6" with resultant surface speeds of 2800-3100 ft/min. These speeds provide the impetus necessary for uniform burr removal.

Deburring Brushes

Brushes used for this operation include 180 grit or 240 grit bristle brushes and reinforced non-woven abrasive wheels. Bristle brushes rely on the stiffness of the individual bristle to bring abrasive in contact with the burr. Flexing of the individual bristles occurs under production brush loads. The bristle tips penetrate the hole as they contact the burr. The fore edge of the hole receives an exaggerated radiusing with complete burr removal. The bristle action at the trailing edge removes part of the burr and forces the remaining portion into the barrel of the hole.

Reinforced non-woven wheels deliver more cutting abrasive to the burr by virtue of their mass construction. The level of brush

pressure required to attain a burr free surface with a reinforced non-woven wheel is typically 50% that of a bristle brush. The combination of increased abrasive and reduced brush load contributes to the elimination of burrs in the hole, while providing a minor radiusing for electroless copper deposition and component insertion.

Scrub Before Image

Surface finish requirements become more critical during the scrubbing prior to photoresist applications. Scrubbing objectives in this operation are twofold; removal of any surface contamination and imparting a roughened copper surface for optimum resist adhesion. The criteria are the same for either photo polymer film, ink emulsion or liquid resist use.

Scrubbing machines are identical to deburrers, except that most use 3.5"-4" outside diameter brushes with a corresponding surface speed of 1650-2100 ft/min. Common brush grades for this operation are: the 320 grit bristle, the non-woven type aluminum oxide - very fine, and the non-woven type silicon carbide - super fine. A silicon carbide particle has a sharper cut and is slightly harder than one of an aluminum oxide type. Therefore, scrubbing wheels made of silicon carbide abrasive, as with deburring wheels, provide better performance on copper.

Copper Removal

While oxide films and oils are two of the contaminants removed during this process, copper is also removed. Differences in effects on copper between abrasive bristle and non-woven abrasive wheels are of particular concern in the through-hole areas. Non-woven abrasives remove less copper and impart depressions of less depth than bristle brushes, thus reducing the potential for rim voids. Figure 1 plots conveyor speeds, showing how copper removal can be further minimized. Conveyor feed rates of 6-9 ft/min. give the best results. In cases of extreme oxidation, a 5% sulfuric acid dip and rinse prior to scrub is preferable to slowing the conveyor speed. Brush pressure should be maintained at .75-1.25 amp/min above idle. Excessive brush load will contribute to loss of surface copper related problems (Fig. 2).

Surface Roughness

Photoresist performance hinges on a contaminant-free surface of a specified roughness. Conveyor speed, brush pressure and the brush type used in the scrubbing operation determine the surface roughness. Control of the surface finish will ensure a good bond between the resist and the copper panel. Fig. 3 charts the effects of conveyor speed on surface roughness. The optimum feed rate is 6-9 ft/min. Slower rates will yield an increase in the depth of the microscratches on the copper. A brush load of .75-1.25 amp/min. above idle will, with the proper brush type, provide the amount of roughness necessary for resist adhesion without imparting deep scratches (Fig.4).

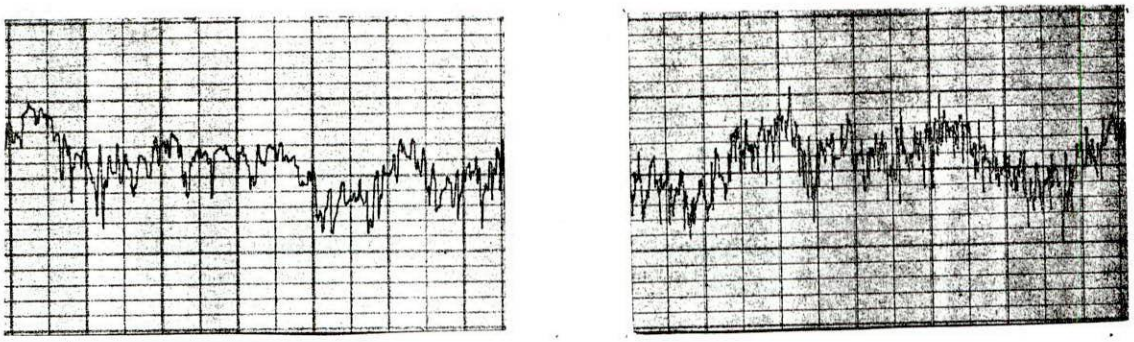
Photoresists laminated to an electroless copper surface adhere best with an RMS roughness of 11.8-15.7 mil[1]. Surface profilometers reveal effects of the scrubbing process by determining RMS roughness and the important values of RT roughness and the high spot count.

Effects of Brush Type on Finish

Conveyor speed and brush load are two variables which can be altered to improve surface finish qualities of printed circuitry. The greatest impact on surface preparation, however, comes from the type of brush installed in the scrubber. Brushes of non-woven abrasive nylon construction provide the best surface conditioning possible via mechanical scrubbing.

Surface profilometer analysis of electroless plated copper substrate scrubbed with non-woven abrasives show a great number of microscratches of minimal depth. Boards processed under equivalent operating conditions using 320 grit bristle brushes always show a much lower scratch density. The scratches which do occur are characterized by their depth (Fig. 5).

Analysis of panels scrubbed by printed circuit manufacturers show the typical range of RMS roughness values are 12.2-18.1 mil for non-woven flap wheels, type S - Super Fine. Similar panels scrubbed with 320 grit bristle brushes produce a 18.5-31.1 mil RMS roughness, well above the optimum range. Averages of high spot count for the same panels are .453/mil for the non-woven abrasive and .149/mil for the bristle brush samples, further evidence of the non-woven's effectiveness in production environments.



320 Grit Bristle Lea Fibral S-Super Fine

(Fig. 5) Surface Profiles of Scrub Prior to Photoresist

The difference in surface finish quality between the two types can be traced to the supply of available working abrasive. Scrubbing with a bristle brush produces unequal rates of wear between the nylon and the abrasive that it carries. As the abrasive is worn away the smooth nylon bristle tip remains; it buffs rather than scrubs the surface. Increasing the brush load to compensate for this lack of abrasive, results in nylon smear and gouging of the copper. Surfaces prepared with bristle brushes show widely spaced cavities to which photoresist will not readily adhere (Fig. 6).

A generous three dimensional abrasive count carried on a lattice of non-woven nylon provides equal wear between the abrasive and nylon. Therefore, an abrasive rich media is always applied to the substrate. (Fig. 7). This enables the scrubbing operation to be performed with a large degree of predictability and control. Photomicrographs of surfaces prepared by non-woven abrasives show a random microfinish with little penetration of the copper (Fig. 8)

Final Finishing

The adhesion of solder mask over bare copper depends primarily on an oxide-free copper surface. The comparatively aggressive nature of 500 grit bristle brushes makes them generally unsuited for the surface finish criteria of this operation. Our research shows that the non-woven flap wheel with Ultra Fine silicon carbide abrasive is the most effective means for mechanical SMOBC surface preparation. The flap wheel's construction has the resilience necessary to lightly conform to circuit traces and nomenclature while imparting an extremely fine 6.4 mil. - 9.1 mil RMS roughness. The sensitivity to adjustment of this construction permits users to prepare boards for SMOBC without any registration of brush load above idle on the scrubber's ammeters.

Conclusions

Control of the surface finishing operations of a printed circuit board can be exercised with the same degree of accuracy as drilling, plating and imaging Each finishing operation has a different set of defined objectives. Optimum brush selection used with a minimum of dwell time and brush load will, regardless of the operation, always lead to higher board processing yields.

The relative life span of a bristle brush must be viewed against the non-woven abrasive's ability to give better performance in all measurable aspects of surface finish quality. Non-woven abrasives reinforced with synthetic resin yield 75-85% life of bristle brushes, eliminate nylon loss and retain the benefits of traditional non-wovens. The printed circuit of the future will routinely incorporate 5-mil lines and spaces.[2]

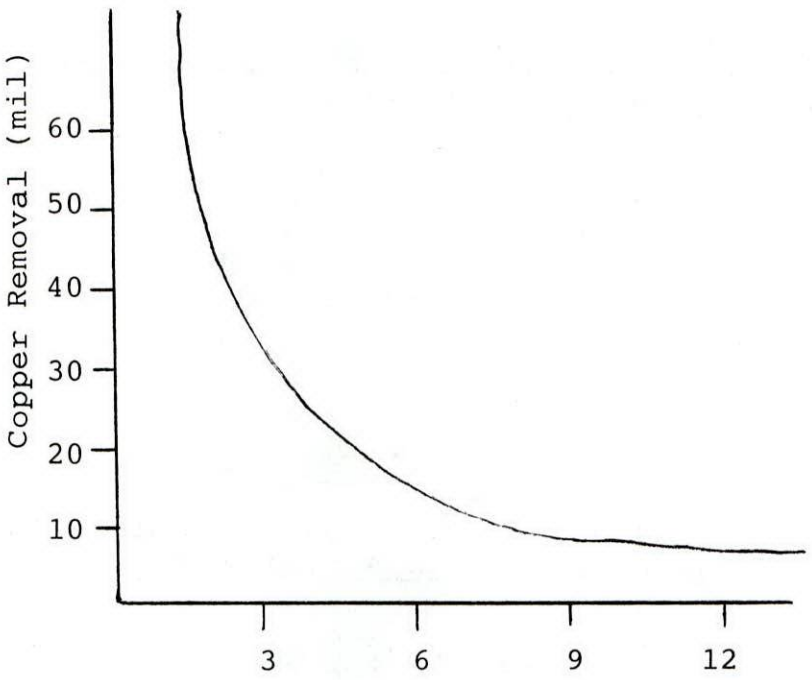
This new standard will demand surface finishes of the greater density provided by non-woven-abrasives.

Summary
The interdependent nature of printed circuit manufacturing operations requires that each surface finishing process be performed with the best available media. Non-woven abrasives installed in deburring and scrubbing machines combine easy operation, economy of use and the best surface finish quality of any brush type.

REFERENCES

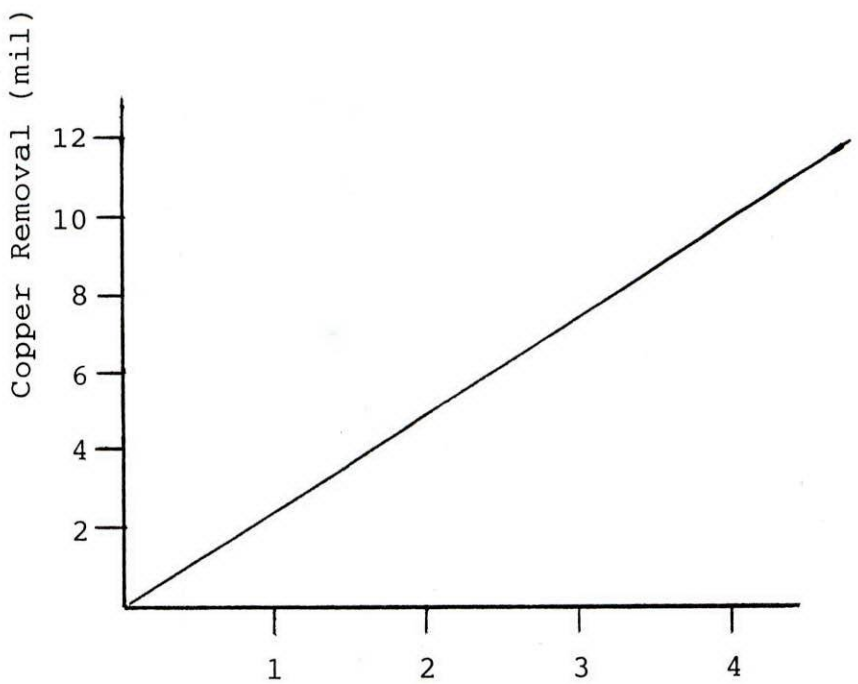
1. W. Hamilton "Dry Film Performance On Electroless Copper", Electronic Packaging and Production, January 1981.

2. F. J. Dance "Can PWBs Meet The Surface Mount Challenge?" ELECTRIONICS, May 1983.



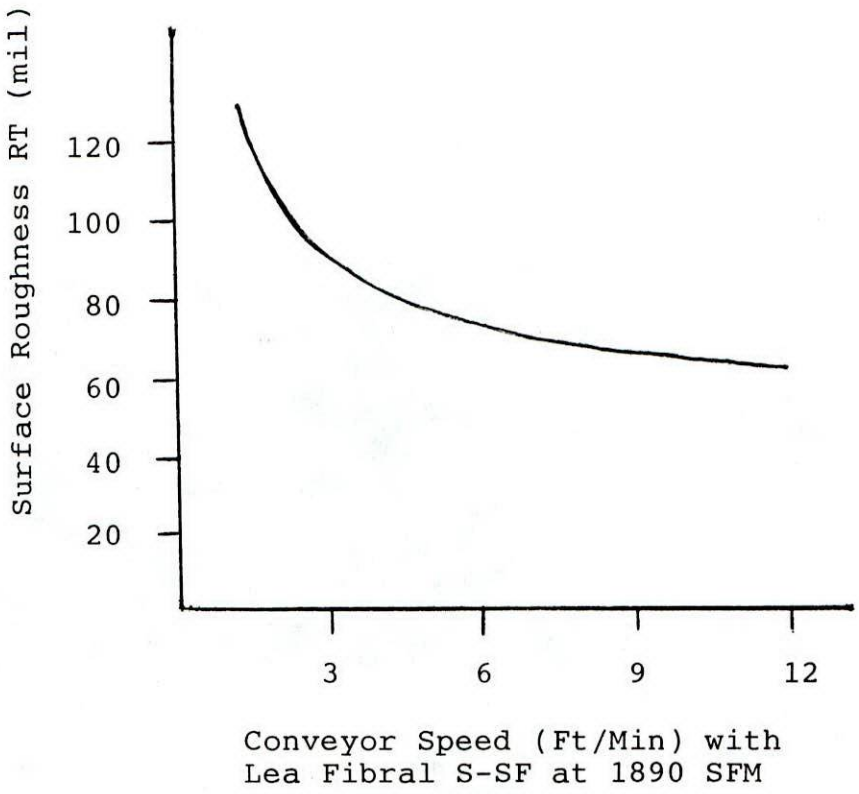
Conveyor Speed (Ft/Min) with
Lea-Fibral S-SF at 1890 SFM

(Fig. 1) Copper Removal vs. Conveyor Speed

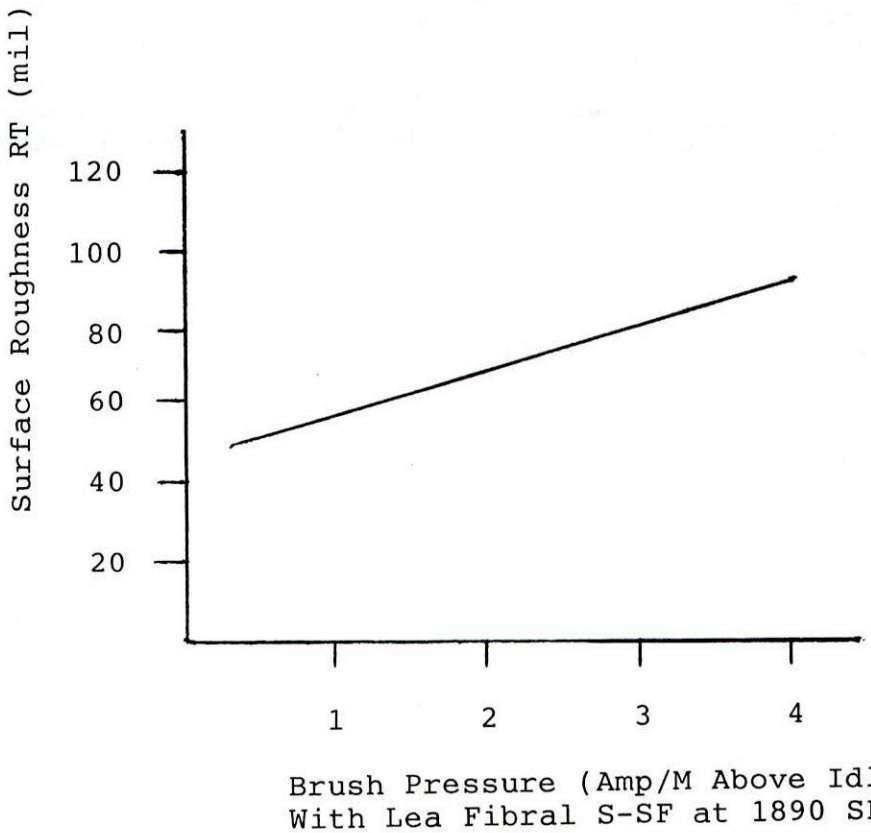


Brush Pressure (Amp-M Above Idle)
With Lea Fibral S-SF at 1890 SFM

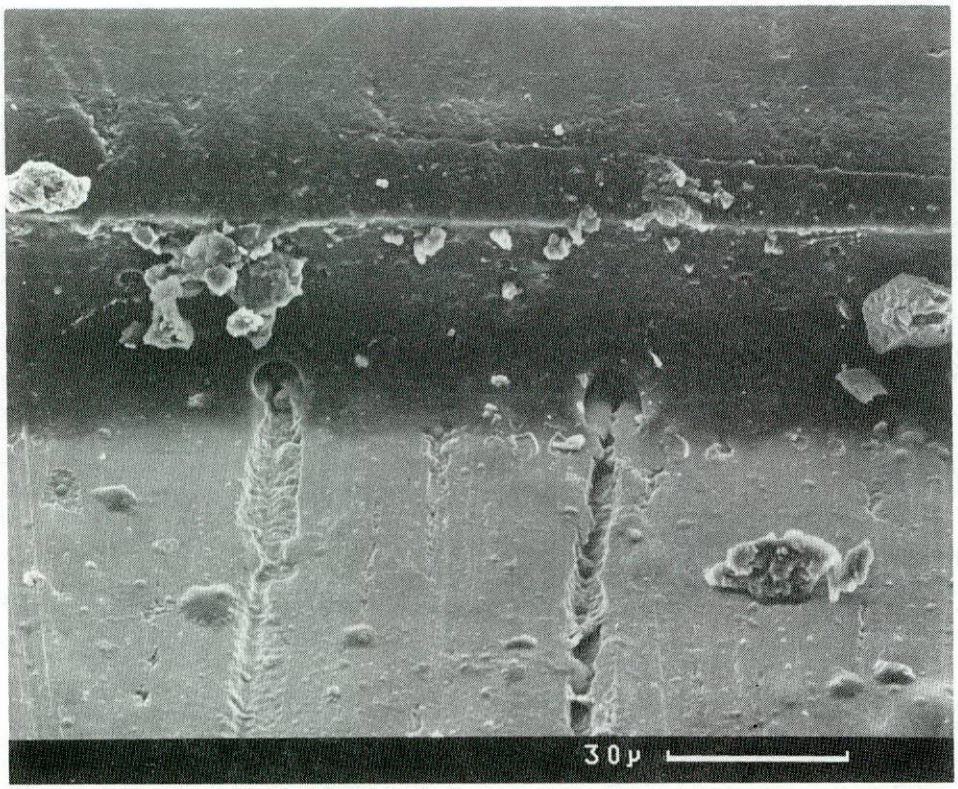
(Fig. 2) Copper Removal vs. Brush Pressure



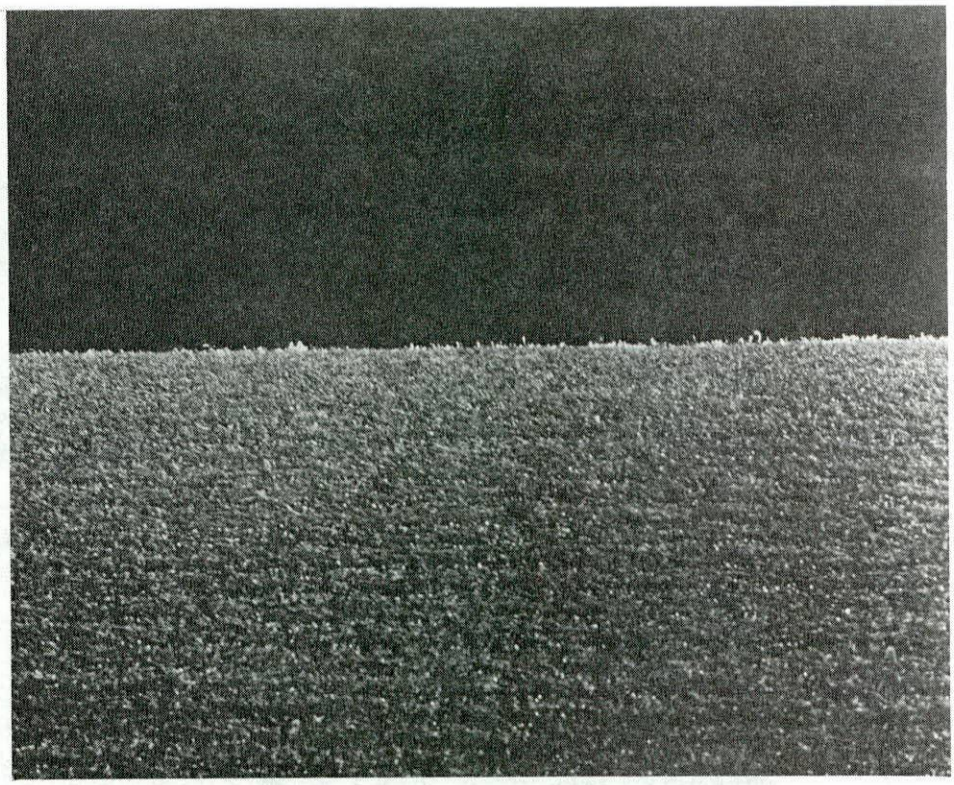
(Fig. 3) Surface Roughness vs. Conveyor Speed



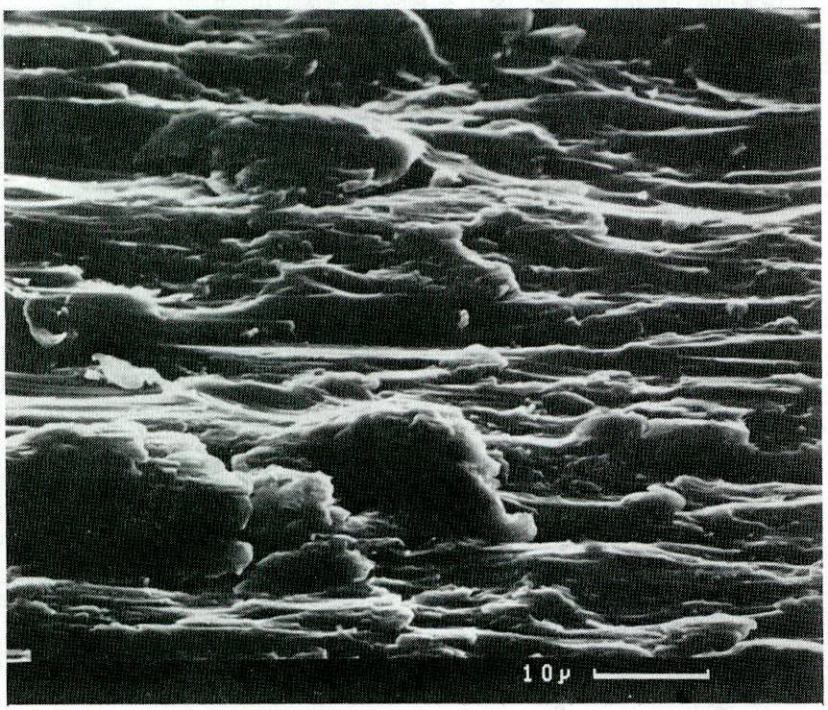
(Fig. 4) Surface Roughness vs. Brush Pressure



(FIG. 6) 320 GRIT BRISTLE BRUSH FINISH
ON ELECTROLESS COPPER



(FIG. 7) NON-WOVEN ABRASIVES WITH SELF-DRESSING PROPERTIES ALWAYS PRESENT AN ABRASIVE RICH WORKING SURFACE.



(FIG. 8) FIBRAL TYPE S-SUPER FINE FINISH
ON ELECTROLESS COPPER

C-2

Mechanical Finishing Session C

The Basics of Preplate and Final Finish

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THE BASICS OF PREPLATE AND FINAL FINISH

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The most effective process ever encountered is the hands-on, get-your feet-wet active involvement in the task you are attempting to master.

The beginning of the metal finishing process that prepares the work piece for final operation is always determined by the condition of the part from its origin. If it's a casting (for instance, zinc die cast, aluminum, brass, bronze, etc.) the surface imperfections should be corrected, whether they are in the die or the die cavity. Also any bad habits acquired by the operators, such as the mis-use of coolants, lubricants or faulty die cleaning methods, should be corrected.

This is true of any metal finishing operation. This is true of any metal whether ferrous or non-ferrous. All these factors determine the costs involved in getting the pre-finished quality and weighing the possibility of whether or not to correct those imperfections or remove them in the finish operation. My experience has always been that the part never reaches the first finishing operation without those blemishes. So, taking that into consideration, follow these steps:

chart your quality course

1. determine quality desired
2. select equipment necessary
3. select proper tools
4. put tools and equipment together
5. run product for determination of quality and quantity desired
6. MOST IMPORTANTLY: determine at what point you have achieved your goals for quality

Determining the quality that must be reached, of course, is usually a group effort involving many people. If it's a cosmetic finish, sometimes it is more difficult to reach an agreement, so some compromises are usually made. The same holds true for functional parts. Determine where metal flash, rough edges, nicks and scratches are undesirable in any situation. Now that we know what our quality must be, we can start our finish operations.

The selection of equipment is determined by the shape and configuration of the part, and quantities involved. The end result of all these considerations is making sure the quality

is achieved. If it is an automatic, semi-automatic, or just a simple hand method, the end result must be the same. The quality must be built into the product.

The selection of tools to do the job is extensive: a pair of gloves, design for fixture to secure, clamping devices, if needed, the fixture to the machine, polishing belts and grain sizes, contact wheels, for each operation in sequence, buffs, buffing compounds, color buffs and color compounds, and containers such as trays, boxes, crates, separators, or possibly special molded plastic containers to conform to the shape of each part for proper nesting to keep handling defects to a minimum.

Before deciding what finishing tools are necessary, a determination must be made as to what operation is involved. If the part is free of grease or lubricant, so the surface can be seen plainly, look for the obvious defects. Such defects include deep nicks and handling scratches, heavy extrusion or die lines, stress lines, orange peel, gouges from the die, etc. If you cannot make these determinations by simply examing the surface, due to surface residue, which is usually the case, take a 12 or 14 inch loose cotton buff and some chrome rouge and hand color (polish to high luster) at least one dozen parts. Now take these parts and go over them carefully and do a check on those defects to see if they are repetitious. If they are, the chances are that they are a part of your production process, either in the die, mold, stamping or any forming process. If they are repetitious, make sure that the defect cannot be eliminated in the prefinish operations. If they cannot, then it's time to start the sequence of operations necessary to get the quality desired.

If we have to belt polish, let's take the most common belt size in width and length, 3" x 132" and decide what grain size with which to begin the sequence. In most cases, if it's a die casting, and the surface must be polished, one grain size will be sufficient to remove all defects, as well as deburr the part. Normally, a 240 grit belt will finish the job. This is now a good surface to buff if the belt application is performed properly. This means using the proper durometer back up wheel for the belt, and a good belt grease for lubrication. If the back up wheel is a serrated rubber wheel, it should be in the medium durometer range of approximately 60 duro. If a cotton buff type contact wheel is used, again

the durometer should be in the medium range. This will permit the part to be applied to the belt, with some cushion to prevent leaving flats, gouges, wild grain lines and so forth. This will also achieve a finish prior to buff, that will be easily buffed out. Normally, the finer the grain used in finishing, the less time required in buffing. If the surface of any metal should require more than one polish operation, start off with the finest grain size possible on the first operation. If the final finish belt, or a 240 grit, is not removing all those holes gouges, cuts, etc. then it's obvious that a lower grain size is needed. If you drop back to a 220 or to 180 grit, and attempt to buff either of those, you may get into a dragging situation or more buff time and wear and tear on buffs and compound than you can afford. However, it is feasible to buff after using either of these grain sizes and get a quality part. If you run into quality problems with this grain size, then it is obvious that two belt operations are needed. Use a little common sense and remember that if you need perhaps a 180, make certain you remove all the surface defects with this grain size, so all you have to do is remove the 180 polish lines with your final belt. It is possible that you can jump over that 240 and finish with a 280 or possibly a 320 grit. This makes your buffing easier, and helps make up some of the loss for that extra operation. Make sure that a grease stick or lubrication is used in both operation. It has been my experience that some lubrication should be used in all belt operations. The most important factor for lubricating a belt is to get a protective coating on the grain before it is touched with the work piece. During the polishing operation, the hot metal burns off in most cases in a liquid form as molten metal when it leaves the piece. It solidifies immediately, and welds itself to the nearest solid object, which in most cases happens to be the face of the belt. Without the lubrication to repel it, the belt will develop a welded metal build up and cease to cut. The operator usually says it's dulled out. He'll either pull it off and throw it away, or tear the belt off his machine making it useless. Most manufactured grease stick for belts are made from animal fats or tallow, with a couple of other ingredients thrown in to alter the melting point up or down depending on the heat created by the friction between the belt and work piece. Whether the metal is in the hard categories of steel or has the softness of some aluminum alloys, a beginning lubrication on belts is most advantageous. Since the bonding of most metal working belt is full resin bonded, most any

agent for soaking can be used. The best I've used is a solution of one to one ratio of water soluble cutting oil and kerosene or diesel fuel. Throw a dozen belts in a 10 gallon container, let them soak overnight and then take them out and let them drip dry before using. When the belt is mounted on your machine, start the motor and give it a very light, once-across coating with a good grease stick and you're ready to make your first cut. I've also used 10W-30 or 40 engine oil as a soak and it works. After you have run the belt for some time and it is beginning to slow down in the cutting process, remove it, throw it in the solution, soak it again, and remove the greases and metal build up. Put it on again and many times you'll get as many parts the second time around. This is especially true with the softer metals such as zinc, aluminum and brass alloys. Aluminum requires a tremendous amount of lubrication between the work piece and belt. Often the best polishing is done with a wet operation of kerosene and grease stick. Lubrication is a must for aluminum to prevent burning and dragging the metal. It some times seems the operation can't be too wet. In fact, I have seen some operations running so wet that drums were laid in the floor to carry away excess moisture or wetness. Now I'm not talking about a wet or dry multiple head, spray on type semi grinding operation. I'm describing what most consider a dry belt, grease out polish operation. I don't like using the word "dry" when describing a belt operation. However, common sense must be used in the use of lubricants, especially grease stick. Too often too much is used. Use only enough, in most cases, to put that thin coating of lubrication on the belt.

Now that we have gone through the finer points of polishing, here are the tools we need: one buffing lathe, preferably twin drives with two 7½ horsepower motors with a minimum of six inches of thread shaft, no smaller than 1¼ inch in diameter. A floor or stand mounted backstand belt idler with a crowned pulley with a minimum of an 18" diameter. Make sure the pulley is crowned so your belt will track (the belt on the idler pulls to the highest point to the center point). A crank style for lateral movement will assure good tracking. A good all purpose contact wheel, 14" diameter x 1-1/4 arbor, 4" face, one to one ratio serration, 50 to 60 durometer rubber wheel. A good medium melting range grease stick. 3 x 132 full resin bonded belts in all grain

sizes needed (never go any lower on grain sizes than necessary).

A five or ten gallon container, one quart or more of kerosene, one quart or more water soluble oil (or 10W 30 or 40 motor oil, whichever you prefer), and a good pair of hot mill gloves.

Now let's polish. As a word of caution once more do not polish unless it is necessary.

buffing

Now that we have polished all the imperfections out, and all we have to remove with our buff application is polish lines, let's select a buff. This is a common buff construction and if it is steel we are buffing, it will be sisal, which is used for all ferrous metals. If the metal is non-ferrous, the buff will be all cloth fabric. Example of these buffs: 14 x 5 x 1-1/4, 8 ply, Bias Sisal, 3/8 sewed, medium treated.

for use on steel

14 x 5 x 1-1/4, 16, 86/82, #2, medium treated (for non-ferrous metal)

The selection of a compound with a very aggressive cut with some color, with aluminum oxide grain for steel, or tripoli grain for non-ferrous metals will get the best results. Bar or liquid buffing compound can be used. Fixturing may be used if needed, either for hand buff, semi-automatic or automatic. A good pair of hot mill gloves will work best.

All of the above is based mainly on hand operations. If we take the variables of each one and put it in practice on any automatic, big or small, we come up with the desired result.

All of the above is based mainly on hand operations. If we take the variables of each one and put it in practice on any automatic, big or small, we come up with the desired result.

The use of the buffing wheel applied to the part to be finished in the buffing operation should be prepared in the preceding operations of polish for easy integration and adaptation to the buffing sequence. If is normally a good

practice, whether it's steel or non-ferrous metal, to buff across the polish lines. In most cases, an angle of anywhere from five degrees up to perhaps thirty degrees is the best. I have found a radical cross buff of 90 degrees is not the best. If the buff operation is such that a few degrees one way or the other in the polish operation will simplify the set up or buffing time, then take advantage of that situation. Also, in the conveyance method between operations, whether it is packed in a box, crate, tray or basket type conveyor, the part should be placed in the best position for pick up and loading or adapting to the conveyance for that buff operation. Most hand operations run from 1400 R.P.M. to 2000 R.P.M. with a buff diameter from four inches to 18 inches. Automatic operations, depending on the type of equipment such as rotaries, in line or straight line or universal type machines normally use buff diameters from four inches to 24 inches with R.P.M. from 450 to 2200. The lower R.P.M. is normally used with a large diameter buff from 16 inches to 24 inches with spacing in between using one section or buff or sometimes two sections and from 1/2 inch of spacing to three inches. This spacing usually depends on the depth of buff lap required to reach the deepest point of the part for finishing with the buff. This is called mush buffing. The part is completely buried into the wheel. A good way to see what takes place is to go through a "Robot Car Wash" and observe the nylon wheels that wrap around your car and gets into recesses. Now buffing is not that simple. Too often, I see automatic machines set up with large heads, with 80 inches of face or a seven foot head or 168 inches on a 14 foot head pulled down on the part to be buffed with no regard paid to whether or not the head position is in the right place. Obviously, there is a point on each section of that entire wheel, (the 7 ft or 14 ft), that is most effective when it makes contact with the part. If there are recesses, sharp corners, edges, grooves or any surface that is not flat, the buff must be set to pull into those areas and remove all those undesirable blemishes in the metal. Avoid a common mistake: Often, the head looks so big and the area to buff out looks so small that you set the head to produce a scatter load or bird shot effect. It seems that you can pull the head down on the part anywhere and still hit the spot you want to buff. If you shoot into a covey of quail or a flock of ducks, you aim directly at one and perhaps the scatter will get more. Don't use the spindle of your fixture as a center point and the shaft supporting your wheel for location points only, pull the head over your part, and set the shaft of your wheel over the center point of your conveyor. Line it up

parallel to the travel of your conveyor. This is your starting point. Now regardless of the rotation of the buff, clockwise, or counter clockwise, the pressure point of your wheel will be directly over the center line of the conveyor. So if you move the entire shaft of the buff head a fraction one way or the other, you move that contact point. Theoretically, by using mathematical equations, you could fixture your work piece, scribe a center line and measure out to that point you wish to reach. If it's six inches off center, then move all or a portion of that buff out that six inches and lower the buff into that area. Pass a part through and see if you've made contact with that area. Adjust it in or out until you get the desired result. If you can buff that area with one-fourth of that head, then angle your shaft and use the other three-fourths to reach other areas that need buffing. In other words, use each section of buff to your best advantage for exceptional quality and economics in cost. Set each wheel to do a particular part of your work piece, and know where on that wheel any specific area is being buffed. A good way to check that out is to pull a part off every six inches and see what areas are being buffed. You may find that after passing half way through that head, your part is buffed. If it is, then you will over buff if the part goes on through the entire buff. Conceivably, you could do one of two things, take off half of your buffs or double your conveyor speed. This can result in more parts per hour. If daily quantities warrant it, and one person can't handle the out put, add more personnel. If quantities do not require that many parts hourly, leave your conveyor speed slow, and remove some buffs. The theory in buffing is the amount of S.F.M. passed over a given point in a given amount of time produces the quality desired. In cloth sheeting this could be computed into yards of material depending on the type of buff or the pack in the buff. Use a number 2 pack, 16 ply or 6, 8, 10 pack and as the number goes up, the yardage increases. So the contact time can be lessened by dropping the pack in the buff or speeding up the conveyor. This should be true if its flat, round, orbital, or any unbroken line part. If the part is odd shaped, such as a swing spout for a kitchen sink faucet, then care must be taken in making the pack sufficent to flex and lap into the recesses. I've always used the rule of thumb that anything being lapped in depth by over 1/2" deep should have at least a #2 pack. The pack must be increased for flexibility as it has to dig deeper. The inside flexing of a buff can break the buff down quicker than the surface wear against

the part. Ripping or tearing from the outer periphery of the buff toward center is caused in most cases by extreme flexing of the buff. When the machine is set and the quality product is produced, turn the conveyor speed up to the point where you lose your quality. Then, after inspection shows you are losing your quality, slow your conveyor speed back to the point that your part is acceptable, and this should be your "quality break point". What is proven is that the theory of cloth yardage and surface feet of buff in conjunction with conveyor speed or dwell time is quality start point. This is true on any piece of buff equipment. (Compound application) The other integral part of this operation is compound application. My experience with this phase of buffing is that in more than 35 years of applying compound, liquid or paste, when applied properly is best. There are several pressure systems being used to a good advantage. Beginning with the pump system, if you supply very many guns, five or over to one machine, the best trouble free system I've found is to start as soon as you can, from your pump, pressure tank, etc. with the shortest hose hook up possible. Anything over 18 inches of one inch I.D. hose is too long to your main compound line. Remember this is your reservoir line and should be restricted no more than necessary. Use 3" black iron pipe or 3" PVC plastic pipe. As you cut and erect either one, treat them as an important part of your equipment. Wash each piece after it is cut and swab it like a gun barrel to remove all chips and dirt from the pipe. Keep the 3" diameter all the way for the full length. Use 3" tees, 3" nipples and 3" ells. Do the same with the pipe to each gun. Bring the 3" diameter all the way down and as near the gun action as possible. The shortest hose possible should be used to accommodate a petcock shut off and a solenoid valve. By using the 3" header, you eliminate the risk of line plug ups due to heavy or thick compound. Before the guns are connected, and after all the other components are in place, take a 55 gallon drum of water at about 140° to 160° Fahrenheit, and flush the entire system to again clear out all dirt, chips, etc. before you fill it with compound. Go back to the pump or supply system, and put a 3" "Y" type steam trap filter with a 20 mesh screen of stainless steel as close to the pump as you possibly can. This 20 mesh strainer will pick up all foreign matter from the compound and keep the gun tips from plugging up. This saves a lot of wear and tear on the guns. It's a good practice to construct the air supply line of the same size pipe - three inch diameter all the way. Remember the air in

some cases serves a dual purpose. The air supply opens the gun tip for spray and is the atomizer to spray the compound in a mist. By using a 3 inch supply line all the way, there is always an air supply to operate the gun as long as it is open. You will not use anymore air than needed, but there will never be a bleed down of the line and a malfunction of the gun. Some engineers install from one-half inch to one and one-half inches, and the size is inadequate. Using a solenoid control at each gun and a timer at each gun, control is established for economical, trouble-free application of compound. Any pressure system can be used with this set-up whether pressure pots, etc. If at all possible, mount the gun on any bracket, stand or device and attach it to anything except the buffing machine. This takes away all chances of vibrations from the machine shaking the gun apart. My best recommendation is a tripod-type floor stand with one adjustment, up or down, the less adjustment - the better. The gun can be aimed at the proper point on the wheel by moving the entire stand. The stand is portable and can be moved out of the entire stand. The stand is portable and can be moved out of the way for maintenance, sweeping floors, or gun repair. The best place to spray the compound is in the "V" where the buff makes contact with the part. This is on the downwind side, so any peripheral air will blow the excess compound down on the part where the wheel will pick it up to cut down on compound loss. Remember also, it's better to spray a little bit more often than to apply an over amount, and have a few parts muddy tapering off on the last few parts until the wheel is almost dry before spraying again. This causes inconsistent quality, use these adjustments to set your pattern. A moderate air pressure on your supply point, pump or pressure tank of about 45 pounds of air P.S.I. If your compound is in the 40,000 (on a Brookfield Viscometer), it can be controlled by each timer, at each gun, to the exact amount for any requirement even if it's hand buffing. I advocate spray compounds on any buff application over bar materials including color buffing. When you insert a 55 gallon drum of compound under your pump or in your pressure tank, each particle in that drum must pass through your orifice or gun tip as small as 25 thousandths of an inch. That is why the filter at the pump is so very important.

Now we have all the tools, parts equipment and knowledge, let's choose a compound. If you're going to plate copper, nickel or chrome and have good brightness and levelers in

your nickel, you can use a very heavy cut, even on the scratchy side, that will leave the part dull and cloudy. This will speed up your buff operation.

If you can't cover scratches and clouds and need a clean semi-bright part you can see readily without wiping, then a cut and color combination compound in the medium range is desirable.

If you are plating brass or some precious metals, then a two compound system should be used on the same machine. This is established by picking a fairly aggressive property with some brightness, and then a rouge for high luster. In some cases, this may have to be a two operation procedure if your final finish is very critical such as bright silver, gold, brass, or a clear lacquer over the final finish instead of electroplate.

C-3

Mechanical Finishing
Session C

Aluminum Buffing - The Part Tells You How

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ALUMINUM BUFFING - THE PART TELLS YOU HOW

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Aluminum buffing, or the mechanical finishing of aluminum, refers to an operation which changes the surface of an aluminum part by physical means. The reason for such mechanical finishing is generally to remove mechanical defects such as mill scale, slight burrs that might be retained, parting lines, or extrusion marks. All of these of course are the result of the basic manufacturing process itself. The end result then is to produce a part with a high degree of lustre or color having a black mirror finish.

This mirror high finish is an important and necessary prerequisite to all parts that are to receive either an anodizing or lacquer finish. Such defects as scratches, pits, draw marks and die lines must be removed prior to final finish or they will be visible in the finished part. This is where buffing comes into play. The type of machinery, compound, buffing wheels, and compound application systems, all play a major role in the degree of final finish obtained.

There are many aluminum parts that can be taken directly from the fabricating stage of manufacturing and totally finished by buffing alone. Those parts however with deep draw marks, extrusion lines and rolling marks may have to go through a polishing operation prior to buffing. Aluminum castings generally always require belt polishing so as to remove the parting line.

When reviewing or analyzing the buffing requirements of any particular aluminum part, it is well to consider whether such things as drawing oils and/or lubricants may be present on the part and therefore have some effect on the color of the final finished product. These particular materials sometimes are not totally compatible with buffing compounds and can create adverse problems. A typical example would be where a buffing head or wheel becomes impregnated with grease and fine aluminum particles begin to cling to that head with the result of metallic particles imparting wild scratches in the finished product.

We will then be looking at four particular aluminum parts, running through the mechanical finishing or buffing processes necessary to create the desired finish. These parts are tennis racquets which are tubular extrusions formed and bent, spray guns which are die castings, extrusions and cosmetic shells which are drawn.

We will try to analyze the needs of each of these parts and determine individually the type of machinery, compound application system, and buffing wheels, required to produce the maximum finish at the minimum cost.

Part #1
Tennis Racquets

This part starts out as a hollow tubular extrusion and is subsequently formed to the shape of the final racquet. It also has drilled holes around the loop, evenly spaced, for stringing the web on the racquet. The part is loaded onto a fixture which secures the racquet in four areas:

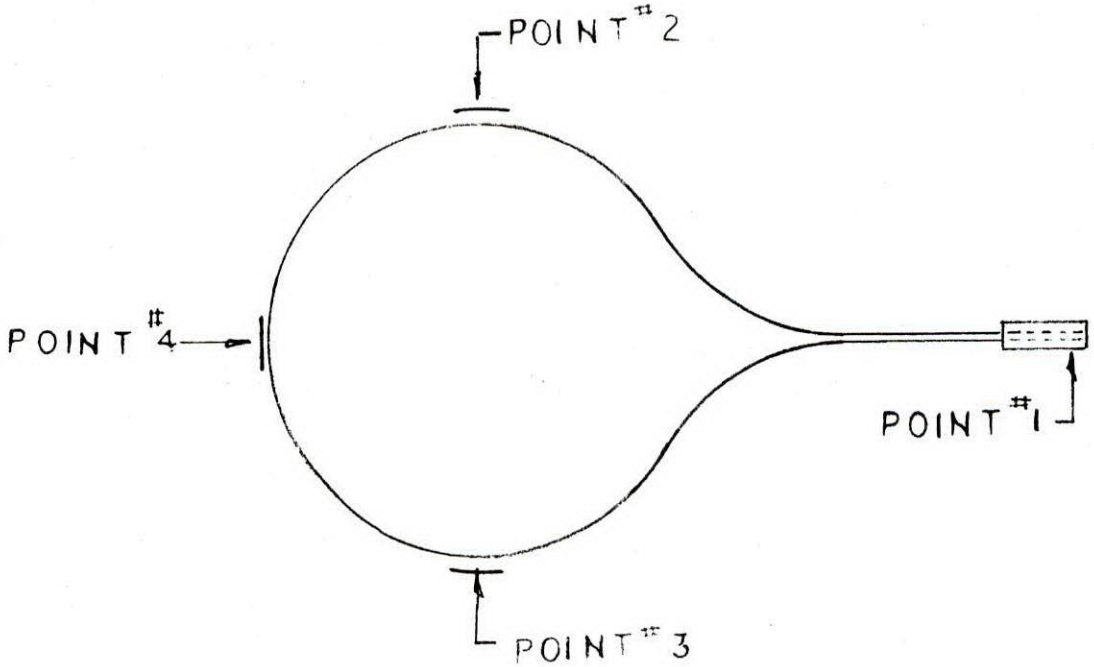


Figure 1

Figure 1 shows the points in which the part is fixtured. No. 1 point is the throat, No. 2 and 3 points the sides of the loop, and #4 point the top of the hoop on the racquet. Fixturing of such a part becomes a rather important factor in that during the forming of the racquet, there has been stretching of the aluminum. Proper fixturing of the part not only helps to keep the part in dimension, but allows the buffing operation to maintain an acceptable finish where the metal has changed from its original shape, creating in some areas severe stretch marks.

Since the part must exit the buffing machine with a uniform finish, wheel time over those areas with the stretch marks become important.

We are also required to remove any mill treatment which is generally present and do some slight deburring on the series of drilled holes. These holes however must be kept free of both buffing compound and buffing lint, since packing such materials into the holes creates a rather severe cleaning problem prior to anodizing.

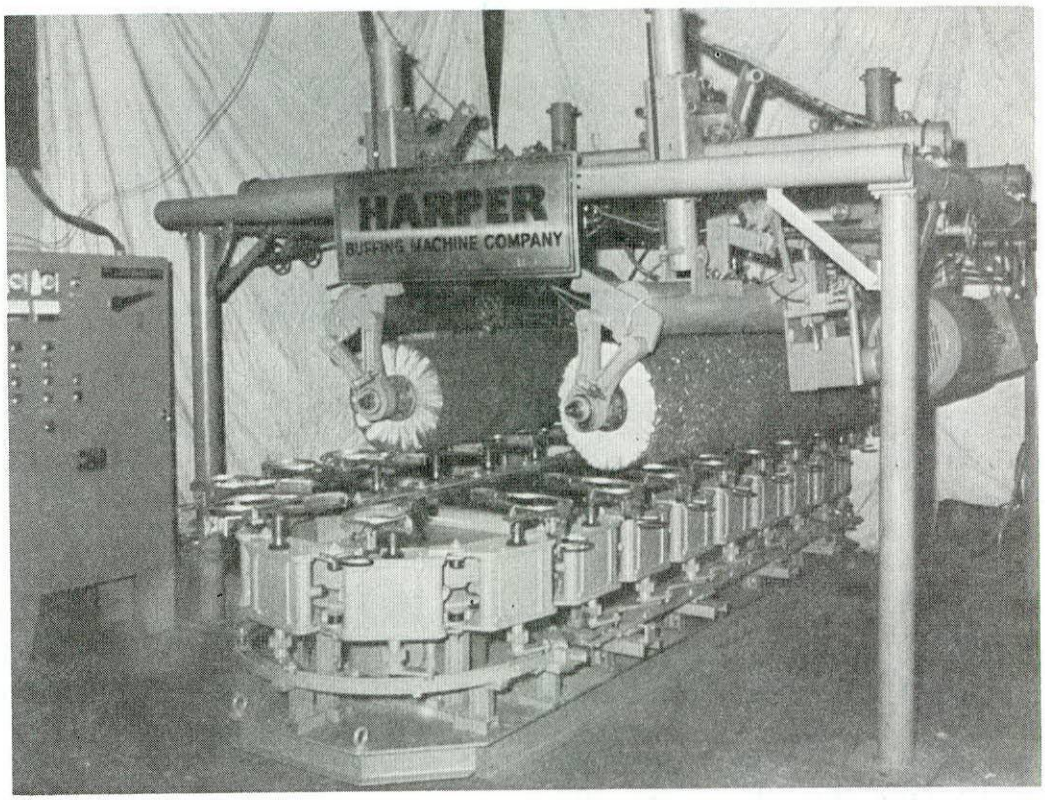


Figure 2

Figure 2 shows the conveyor on which the parts ride. It is loaded in the front of the machine and goes through one 7' cutdown head and through 2/3 of a second 7' cutdown head. The last third of the second head is devoted to wipe-up. The part then comes back to the load area and is flipped over to do the opposite side where it is then run through the two heads again as in Step #1, whereupon the part is unloaded and a new part snapped into the fixture.

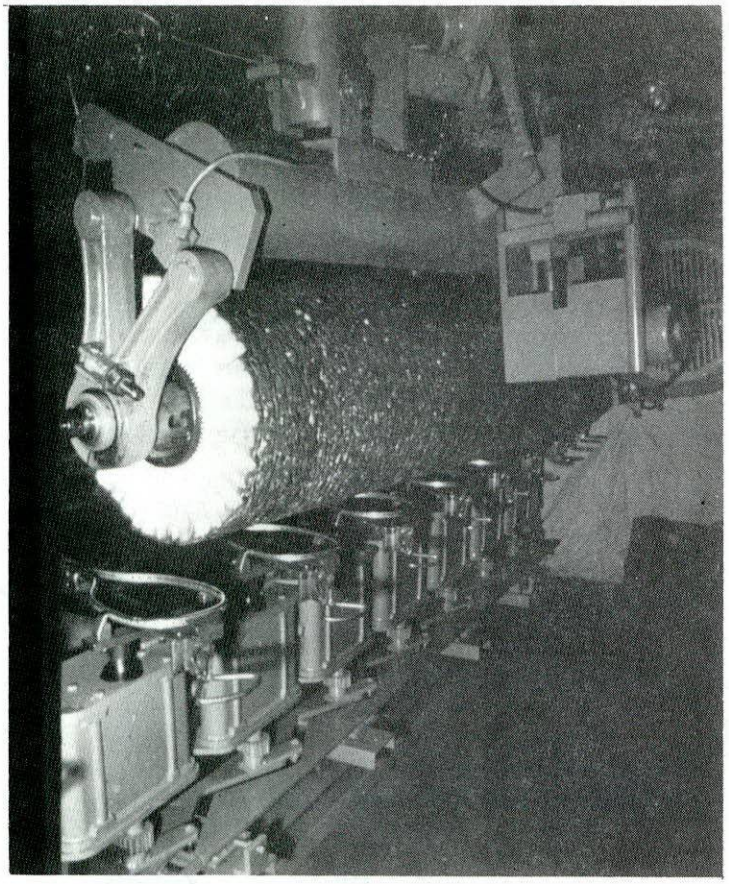


Figure 3

Figure 3 shows the part in relationship to the buffing head where it is moved in a wig-wag type configuration so that the 7' wheel completely engulfs the section of the racquet that has to be buffed.

Part #2
Spray Guns

This part is fabricated as a diecast. After the part is cast, a parting line of flashing is left around the outside edge of the part and must be removed generally by a polishing operation prior to buffing. Usually a 240 or 320 grit belt quite readily removes the flashing.

The part is then loaded on a revolving fixture. Two of the spray guns face each other and revolve under one 7' buffing head for cutdown and then through another 7' head. The second head is still in the cutdown phase for approximately 4' whereupon a coloring compound is applied for the remainder of the 7' head to bring up overall lustre. The parts in the fixture then exit the machine to be flipped to the opposite side. After both sides are finished, the parts are racked and sent to cleaning.

Again we are looking to remove both the belt polishing line and some diecast scale that has remained on the gun. We should note however that the buffing operation is not intended to remove

deep pits or casting chill which is the result of poor quality diecasting. The part is colored with a high chrome green coloring compound so as to develop a black mirror depth of color.

The buffing wheels used for the cutdown operation are the Brute soft impregnated buffing wheel and are chosen so as to avoid the normal blemish marks formed at the time of compound spray. The coloring wheels are Bearcat 64/64 cloth so that the flap of the wheel will not show a haze line on the other side from buffing.

Part #3
Cosmetic Shells

These parts are generally lipstick tubes, eyebrow pencil tubes, perfume and cosmetic container caps, etc. They are formed prior to buffing on progressive die eyelet machines.

The finishing requirements of such cosmetic shells demand the complete removal of all draw marks and scratches from the eyelet machine while producing an ultra high lustre totally haze-free. All of this of course has to be done regardless of the configuration of the shell.

The machinery used for this type of finishing is generally a 4 head or 5 head rotary type table machine, with the 5 head type the preferable choice.

The first head which is a cutdown on the side of the shell uses a full disc sewn buff. This added stiffness or hardness to the buff is necessary to enhance the cutting ability. The second head is similar and is used in cutdown of the top of the shell. The third head is used to color the side of the shell, whereas the fourth head colors the top. Both heads #3 and #4 use 86/92 Elk type buffing wheels. Head #5, when present, would use a 64/64 Bearcat type buff and is used for full wipe-off of the shell prior to degreasing.

There are two critical factors in the finishing of cosmetic shells and both demand they receive constant attention. Firstly, the part has to be completed in one revolution of the buffing machine, since the extremely thin wall of a cosmetic container would generally be destroyed in a second pass. Secondly, the angle of the buff on the sides and top are critical. The wheel covering the side of the container must hit the entire side surface, but stop precisely at the line of demarcation, separating the side from the top, but totally covering the shell all the way down to the chuck on the fixture. It is important that the wheel be kept well lubricated with compound so that metal build-up on the wheel is kept at a minimum. Too dry a buffing wheel is a common cause of metallic head scratching.

The finishing of the top is basically the same, only the buff must hit the top from edge to edge in both the cutdown and color operations. The reason for this is to avoid the appearance of a ring which will show on either the top or the side where the buff leaves off. If this fine line of demarcation is not scrupulously followed, then of course this line will show in the final finish.

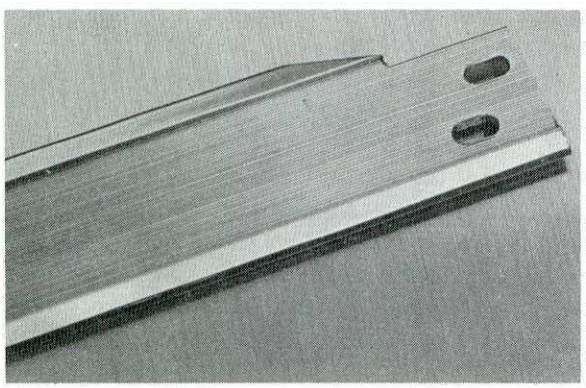
Part #4
Aluminum Extrusion

Aluminum extrusions are probably the most difficult to mechanically finish or buff. The reason being that flat parts tend to show all blemishes more readily than parts having other configurations.

The machinery that is generally used are flat bed type table machines with the parts passing either under a series of top heads for the desired degree of cut and color and then flipped to the opposite side to repeat the operation, or they can be buffed under a double roll head doing both upper and lower parts simultaneously.

The most severe problem that arises while finishing extrusions is due to the length of the extrusion and the need to spray compound on the wheel while buffing the same extrusion. This is called blushing and occurs every time the compound gun is fired. This comes about due to a sudden surge of compound hitting one spot across the face of the wheel and transferring to the part, causing a more aggressive cut at that particular spot. This split second compound firing and initial cutting surge on the part leaves a blush which cannot be wiped off.

To overcome this problem, we have found that small frequent applications of compound to the buffing wheel, combined with the use of a soft abrasive impregnated buff such as the Brute buff, totally eliminates this long-standing and very frustrating problem.



Summary:
Obviously, there are many more problems to buffing aluminum than those we have briefly discussed here, but they are the more ordinary problems which are generally solved through minor adjustments of either equipment or compound. What we have attempted to do is show that the large, very tough buffing problems that plague most aluminum finishers are now being attacked through engineering.

Engineering as exemplified by the use of 7' heads which totally engulf the part. Engineering the proper degree of dryness in terms of compound formulation and finally engineering the proper buff construction and selection utilizing abrasive impregnation. It is only by the coordination of compound, buffs and machines that the automatic buffing of aluminum parts can produce finishes which heretofore were obtainable only through hand buffing.

C-4

Mechanical Finishing
Session C

Resin Bonded Media In Mass Finishing Applications For Plating

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RESIN BONDED MEDIA IN MASS FINISHING APPLICATIONS FOR PLATING

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Mass Finishing with resin bonded media accounts for 30-50% of all mass finishing processes, of zinc and aluminum parts, especially of diecast work.

Resin bonded media consist of a plastic matrix, usually polyester, cross linked urea formaldehyde or nylon. The matrix incorporates one or more types of abrasives, selected to achieve a specific degree of surface refinement of the metal processed.

The main advantage of resin bonded media is their light weight, with an average density of 70-90 lbs. per cubic foot.

This characteristic, along with their inherent resiliency, allow the deburring and surface refinement of light metals without impingement or gouging of the surface. Since resin bonded media are manufactured by a molding process, a variety of shapes and sizes can be produced to suit most applications.

Media Classification

There are three primary types of resin bonded media classified according to their degree of abrasiveness.

1. Fast cut.
2. Medium cut - or general purpose.
3. Preplate - or light cut.

Several subgroups exist between these types for intermediate levels of surface finishing.

- Fast cut media generally consist of blends of aluminum oxide and silica. They are used for removal of heavy burrs, grinding lines and refinement of the coarse surface left by sand casting. The metal removal rate with this type of media is the highest, and so is its wear rate.

- Medium cut media contain very fine aluminum oxide, and or silica. This type is often used on machined parts and castings that are relatively free of heavy parting lines or burrs. The metal removal rate is lower than the previous type, as well as its wear rate.

- Preplate media, are generally formulated with very fine silica and pumice abrasives. They are primarily for surface refinement to provide a very low RMS value, typically between 1 and 3. Plating appearance of surfaces processed with this type of media are excellent and approximates that are obtained on buffed parts. Generally, the softer abrasives are selected in order to avoid deep impregnation of abrasive particles into the surface. Harder abrasives, such as aluminum oxide, once embedded into the surface of light metals, invariably lead to plating problems such as pitting or lack of adhesion.

Applications for Plating

As mentioned earlier, surface refinement of castings by mass finishing with resin bonded media is a very popular process used to prepare parts for plating. Diecast buckles, hardware items, lamp fixtures, automotive components, etc. are all examples of parts finished with this process.

The base metal preparation plays an important role in the final appearance of plated surfaces. Leveling of plating, uniformity of appearance and adhesion, are all directly influenced by the process selected for mass finishing.

Surface Evaluation

In order to assess the effect of mass finishing techniques on plating, relevant surface characteristics were selected and compared. These characteristics are:

A. Before Plating

   Degree of surface smoothness expressed in RMS value as a function of media type.

B. After Plating

   Reflectivity and appearance of the surface as a function of media type and compound.

The evaluation was carried out by processing identical castings (see fig. 1) in a 3 cubic ft. vibratory machine using the same size and media shape. A mildly alkaline liquid compound was used at a concentration of 0.5% by volume, and fed into the machine at the rate of 3 gallons per cubic foot per hour. The drain on the machine was left open to maintain a flow through system.

After mass finishing, parts were racked and processed equally through a copper-nickel plating cycle.

A. Degree of Smoothness Before Plating

Table (1) shows the average RMS values obtained as a function of media types and processing time.

Types:	Fast Cut RMS	Medium Cut RMS	Preplate RMS
Time			
1 hr.	28	10	6
2 hrs.	27	8	4

Photomicrographs of the surfaces processed were taken to examine the effect of media selection more closely.

100X magnifications, as well as Nomarski techniques, were used to define the scratch pattern and depth left by each type of media. Fig. 2-3-4.

The pattern obtained with the fast cutting media generates higher RMS values and shows deeper and wider scratch lines across the surface.

By contrast, the preplate media generate very low RMS values and show much finer, superficial scratch lines.

B. Appearance After Plating

Surface reflectivity was visually noted, and a series of photomicrographs taken to examine the degree of leveling and plating coverage. Figs. 5-6-7.

Although the resin bonded media usually produce matte, non reflective surfaces, bright plating is generally obtainable. The degree of brightness, however, is a function of the media type, and the RMS value produced on the surface.

As illustrated, the lower the RMS, the more levelled and brighter the plated deposit obtained. This could readily be explained on the basis that crystals grow more evenly across surfaces with the least degree of imperfection.

This is in variance to the common beleif that a bright surface is needed to obtain bright plating.

It was also noted that increasing the compound concentration and working with a closed system (rather than flow through), generated a lower RMS even when fast cutting media were used. Residue of resin and abrasive particles build up with such a process, resulting in gradual media loading with residue and loss of cutting efficiency.

This residue tend to accumulate in recessed areas of parts, and is extremely difficult to clean, resulting in defective plating.

That same residue was obtained on parts processed with flow through systems that used very little or no compound in the water feeding the load.

To overcome this problem, a low concentration of a properly formulated compound should be used in a continuous flow through system.

Conclusion

Plating is a build up of crystals that follows the topography of the base metal.

The selection of the correct type of media will determine the degree of smoothness of the base metal and consequently affects the appearance of plating.

Preplate resin bonded media when used with recommended compounds in flow through systems, generate the most adequate surface finishes for good plating.

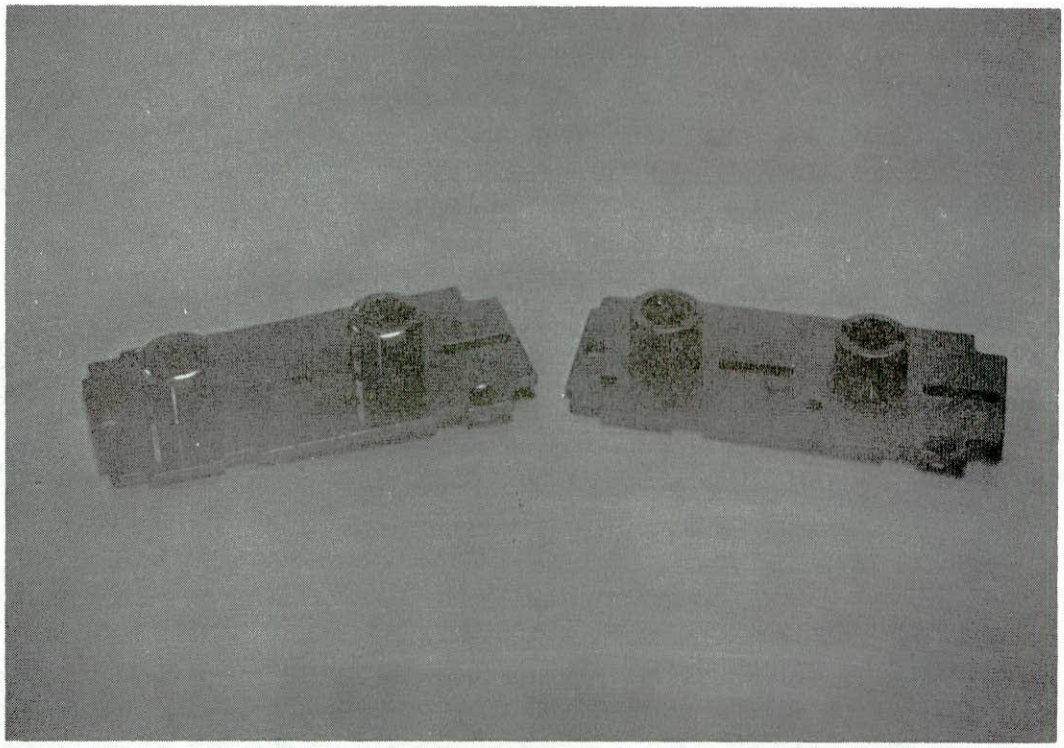

Fig. 1
Zinc diecast parts, mass finished with resin bonded media
Before and after plating

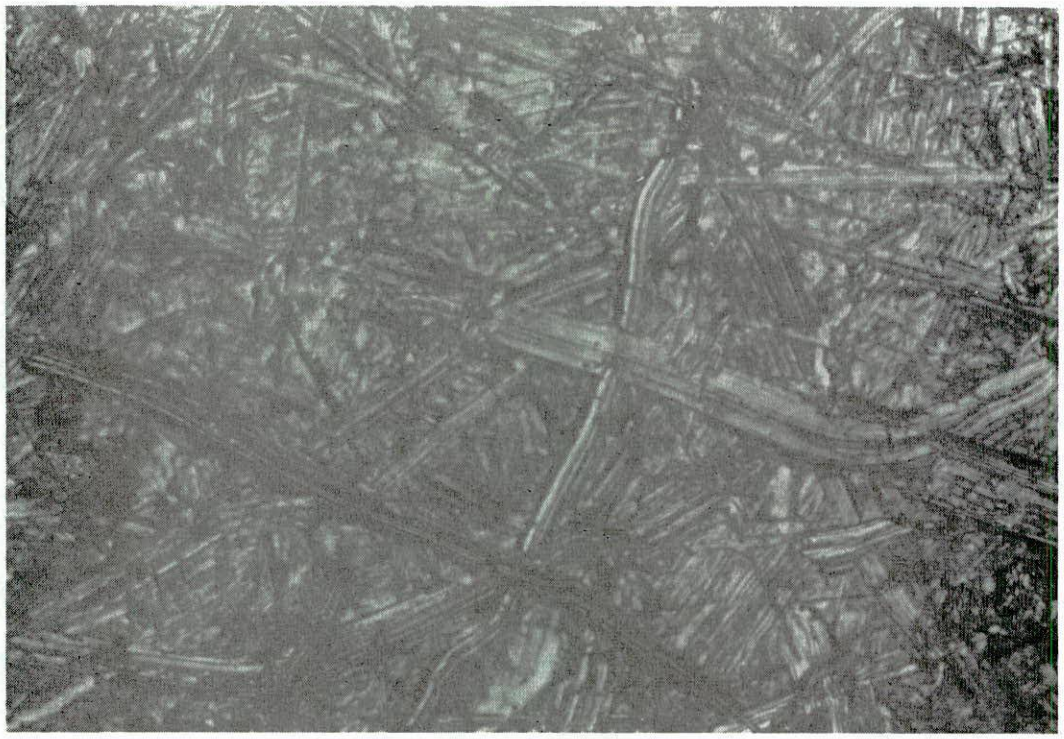

Fig. 2 100X Magnification
Surface finished with Fast Cutting media

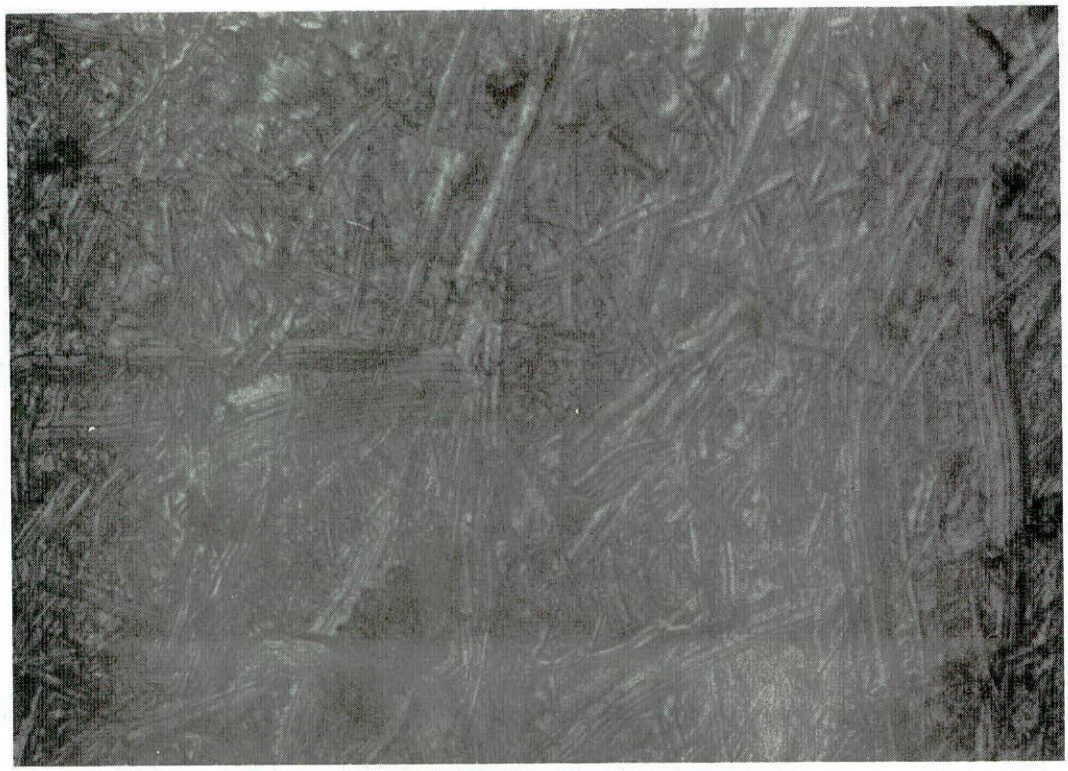

Fig. 3 100X
Surface finished with Medium Cutting media

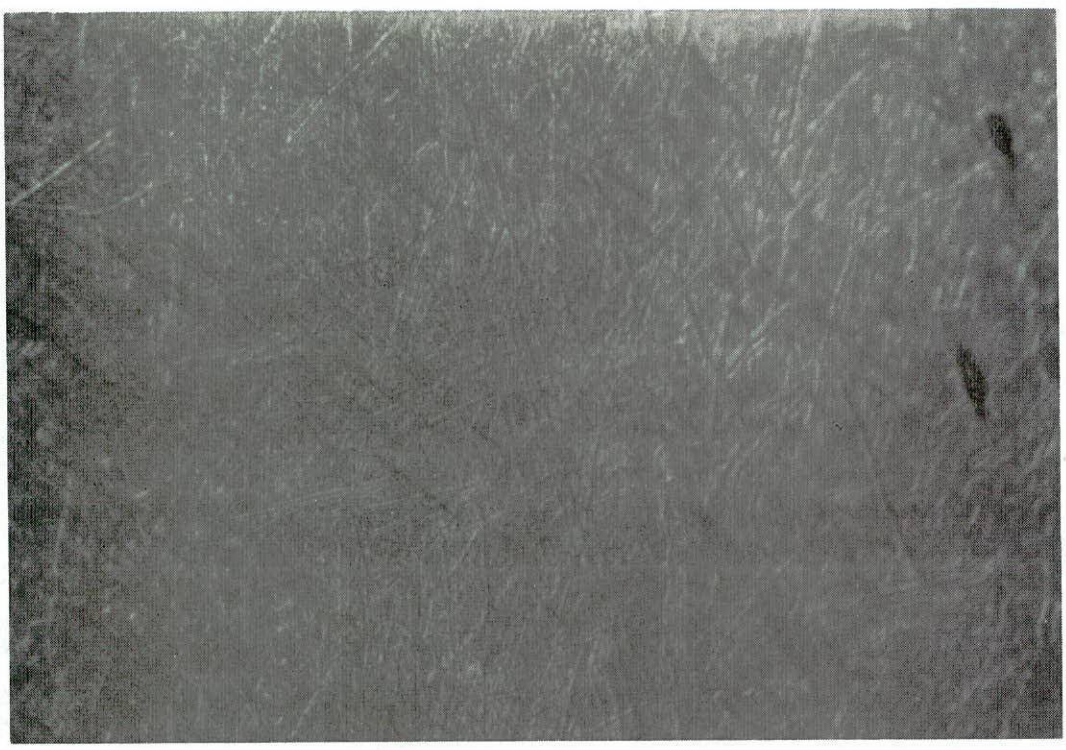

Fig. 4 100X
Surface finished with Preplate media

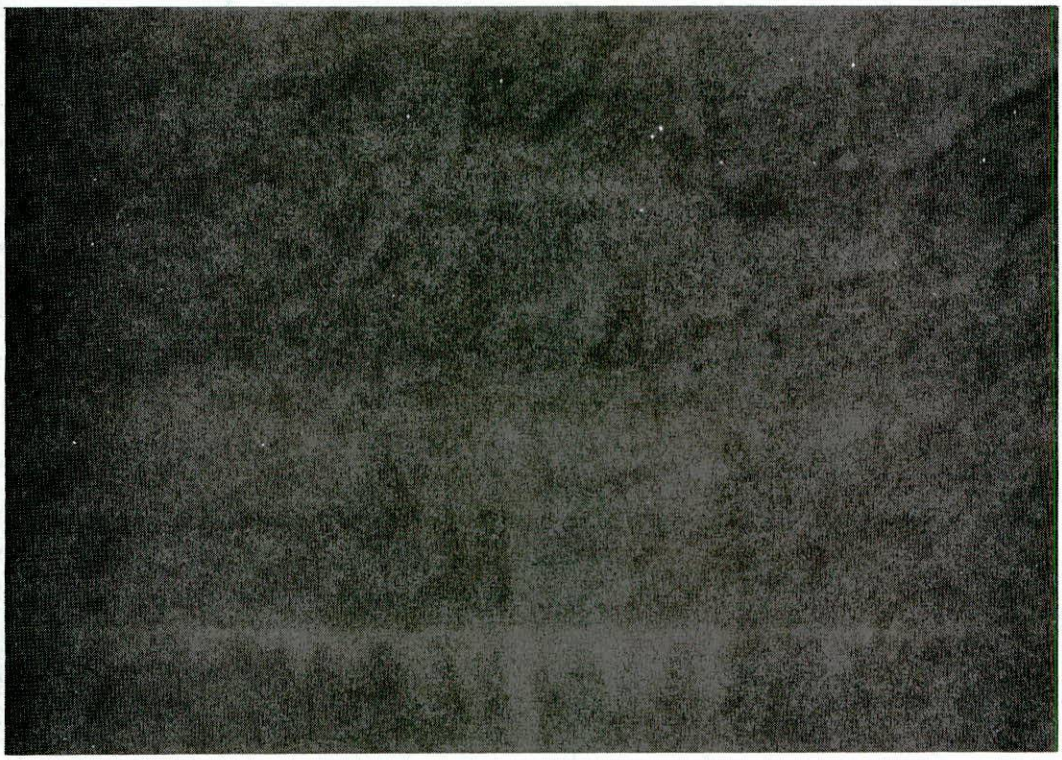

Fig. 5 100X Magnification
Plated surface after processing with fast cutting media

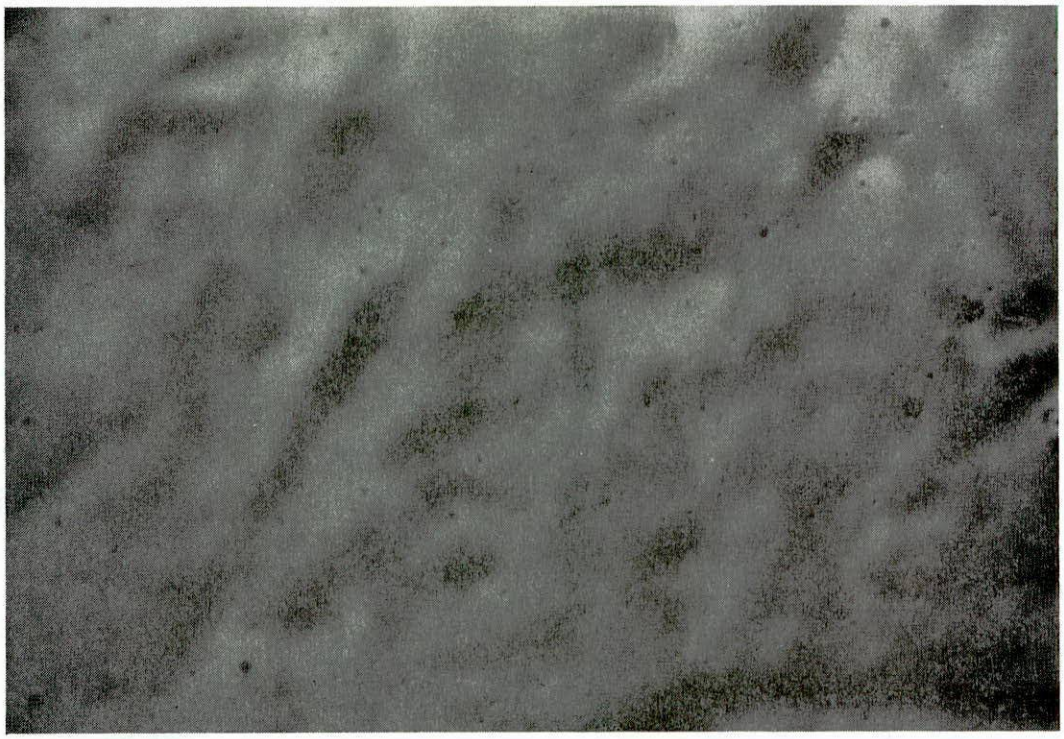

Fig. 6 100X Magnification
Plated surface after processing with medium cutting media

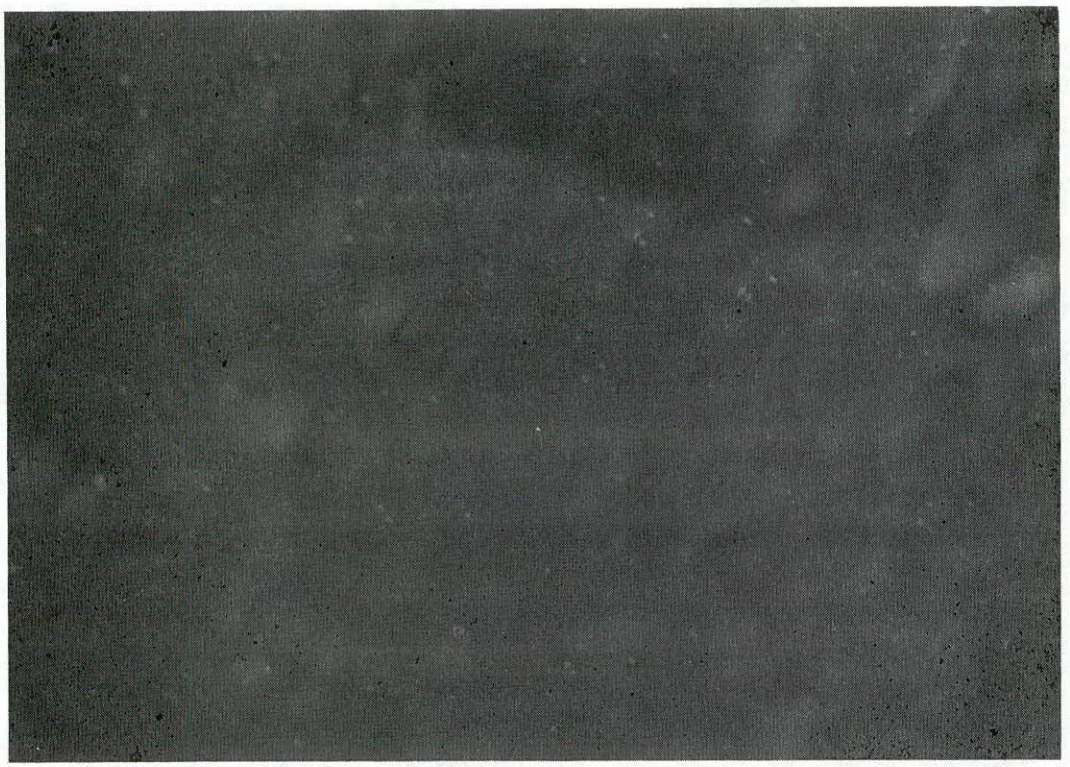

Fig. 7 100X Magnification
Plated surface after processing with Preplate media

D-1

Decorative I
Session D

Uniform Satin Nickel as a Decorative Finish

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UNIFORM SATIN NICKEL AS A DECORATIVE FINISH

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WHAT IS IT?

A nickel plating deposit that enables the plater to deposit a uniform satin nickel finish on either plastics or metals without:

1. Mechanically abrading the surface
2. Introducing an insoluble particle in the nickel bath
3. Any additional steps or baths

The satin finish effect is accomplished by a brightener system that intermittently disrupts the nickel deposition process. The stability of this brightener system is maintained by a unit that continuously filters the plating bath and regenerates the plating additives. This unit releases the plater of intensive labor costs and additional steps.

HOW IT WORKS

To a standard electrolytic nickel bath an organic emulsifier and a primary brightener are added. The emulsifier, referred to as the velvet forming agent, is primarily responsible for producing the satin-nickel effect. This emulsifier produces a homogenous solution below the cloud-point temperature in the electrolyte solution; and, above the cloud-point temperature, it gives rise to an emulsified liquid state.

During electroplating, the positively charged emulsion globules in the dispersed phase are continuously interacting at the cathode (the part) which intermittently attracts and releases the globules. The globules blanket the part in a random fashion, thereby interrupting the plating process on the surface. As these emulsion particles are impacted on the part, they produce flat circular indentations, not spherical. The typical diameter of the indentations ranges from two to thirty microns with a depth of between 0.15-0.25 microns. The end effect is a diffused reflective nickel surface of uniform, matted, satin appearance.

A minimum thickness of 8 microns is required to achieve this effect. Higher thicknesses do not adversely affect the satin finish.

For a production feasible system, the process must function economically and continuously; therefore, the emulsion must be maintained at optimum operating level while at the same time restraining contaminants within a tolerable level.

This is readily accomplished by a highly efficient regeneration system we call the aggregate. The aggregate system continuously draws off the electrolyte from the bath, cools it, filters it, reheats it, and returns it to

the plating cell. The unit can be located anywhere within 30 feet of the nickel tank and takes up a space of approximately 3 feet by 3 feet.

41 Slide -- Aggregate
42 Slide -- Schematic of Aggregate

In the nickel bath, the solution is operating in a temperature range of 49-60°C. (120-140°F.), a temperature well above the cloud-point of the emulsion. The solution is producing breakdown products that rise to the surface of the plating tank and are being skimmed off into overflow tank (a tank capacity of 5-10% of the operating bath is sufficient to carry out the process). The solution first goes through the highly efficient cooling system and is cooled down to 21-27°C. (70-80°F), a temperature well below the cloud-point of the emulsion. Now the solution is a completely homogenous solution; it moves next to the filter with a 10-15 micron grade filter. Here contaminants and breakdown products are removed without removing the fraction emulsion droplets. The solution then moves back to the heating chamber when it is reheated to 37°C. (99°F.), a temperature above the cloud-point so the electrolyte is once again in the emulsified liquid phase. Now the solution is returned to the plating tank in the area of the tank heater, and is reheated to the operating temperature 49-60°C. (120-140°F.). The solution has been regenerated and contaminants removed; it is available to the plating tank to continue the deposition of a uniform, matte, satin finish on all surfaces of the part, regardless of local current density conditions.

The emulsion causes no interference of subsequent plating such as gold, copper, chrome, silver. The deposit does not detract from salt spray requirements. Any part at the point of processing that is receptive to nickel plate is receptive to satin nickel. The activity of the satin nickel is excellent and, thus, chrome coverage is equally excellent.

Why haven't you heard of it before? Why now? Simply put. It has taken a long time to get to "Mr. Decision Maker" in styling, but it is happening. More important to the plater, growth in bright plate requirements is not dynamic. You need all the flexibility you can find. The search for satin nickel is over, your search for new ways to get plating customers continues. Satin nickel just may be one of the ways to assist you.

WHAT TYPE OF PARTS?

First, let us list types of parts presently being processed (granted, mostly being done in Europe and Japan).

Typewriter and calculator parts
Photographic equipment, cameras
Electrical appliances - push buttons, nameplates, tools and hardware
Plumbing fixtures - knobs, soap dishes
Building hardware - knobs, push plates, kick plates
Eyeglass frames
Car radio, stereo buttons
T.V. buttons and plates

Office furniture - chair rollers
Electric razors (the famous T.V. ad for Remington)
Microscope parts
Pens
Attache case hardware
Rear tail light reflector

One of the problems with decorative plated parts, shiny or otherwise, is that of fingerprinting. Because of the rounded configuration of this type of deposit, moisture and oils from the skin are not as readily scraped off as they are with conventional nickel deposits. Therefore, fingerprints are less apparent and readily cleaned from this satin finish.

The ability to produce uniform matte finishes from mechanical induced blasting or scratching has and probably always will be a problem. The ability to produce constant uniform satin finish over the entire part is a big plus, and slight surface imperfections are readily "hidden" by this application of this satin finish.

BITS AND PIECES

1. Standard Ni - $NiSO_4$ - Ni Cl - Boric - Formulations are used, one difference, the ratio of nickel metal to nickel chloride should be 1 metal to 4 nickel chloride - otherwise the work will be too bright.

2. Current Density - Cathode 1.5 - 8 A/dm^2 (15-80 ASF) normally 2-4 A/dm^2 (20-40 ASF)

   Anode - 2.5 A/dm^2 (25 ASF)

3. Bath Voltage - 4-12 volts

4. pH - 3.8 - 4.8

5. Plating time - 13-15 minutes for 8 microns (.0003")

6. Agitation - mechanical only - not air

7. Tank size - most baths are 250-800 gallons (using 2 units)

8. Preplate Cycle - Bright copper, rinse, acid, rinse, plate
   Have seen many cycles with 2% sulfuric, directly into the satin nickel.

9. E.P. Tank - Good practice to have these especially in zinc D.C. and brass lines. The E.P. tank is located between the plating tank and the aggregate. This is an ideal place to make additions because the E.P. treated solution goes through the filter from here.

10. Carbon Treatment - will vary - about once/month

11. Cathode Rod Agitation - vertical or horizontal being used with a 4-6" stroke.

12. Solution movement - around heating coils is important.

13. Centrifugal Pumps - Out - they bruise the emulsifiers.

14. Flow rate - 1/3 of the solution through the filter per hour.

15. With cathode rod (vertical movement) jerk motion at start of upstroke tied into horizontal paddles to give better solution movement.

16. Anode bags - tend to pick up breakdown product at the solution/air interface. A 4-6" strip of plastic mounted next to the anodes, on the plating cell side, collects this breakdown product. It can be scraped off periodically and extends carbon and filter treatment maintenance.

17. Resolution time - 2 minutes time to cool bath below cloud-point is important. Additional time can be built in by adding a length of flexible tubing or a separate chamber.

18. Shutdown - Bath will require 4-6 hours to properly emulsify the addition agents. Temperature should not be allowed to drop below 35°C. (95°F.) as boric will drop out and clog the filtration system.

19. Heating water should not be more than 80°C. (170°F.) for a safety factor. At 90°C. (180°F.) the emulsifiers are evaporating.

20. Cooling water consumption - if water below 60°F. is not available, a separate chiller is recommended (7 tons for 800 gallon tank).

21. Sulfur deposit as nearly as we can tell is 0.14%.

22. For plating on plastics - the deposit over 2.0 - 2.5 - 1 ratio of copper to nickel passes stress tests and hot-cold triple cycle.

23. The Hull Cell or Jiggle Cell can be used for control.

TYPICAL TEST PANELS OF SATIN NICKEL BATH

Fig. 1
Normal concentration of satin additives.

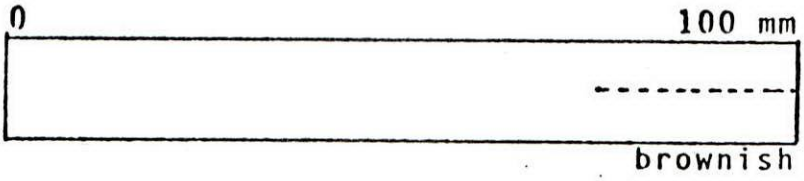


Fig. 2
Half concentration of satin additives.

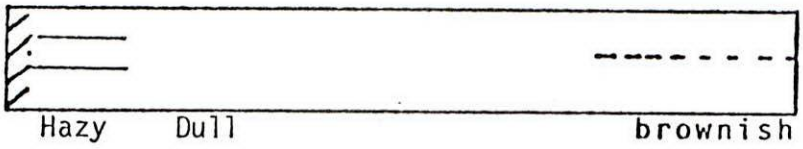


Fig. 3
Low satin additive.

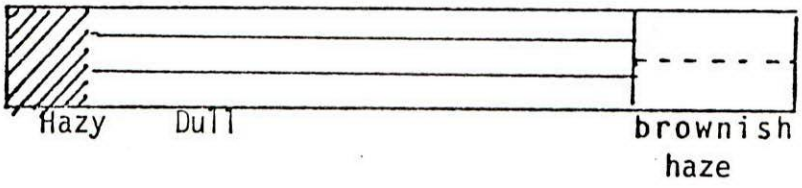


Fig. 4
High satin additives.

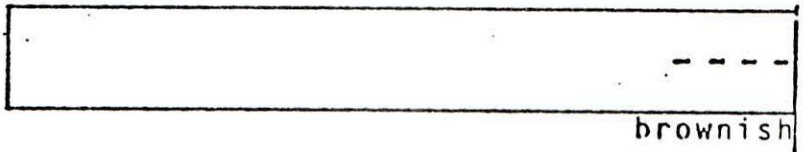


Fig. 5
Normal concentration of primary additive

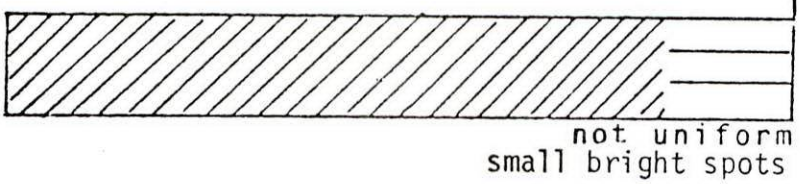


Fig. 6
Low primary additive.

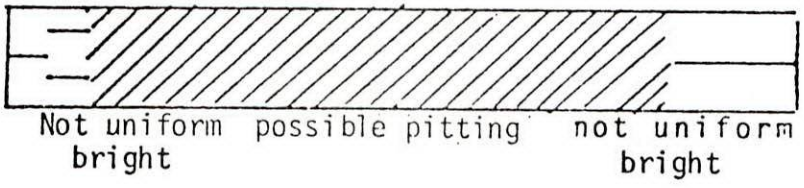
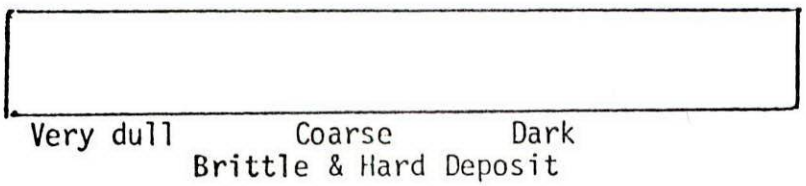


Fig. 7
High primary additive.



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Decorative I
Session D

Electrodeposition of Bright Zinc-Nickel Alloys

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ELECTRODEPOSITION OF BRIGHT ZINC-NICKEL ALLOYS

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ABSTRACT

The bright zinc-nickel alloy plating process reported at the 69th AES Annual Technical Conference has been commercialized in Japan for use in automotive applications. This new technology is far superior to conventional pure zinc plating processes in corrosion resistance and thermal stability.

Our experience with production scale operations during the past few years has resulted in several improvements. The additive system retards a tendency of high nickel codeposition at low current density areas, which may influence chromating coverage. In addition to the initial rack plating applications, mass production under barrel plating conditions is now underway. Finally, a pretreatment process has been developed to avoid hydrogen embrittlement.

INTRODUCTION

At the AES Sur Fin '82 conference, we described a new bright zinc-nickel alloy plating process and chromating method.[1] This new technology[2] has made it possible to plate zinc-nickel alloy deposits, which are far superior to pure zinc deposits for both corrosion resistance and thermal stability, using the same methods as for conventional zinc plating.

During the past two years, this bright zinc-nickel alloy plating system has been adopted by several automotive manufacturers and parts suppliers in Japan. The experiences with these production-scale operations have led to several new developments, including modifications of the process which now permit operation in commercial barrel, as well as rack installations.

One of the key aspects of zinc-nickel alloy technology is to control the amount of nickel codeposited, especially under low current density (LCD) conditions such as barrel plating. Since LCD conditions favor high nickel levels, this can lead to problems with chromate coverage and corrosion resistance. The improved additive system controls nickel codeposition under LCD conditions, thereby producing alloy deposit with the desired nickel content in the range from 8-15%.

Another feature of importance is the ability to plate bolts, springs and other high strength steel parts without hydrogen embrittlement. To avoid this problem, which is common with some pretreatment and zinc plating process cycles, many specifications require a 200°C heat treatment for 4 hours. We have demonstrated that when the bright zinc-nickel alloy process is used in conjunction with an appropriate pretreatment process, there is no hydrogen embrittlement; hence, the heat treatment process can be avoided.

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*A joint venture partner of OMI International Corporation, Warren, Michigan.

ALLOY COMPOSITION

Figure 1 shows the dependence of the nickel content of alloy deposit on the cathode current density. The data for this figure were obtained using the bath composition and operating conditions given in Tables I and II, respectively. As indicated in Figure 1, alloys with >25% Ni are dark and unacceptable, whereas alloys in the range 15-25% Ni do not lend themselves to chromate post-treatment. Below 15% Ni, bright uniform alloy coatings that readily accept chromate are formed. Since uniform chromate films enhance the corrosion resistance, most applications will require that the Ni content be maintained below 15%.

Barrel operations normally use current density values of less than 2 ASD (2 amperes per square decimeter is about 20 ASF). Therefore, successful operation of this process in barrel applications requires that the tendency to codeposit Ni at LCD be controlled. As described below, appropriate chemical additives have been developed to accomplish this task.

NICKEL CONTROL

Various compounds have been evaluated in this bright zinc-nickel alloy system for their ability to control nickel codeposition at low current densities. This work successfully identified a number of additives which achieve this result. The effects of the primary brightener A and the secondary brightener B on the control of the nickel content is shown by the open circles in Figure 2, which also corresponds to the results shown in Figure 1. An additional control is evident from Curves C, D which represent the addition of 0.015M of proprietary[3] controllers C, D.

The effects of these same additive chemistries on the cathode efficiency for zinc, nickel and on the total alloy are shown in Figures 3, 4 and 5, respectively. The data for these figures were obtained using the bath composition and operating conditions given in Tables I and II. It is evident that the decrease of the nickel content is associated with the increased cathode efficiency for zinc deposition caused by the additives. There is also a contribution from the reduced efficiency for nickel deposition. The combined effect of the additives developed is to improve the covering power of the alloy deposits, especially in LCD areas.

BARREL PLATING

Due to the large amount of dragout of solution in barrel plating, the metal concentrations in a barrel operation should be kept at the lowest possible level so that the process will be economical. The bath composition given in Table III has been established by testing to be the most effective composition for barrel operations. The operating conditions are listed in Table II. An example from an installation producing bolts is given in Table IV(a).

CORROSION RESISTANCE

Deposit thickness and corrosion test[4] data for the yellow chromated-parts described above are given in Table IV(b). In comparing these results with pure zinc of similar thickness we note that the alloy deposits provide a two-fold improvement in resistance to white corrosion and a three to five-fold improvement in resistance to rust prevention.

HYDROGEN EMBRITTLEMENT

It has been reported previously[5] that zinc-nickel alloy plating does not have problems due to hydrogen embrittlement, and the same favorable result has been demonstrated in our work.

Hydrogen embrittlement of work pieces can occur during the pretreatment and/or plating stages. The amount of hydrogen embrittlement can be related to an embrittle ratio (ER), which is measured by the use of a Delta gauge[6] (Figure 6). A test piece of sheet steel, Rockwell C hardness 52, with dimensions 100x10x1 mm, is plated and placed in the test fixture, which then is tightened until it breaks. The embrittlement ratio is given by

$$ER\ (\%) = 100 - \frac{(L)}{Lo}.100$$

where Lo and L are the distances that unplated and plated test pieces can be compressed before breaking.

Table V lists the ER values measured when various plating processes are used. These results show that the zinc-nickel alloy process causes very little hydrogen embrittlement.

As stated above, hydrogen embrittlement can also be caused by the pretreatment stage, especially during cathodic electrocleaning and the acid dip (pickling). By using anodic electrocleaning and an inhibitor in the acid dip, hydrogen embrittlement can be nearly eliminated. Thus, the following pretreatment cycle is recommended.

- alkaline soak or anodic electrocleaning
- acid dip (10-20% HCl with inhibitor)
- alkaline soak
- anodic electrocleaning
- acid activation (1-2% HCl)

When this pretreatment cycle is used prior to zinc-nickel alloy plating, the ER is reduced to a value which is less than that obtained for heat-treated zinc deposits. This result is apparently due to the low diffusivity of hydrogen through zinc.[7]

Thus, the productivity is improved and costs are reduced due to eliminating the heat-treatment process. This approach is especially useful when processing steel compositions that do not maintain optimum properties when subjected to heat treatment.

CONCLUSION

The previous work on bright zinc-nickel alloy plating has been extended to facilitate commercial scale rack and barrel operations. The best results are obtained with alloys in the range 10-15% Ni. An improved chemical additive system has been developed to avoid problems due to high nickel content and poor chromate coverage at low current density.

Exceptional corrosion resistance in neutral salt spray tests and the ability to plate high strength steel without the need for a heat-treatment to avoid hydrogen embrittlement are two of the major benefits now being realized by the users of this new technology.

REFERENCES

1. H. Tsuji and M. Kamitani, "Electrodeposition and Passivation of Bright Zinc-Nickel Alloys" presented at 69th Annual Technical Conference, AES (1982).

2. The process is sold under the name, ZIN-LOY™, Ebara-Udylite Co., Ltd.

3. Patent application pending.

4. Corrosion tests based on neutral salt spray, equivalent to ASTM B137.

5. G. Hsu, "Zinc-Nickel Alloy Plating: An Alternative to Cadmium", PLATING AND SURFACE FINISHING, 71, 52 (1984).

6. T. Doi, I. Saito and K. Takada, "Measurement of Hydrogen Embrittlement in Zinc Plating Process by Bend Fracture Test", JITSUMU HYOMEN GIJYUTSU 31, 457 (Oct. 1984).

7. K. Yamakawa, "Hydrogen Absorption and Hydrogen Embrittlement of Steel", ibid., 30, 240 (June 1983).

TABLE I

BATH COMPOSITION FOR RACK PLATING OPERATION

Component	Range	Optimum
$ZnCl_2$	80 - 120 g/L	100 g/L
$NiCl_2.6H_2O$	120 - 160 g/L	140 g/L
NH_4Cl	180 - 220 g/L	200 g/L
NH_4OH (25%)	30 - 60 mL/L	40 mL/L
Primary Brightener A	40 - 60 mL/L	50 mL/L
Secondary Brightener B	1 - 3 mL/L	2 mL/L

TABLE II

OPERATING CONDITIONS

pH		5.5 - 5.8
Temperature		33 - 37°C
Anodes		Zn and Ni
Agitation		Air agitation
C.D. (A/dm^2)	Rack	2 - 5
	Barrel	0.5 - 2

TABLE III

BATH COMPOSITION FOR BARREL PLATING

Component	Range	Optimum
$ZnCl_2$	60 - 80 g/L	70 g/L
$NiCl_2.6H_2O$	80 - 120 g/L	100 g/L
NH_4Cl	220 - 250 g/L	240 g/L
NH_4OH (25%)	20 - 40 mL/L	30 mL/L
Primary Brightener A	40 - 60 mL/L	50 mL/L
Secondary Brightener B	1 - 3 mL/L	2 mL/L
Controller C, D	1 - 3 g/L	2 g/L

TABLE IV(a)

BARREL* PROCESSING CONDITIONS

Bolt	Parts	Kg	V	A	C.D. (ASD)	Time (Min.)
A	12 mm dia. x 35 mm high carbon steel	80	4.5	300	0.50	45
B	10 mm dia. x 35 mm high carbon steel	70	4.7	350	0.47	45
C	10 mm dia. x 107 mm high carbon steel	60	4.5	350	0.67	40
D	6 mm dia. x 13 mm low carbon steel & washers	40	5.0	400	0.50	30

*Covered rotating barrel: 350 mm i.d. x 950 mm
Perforation: 5 mm dia.
Rotation: 6 rpm

TABLE IV(b)

CORROSION RESISTANCE

Bolt	Thickness (um)	% Ni	Salt Spray Hrs. White Corr.	Salt Spray Hrs. Red Rust
A	5.8 - 6.3	11 - 14	144 - 216	>1000
B	5.4 - 6.6	12 - 15	192 - 264	>1000
C	5.6 - 6.6	10 - 13	144 - 192	>1000
D	5.5 - 6.4	11 - 14	144 - 216	>1000
Control	6	0	72 - 120	300 - 400
	13	0	72 - 120	600 - 700

TABLE V

HYDROGEN EMBRITTLEMENT RESULTS

Plating Bath	Operating Conditions	Embrittle Ratio (%)
Zinc (Cyanide)	2 A/dm^2, 10 min.	68
Zinc (Zincate)	2 A/dm^2, 10 min.	50
Zinc (Chloride)	2 A/dm^2, 10 min.	4
Ni (Watts)	1 A/dm^2, 30 min.	5
Ni (Wood)	3 A/dm^2, 2 min.	1
Zn-Ni alloy	3 A/dm^2, 20 min.	2
Zn-Ni alloy	3 A/dm^2, 10 min.	1
Electroless Ni	90°C, 60 min.	23

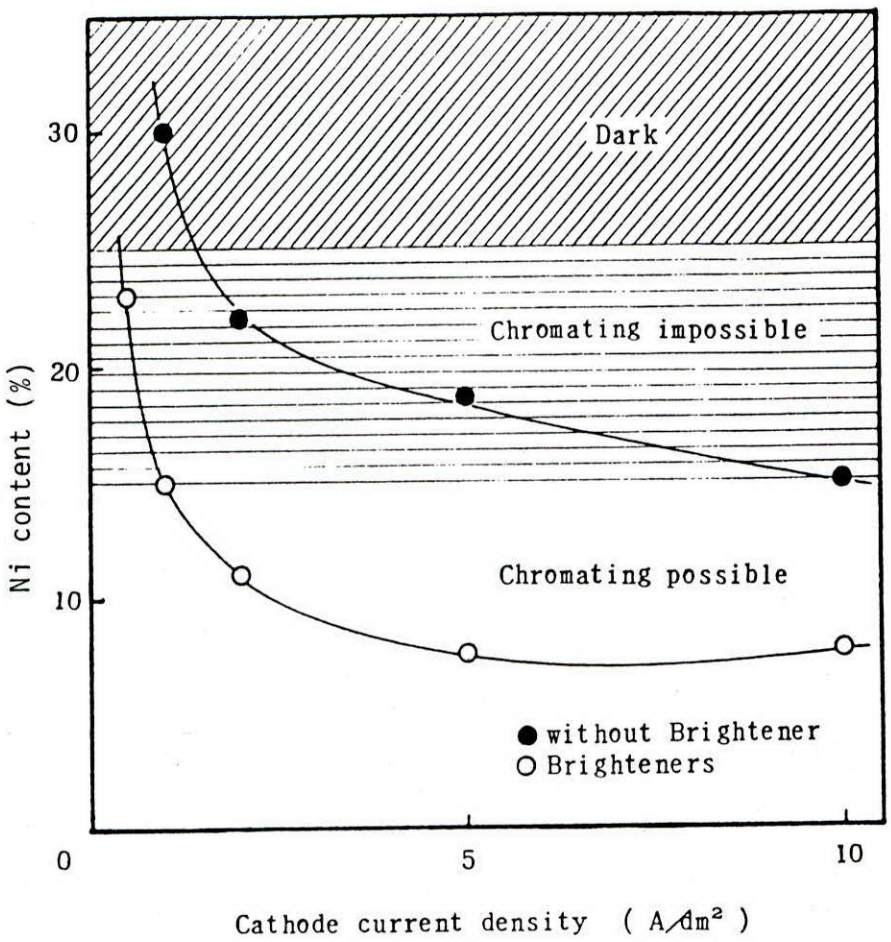

Fig. 1 Effect of cathode current density on Ni content, with and without brighteners

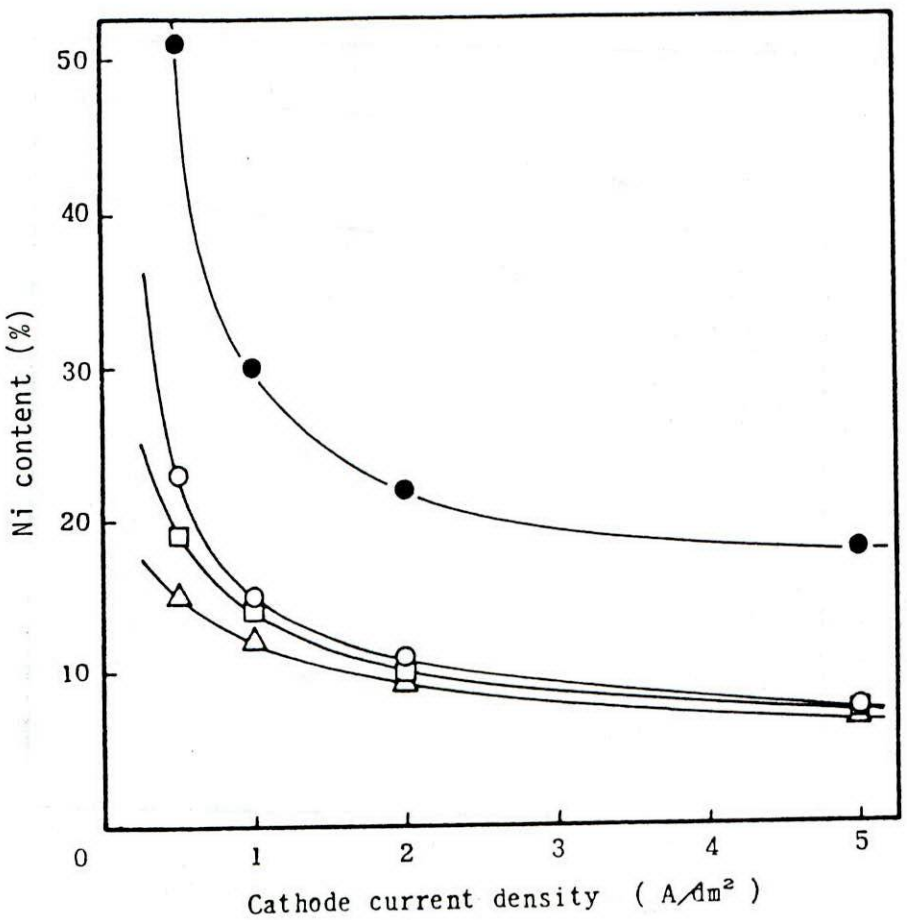

Fig. 2 Effect of Ni control additives

- ● without Brighteners
- ○ Brighteners A and B
- □ Brighteners A, B plus Controller C
- △ Brighteners A, B plus Controller D

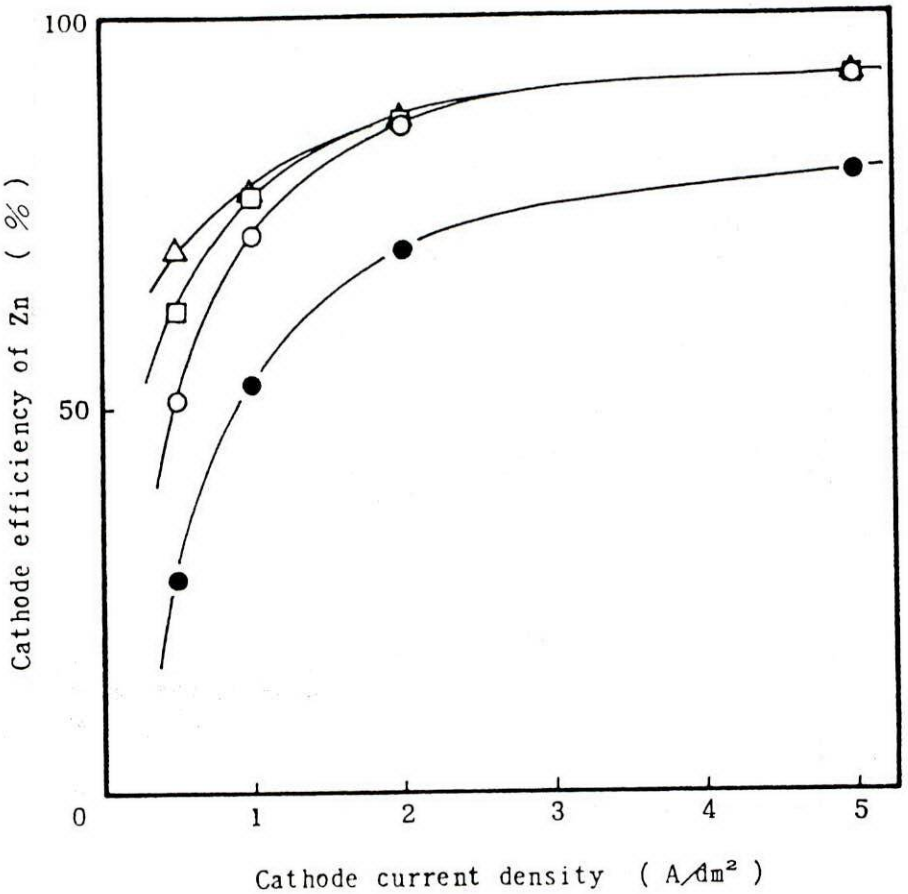

Fig. 3 Relation between cathode current density and cathode efficiency of Zn

● without Brighteners
○ Brighteners A and B
□ Brighteners A, B plus Controller C
△ Brighteners A, B plus Controller D

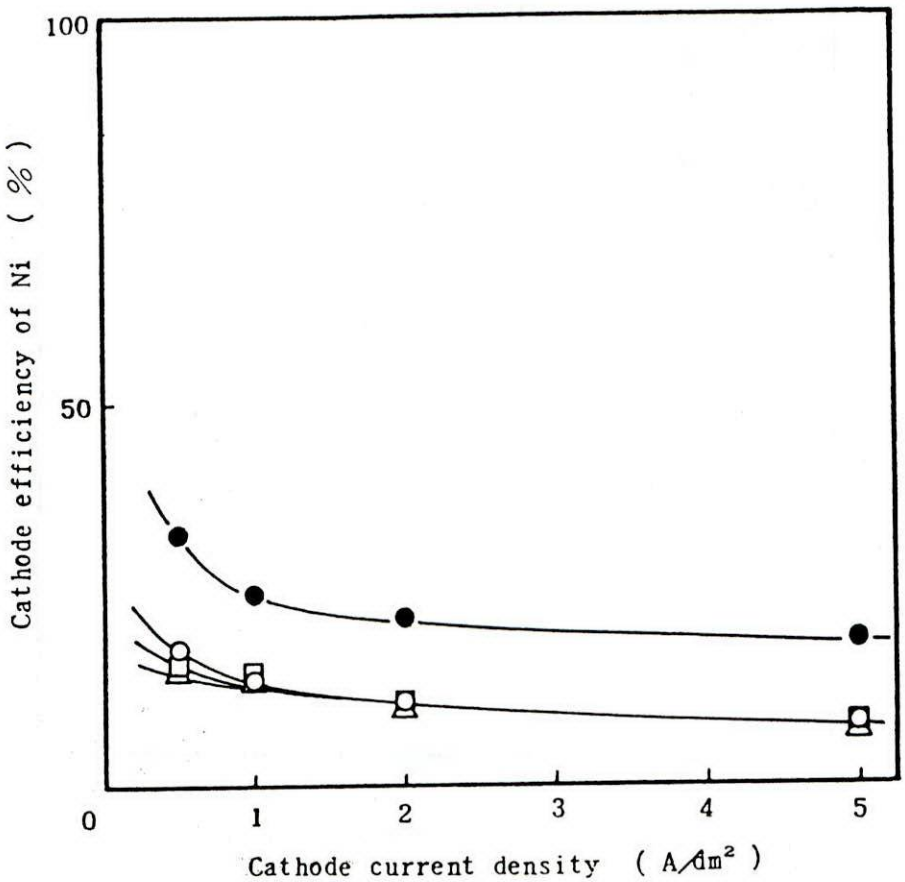

Fig. 4 Relation between cathode current density and cathode efficiency of Ni

● without Brighteners
○ Brighteners A and B
□ Brighteners A, B plus Controller C
△ Brighteners A, B plus Controller D

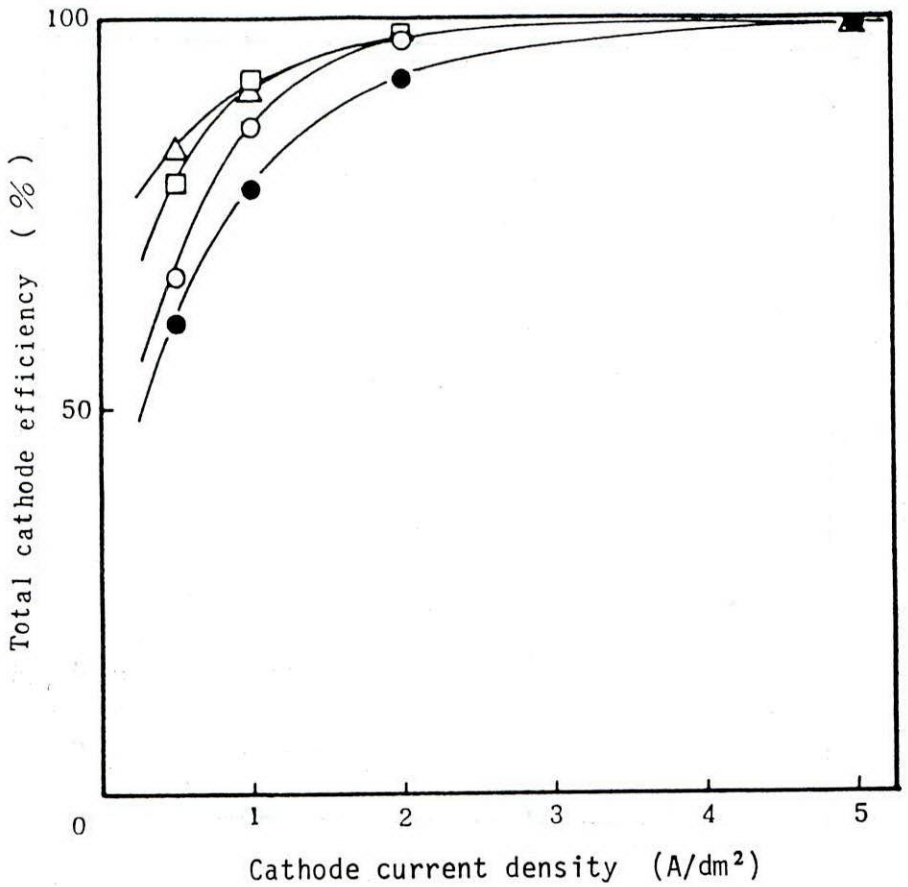

Fig. 5 Relation between cathode current density and total cathode efficiency

- ● without Brighteners
- ○ Brighteners A and B
- □ Brighteners A, B plus Controller C
- △ Brighteners A, B plus Controller D

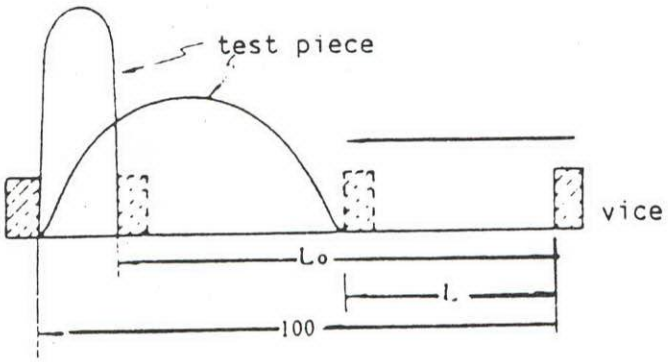

Fig. 6 Test procedure for measurement of hydrogen embrittlement (after Ref. 6)

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Decorative I
Session D

New Alkaline Copper Process: A Novel Alternative to Cyanide Copper

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NEW ALKALINE COPPER PROCESS: A NOVEL ALTERNATIVE TO CYANIDE COPPER

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ABSTRACT

A new mildly alkaline, lightly complexed copper plating solution has been developed as a replacement for conventional copper cyanide baths. The process utilizes a unique soluble/insoluble anode system and chemistry which produces fine grained, ductile, adherent deposits with outstanding throwing and covering power. Acceptable results have been obtained commercially on steel and brass substrates and the potential for use on zinc based die castings is encouraging. The electrolyte contains no cyanide and can be readily and easily waste treated using conventional procedures and equipment.

INTRODUCTION

The medieval alchemists are credited with the first attempts at copper plating. They found that they could transform unappealing iron artifacts into eye pleasing, bright, rose colored works of art, by simply immersing them in an acidified solution of blue vitriol. This instant transformation was not magic, as it had appeared, but merely a simple redox reaction. The iron was oxidized in the acid medium and, in turn, reduced the copper ions to metallic copper which then freely immersed on the active iron surface.

It was not until the mid-19th Century that any serious work was done with copper plating. The discoveries of Faraday and Henry in 1831[1] led to the conversion of mechanical energy to electrical energy and consequently made the electroplating of adherent copper deposits possible. However, it took some forty years to commercialize the first generators to supply power for lighting, heating and electroplating.

The second quarter of the 19th Century produced a rather large number of patents for copper plating, some of which are still used as building blocks for the refined, highly specialized systems of today's world. The precursors of these modern copper-cyanide systems were patents granted to Wright in 1840,[2] and Hallengshead in the 1890's.[3 4]

Towards the end of the 19th Century, copper plating was widely practiced and, along with silver plating, became the backbone of the metal finishing industry.

The 20th Century ushered in a new era of technology, as copper deposits and plating techniques had to be modified to meet the requirements for a new and challenging market. This thrust towards new technology was also spurred by public awareness of industrial health, safety and environmental protection.

Congress yielded to public pressure and in a period of ten years, 1974 through 1984, enacted a series of laws regulating and governing potential health and environmental hazards. Acronyms like EPA, TSCA, NIOSH and OSHA have become household words in the industry. Consequently, metal finishers and suppliers had to reorient their thinking. Cyanide plating systems, which had provided dependable performance and economy for over 100 years, were being threatened by these new governmental restrictions. In order to meet this new challenge, technology was directed towards: (1) The reduction of cyanide concentrations, and (2) The substitution of cyanide with new, nontoxic complexing agents.

To date, at least four different types of commercial electrolytes have been developed. The basic components of each process are summarized below:

Micro Cyanide Bath[5]

Components	Concentration g/L	Concentration oz/gal
Copper Metal	11.7	1.56
Free KCN	2.5	0.33
KOH	12.5	1.67
Rochelle Salts	51.1	6.81
Proprietary Addition Agents		

This very low cyanide formulation was not fully acceptable to the plating industry, since it had limited cathode efficiency and still required the handling, storage and waste treatment of cyanide materials.

Copper Pyprophosphate Baths[6 7]

Components	Concentration g/L	Concentration oz/gal
Copper Metal	30	4.0
Total pyrophosphate	210	28.0
Ammonia	3	0.4

While these baths exhibit high efficiency and good throwing power, they also have inherent limitations: (1) They require a copper strike prior to plating on steel and zinc die cast substrates; (2) Some formulations may to contain up 300 g/L ammonia which presents environmental and waste treatment problems; (3) The baths have limited solution life due to the hydrolysis of pyrophosphate to orthophosphate.

Acid Copper Sulfate Baths[8,9]

Components	Concentration g/L	Concentration oz/gal
Copper sulfate pentahydrate	210.0	28.0
Sulfuric acid 60° Be	60.0	8.0
Chloride Ion	0.060	0.008
Proprietary Addition Agents		

While acid copper plating baths can provide excellent plating speed and outstanding leveling and brightness, they have certain limitations which include the need for: (1) A copper strike prior to plating on steel and zinc die casting parts; (2) Acid resistant ventilation systems to remove "acid mist", and (3) Highly corrosive electrolytes.

Copper Fluoroborate Bath[10,11]

Components	Concentration g/L	Concentration oz/gal
Copper Fluoroborate	224-448	30-60
Copper Metal	60-120	8-16
Fluoroboric Acid	2	0.3
Proprietary Addition Agents		

The fluoroborate system is similar to the acid copper plating baths but is generally expensive to operate and more difficult to control. However, it has a higher solubility than sulfuric acid and, therefore, accommodates higher plating speeds.

Other cyanide free baths have also been developed but were never commercially successful. Some of the more well known ones include: Copper fluoro silicate baths[12], amine complexed baths[4], alkane sulfonate complexed baths[13,14], and alkaline organophosphonate complexed baths.[15,16] The fluoro silicate baths are poorly adherent and require a copper cyanide strike even for steel substrates. Consequently, the use of cyanide cannot be completely eliminated. The amine complexed baths also exhibit poor adhesion on common metallic substrates and the strong amine metal complexors present waste treatment problems. While the alkane sulfonate baths are characterized by high cathode current densities they generally have poor throwing power. Like the fluoro silicate baths a cyanide copper strike is required to assure good adhesion. The alkaline phosphonate copper baths produce excellent fine grained deposits when freshly prepared but continuous electrolysis causes the deposits to become grainy and nonadherent. The use of strong oxidizing agents maintain good deposit appearance but adhesion is still marginal.

It is evident that none of the baths described above provide a reliable alternative to cyanide copper plating baths for industrial applications. In many cases, although cyanide has been eliminated alternate complexing materials pose serious waste treatment problems, reduces deposit quality, and/or are unable to guarantee the required adhesion on steel, brass or zinc die cast substrates.

NEW PROCESS

Table I illustrates the composition of a novel alkaline cyanide free copper plating process which contains copper ions, buffering materials, depolarizing agents, proprietary additives and complexing ligands.

The copper sulfate is simply a source of copper ions, while the buffer salts not only maintain consistent pH, but also help to improve solution conductivity and deposit appearance.

The role of the complexor is to form a soluble complex with the cupric ions which then allows the metal to be uniformly deposited on the cathode. The complex is strong enough to prevent copper immersion on steel, brass and zinc based substrates but also unique in that it allows highly efficient electrodeposition.

The anode depolarizer insures excellent anode corrosion at relatively high voltages and helps maintain the desired concentration of copper ions in solution.

The proprietary organic addition agents include wetting agents which reduce surface tension and improve deposit uniformity and also, special compounds to produce semibright to bright deposits over a wide current density range.

Component additions are generally made on an ampere-hour basis and concentrations are controlled by analysis.

Operating Parameters

The operating parameters are summarized in Table II. While the bath can be operated at a pH as low as 6.0, the optimum pH range for this bath is 9.0 - 10.5. Values below 9.0 will make the deposits brighter but may adversely affect adhesion whereas a pH above 10.5 causes high current density dullness and can reduce the limiting current density.

Both temperature and the degree of air agitation affect the appearance of the copper deposit. The effect of temperature is given in Table III. Clearly, temperature plays a critical role in deposit appearance. At very low average current densities, less than 5 ASF, temperatures as low as 100°F produce acceptable deposits; however, to produce overall uniform fine grained deposits at average current densities of 20 ASF or higher, bath temperatures of at least 140°F must be maintained.

Agitation has a dramatic effect on deposit appearance and cathode efficiency. To insure uniform fine grained deposits over a wide current density range, air agitation is required. Lack of agitation produces dull, burned deposits at average current densities of 20 ASF. When proprietary addition agents are used, vigorous agitation will produce brilliant deposits on complex parts at average current densities up to 30 ASF or higher.

Anodes

In order to consistently achieve uniform, fine grained adherent deposits on a commercial level, a unique insoluble/soluble anode system is required. Soluble anodes consist of electrolytic or nonphosphorized copper to insure a constant source of copper ions. The insoluble anodes are constructed of a special proprietary alloy which is electrodeposited on a conductive core. The anodes provide an oxidizing media which helps maintain the integrity of the plating solution. The ratio of insoluble anodes to soluble anodes can vary from 2:1 to 1:2 while the ideal ratio is 1:1. This ratio provides adequate oxidizing conditions while affording sufficient copper anode area to maintain the desired copper ion concentration. Bar anodes are normally used, however, where anode space is limited, wire mesh anodes are recommended to provide the required ratio of insoluble to soluble anodes.

If the insoluble anodes are not used, or are not properly electrified, the plating solution will degrade after several hours of electrolysis causing the deposit to become dull, brittle and poorly adherent.

Cathode Efficiency

As expected, the cathode efficiency varies with current density. Generally, cathode efficiency decreases as average current densities increase (Fig. 1). However, at optimum conditions, 10-30 ASF, cathode efficiency is 95-100%. The excellent efficiency tends to offset the loss of deposition rate characterized by divalent copper electrolysis when compared to monovalent copper systems. Normally, at higher current densities, the efficiency decreases; however, if the copper sulfate is increased to 56.0 g/L (7.5 oz./gal.), the required complexing agent added, and the operating temperature elevated to 71°C (160°F), cathode efficiencies can be maintained above 90% even at cathode current densities as high as 150 ASF.

Throwing Power

Suprisingly, even though the cathode efficiency is high the bath exhibits outstanding throwing power. Table IV gives a comparison of the throwing power of acid, cyanide and noncyanide copper plating solutions, using standard Haring Cell tests. Thus, it is evident that the new process not only surpasses conventional cyanide copper with respect to throwing power but it even exceeds high throw acid sulfate systems.

DEPOSIT PROPERTIES

The copper deposits plated from the new process, under optimum solution concentrations and operating conditions, are fine grained, ductile and adherent to steel, brass and bronze base metals. Metallurgical analysis of the deposit shows a crystalline structure and surface morphology comparable to that produced by copper cyanide plating baths except that the cyanide free deposit is more uniform and compact (Fig. 2). The addition of proprietary additives produce a full bright ductile deposit, which has a laminar structure and appears to exhibit leveling (Fig. 3). However, surface roughness measurements* indicate that the deposit exhibits little or no leveling characteristics. Therefore, the apparent leveling properties, indicated on the photomicrograph, may be due to exceptional grain refinement and superior microthrowing properties.

Ductility

Ductility measurements were determined on test foils using the ASTM experimental bulge tester. Ductility values were obtained from a calibration curve furnished with the instrument. Fig. 4 compares percent elongation of the bright noncyanide copper to bright cyanide copper at various thicknesses. The data clearly indicate that the ductility of the alkaline cyanide free bath is far superior to a conventional cyanide based electrolyte.

Corrosion Resistance

Standard 4" x 6" steel panels were prepared to compare the corrosion resistance of the noncyanide copper deposits with cyanide copper. Following the thin copper layer, 2.5 um (0.1 mils), 12.5 um (0.5 mils) of bright nickel and 0.25 um (0.01 mils) of chromium were deposited using conventional processes. Salt spray test results reveal that the noncyanide copper deposits offer improved corrosion resistance after 72 hours exposure (Fig. 5).

Another group of steel panels were prepared to evaluate the performance of bare copper in a humidity cabinet. One set was plated with 5.0 um (0.2 mils) of the bright alkaline cyanide free copper and another with 5.0 um (0.2 mils) of bright cyanide copper. After 24 hours exposure the cyanide free copper deposit showed only marginal corrosion and no serious tarnishing. The conventional cyanide copper deposit had numerous irridescent corrosion spots and excessive tarnishing (Fig. 6). These tests were made using the cyanide free copper formulation described in Table 1 without proprietary addition agents (the use of said addition agents tend to cause some tarnishing on plated parts exposed to very humid atmospheric conditions.

*British Surfindicator, Model BL 110

COMMERCIAL ADAPTABILITY AND APPLICATION

Commercial experience indicates that this new cyanide free copper process can be successfully used in both rack and barrel applications on ferrous and brass substrates. Existing equipment and process cycles currently used for cyanide and/or nickel plating can be used and no major modifications are required.

With the exception of iron, the alkaline noncyanide copper plating bath offers exceptional tolerance to contaminants which can be easily introduced into the system via drag-in. This is clearly indicated in Table V. However, iron is generally not a serious problem since it forms the insoluble ferric hydroxide which is readily removed by filtration.

The use of specialized addition agents produce brilliant deposits making the bath suitable as an underlayer for decorative nickel-chromium deposits or as a final decorative coating. While it is not presently recommended for plating on aluminum and zinc substrates, laboratory test results indicate that these applications may be possible in the near future.

Waste Treatment

The cyanide free copper process is an alkaline solution containing a highly selective complexing agent, copper metal ions and phosphorous. However, heavy metals can be removed from the effluent by common high pH treatment procedures. The most effective method is to initially add $CaCl_2$ and then raise the pH to 9.5 with NaOH. A flocculating agent is then added to insure proper settling and the solution filtered. Dragout from this process may be mixed with other plant waste streams prior to heavy metal removal if lime is used as the hydroxide source for heavy metal precipitation. Concentrated dumps or spills should be collected and metered to the treatment facility.

In areas where discharge limits are extremely strict, i.e., less than 0.5 ppm Cu, dragout from this process and any bath dumps or spills should be segregated from other plant wastes, treated and then metered into the other treatment plant effluent prior to discharge. Final pH adjustment may be necessary, in this case, of the total effluent stream.

Since the copper concentration of the new process is low and it is readily waste treatable, considerable cost savings are achieved. Waste treatment cost data for the cyanide free copper process and several conventional processes are given in Table VI. It is seen that the chemical cost for treatment is approximately sevenfold less that for cyanide copper.

CONCLUSION

Through the use of novel bath chemistry and a unique proprietary anode system, fine grained, adherent copper deposits can now be obtained from an alkaline cyanide free system. The deposits have excellent physical properties, including extraordinary ductility, as well as outstanding metal

distribution and very good tolerance to common impurities. Waste treatment is simple and economical. The deposits offer superior corrosion and tarnish resistance. Special addition agents can be used to improve deposit appearance from semibright to mirror-like finishes.

Field results indicate that the process is commercially viable in both rack and barrel installations. Laboratory results indicate excellent potential for high speed applications and plating zinc die cast and aluminum substrates.

As a practical alternative to cyanide based copper processes, this novel alkaline cyanide free process does indeed compare favorably with copper cyanide systems but without the problems associated with cyanide.

ACKNOWLEDGEMENTS

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TABLE I

TYPICAL CYANIDE FREE COPPER SOLUTION COMPOSITION

Copper Sulfate Pentahydrate	37.5 g/L (5.0 oz/gal)
Organic Complexing Agent	162.5 g/L (21.7 oz/gal)
Buffer Salts	20.0 g/L (2.7 oz/gal)
Proprietary Anode Depolarizer	0.40 g/L (0.05 oz/gal)
Proprietary Addition Agents*	

*Optional - Added to provide additional brightness to the deposit.

TABLE II

OPERATING PARAMETERS - CYANIDE FREE COPPER BATH

	Optimum	Range
pH (Electrometric)	9.8	9.0 - 10.5
Temperature	60°C (140°F)	52-71°C (125-160°F)
Average Cathode Current Density	2.2 A/dm^2 (20 ASF)	0.5-3.2 A/dm^2 (5-30 ASF)
Average Anode Current Density*	1.0 A/dm^2 (10 ASF)	0.5-2.1 A/dm^2 (5-20 ASF)
Voltage	3.0V	2-4V**
Copper/Proprietary Anode Ratio	1:1	1:2 - 2:1
Agitation	Moderate to Vigorous Air	

* Anode current density based on copper anode area only.

**9.5 V maximum for barrel plating.

TABLE III

EFFECT OF TEMPERATURE ON DEPOSIT APPEARANCE*

TEMPERATURE	DEPOSIT APPEARANCE
120°F	Dark, nonadherent brittle deposit
130°F	Fine grained adherent deposit with HCD burning
140°F	Uniformly fine grained, adherent, ductile deposit
150°F	Uniformly fine grained, adherent, ductile deposit
160°F	Uniformly fine grained, adherent, ductile deposit
180°F	Uniformly fine grained, adherent, ductile deposit

*Other Operating Parameters

Cu^{+2} - 7.5 g/L (1 oz/gal)

pH - 9.8

Current Density - 2.1 A/dm^2 (20 ASF)

Agitation - Air

TABLE IV[8]

THROWING POWER OF COPPER PLATING BATHS

PLATING SYSTEM	THROWING POWER (%)*
Alkaline Noncyanide Copper	95
High Throw Acid Sulfate	87
High Throw Fluoroborate Solder	80
Pyrophosphate Copper	62
High Throw Acid Fluoroborate	58
Cyanide Copper	50
Conventional Fluoroborate Solder	18
Conventional Acid Fluoroborate	14
Conventional Acid Copper	14

* Tests made using Haring Cell measurements with a ratio of 11:1 as in Ref. 8, from which other data are presented for comparison.

TABLE V

EFFECT OF COMMON PLATING CONTAMINANTS ON NONCYANIDE COPPER DEPOSITS

CONTAMINANT	CONCENTRATION	DEPOSIT APPEARANCE
Ni^{+2}	4.7 g/L	No effect
Zn^{+2}	6.4 g/L	Slightly brass colored
Cr^{+6}	0.24 g/L	No effect
Sn^{+4}	0.02 g/L	No effect
NH_4^+	2.18 g/L	Poor Adhesion, HCD Burning
Pb^{+4}	0.04 g/L	HCD Burning/Poor Adhesion
Cl^-	1.00 g/L	No effect*
Fe^{+3}	0.32 g/L	HCD Burning
Electrocleaners	6.5% by vol.	No effect

*Cl^- concentrations exceeding 0.50 g/L can cause the insoluble anodes to corrode.

TABLE VI

WASTE TREATMENT COSTS: ALKALINE CYANIDE FREE COPPER VS. CONVENTIONAL BATHS

PLATING BATH	CHEMICALS REQUIRED (LBS.) TO TREAT 1 GAL.		COST/GAL. ($)	SLUDGE* (Ft^3/Gal.)
Alkaline Noncyanide	0.690	H_2SO_4		
	0.803	CaO	0.172	0.022
	0.208	$Al_2(SO_4)_3$		
	0.004	A-23 Floc		
Bright Acid Copper	1.01	CaO		
	0.004	A-23 Floc	0.103	0.013
Woods Nickel Strike	0.085	H_2SO_4		
	0.650	CaO	0.092	0.013
	0.004	A-23 Floc		
Bright Cyanide Copper	2.000	NaOCl		
	0.890	H_2SO_4		
	0.699	CaO	1.47	0.019
	0.004	A-23 Floc		

Chemical Costs ($/Lb.):		
	CaO	0.10
	NaOH	0.22
	66°Be H_2SO_4	0.06
	NaOCl (15%)	0.66
	A-23 Floc	5.25
	$Al_2(SO_4)_3$	0.13

*Air dried sludge at a density of 80 lb./$ft.^3$

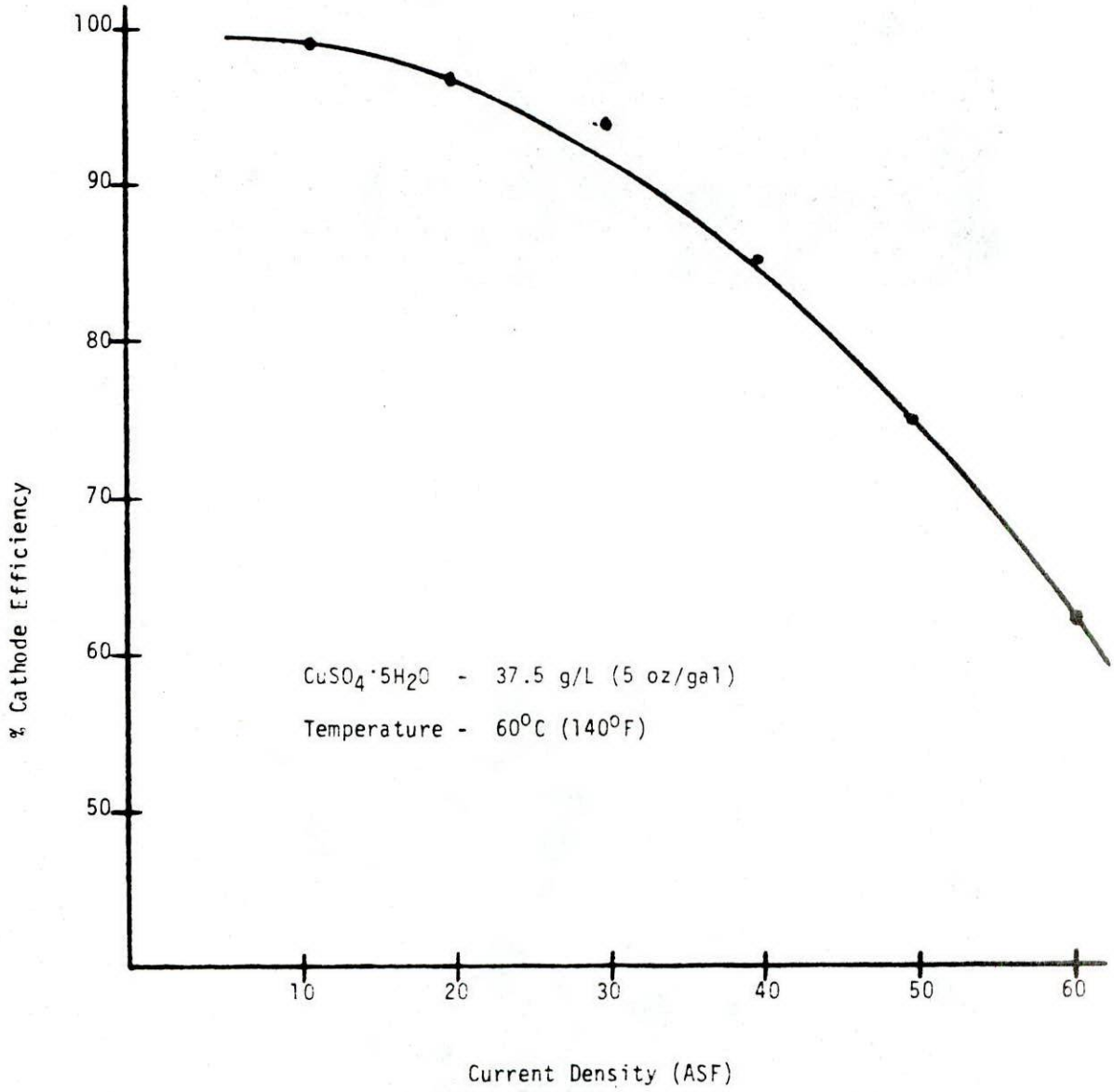

Fig. 1 The cathode efficiency of the cyanide-free copper system as a function of of current density.

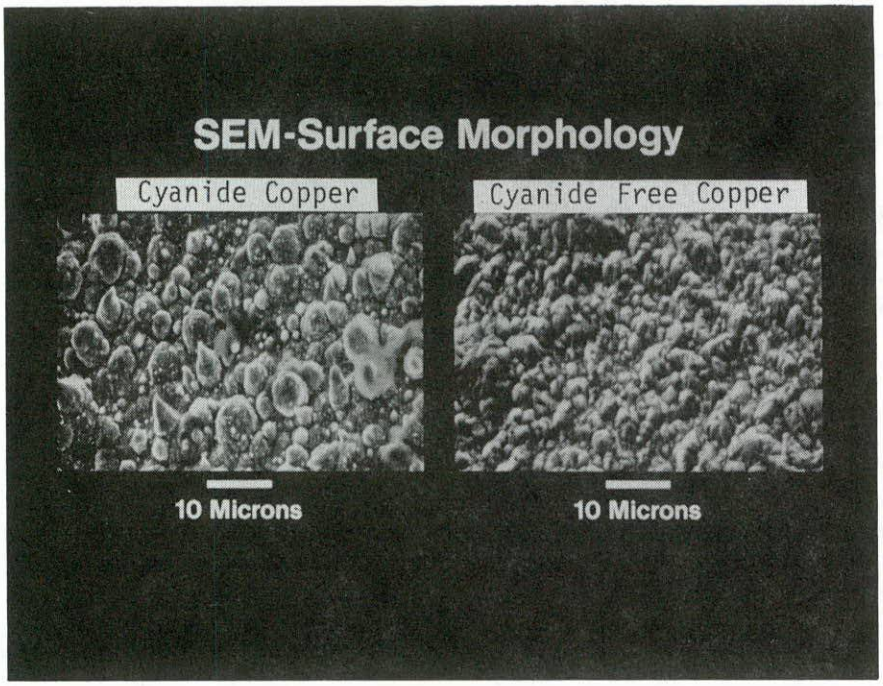

Fig. 2 - SEM photomicrograph comparing surface morphology of conventional cyanide copper and new cyanide free copper deposits.

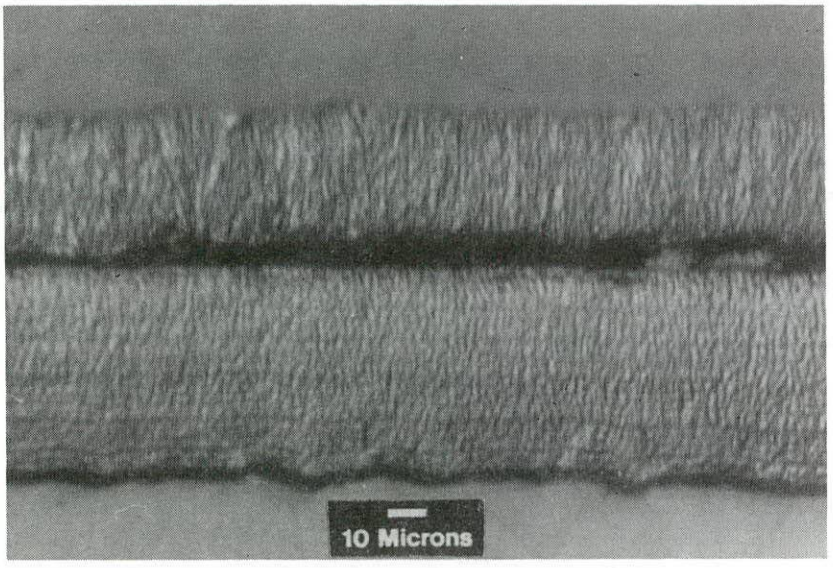

Fig. 3 - Photomicrograph comparing columnar structure of bright cyanide copper (top) and laminar structure of bright cyanide free copper (bottom).

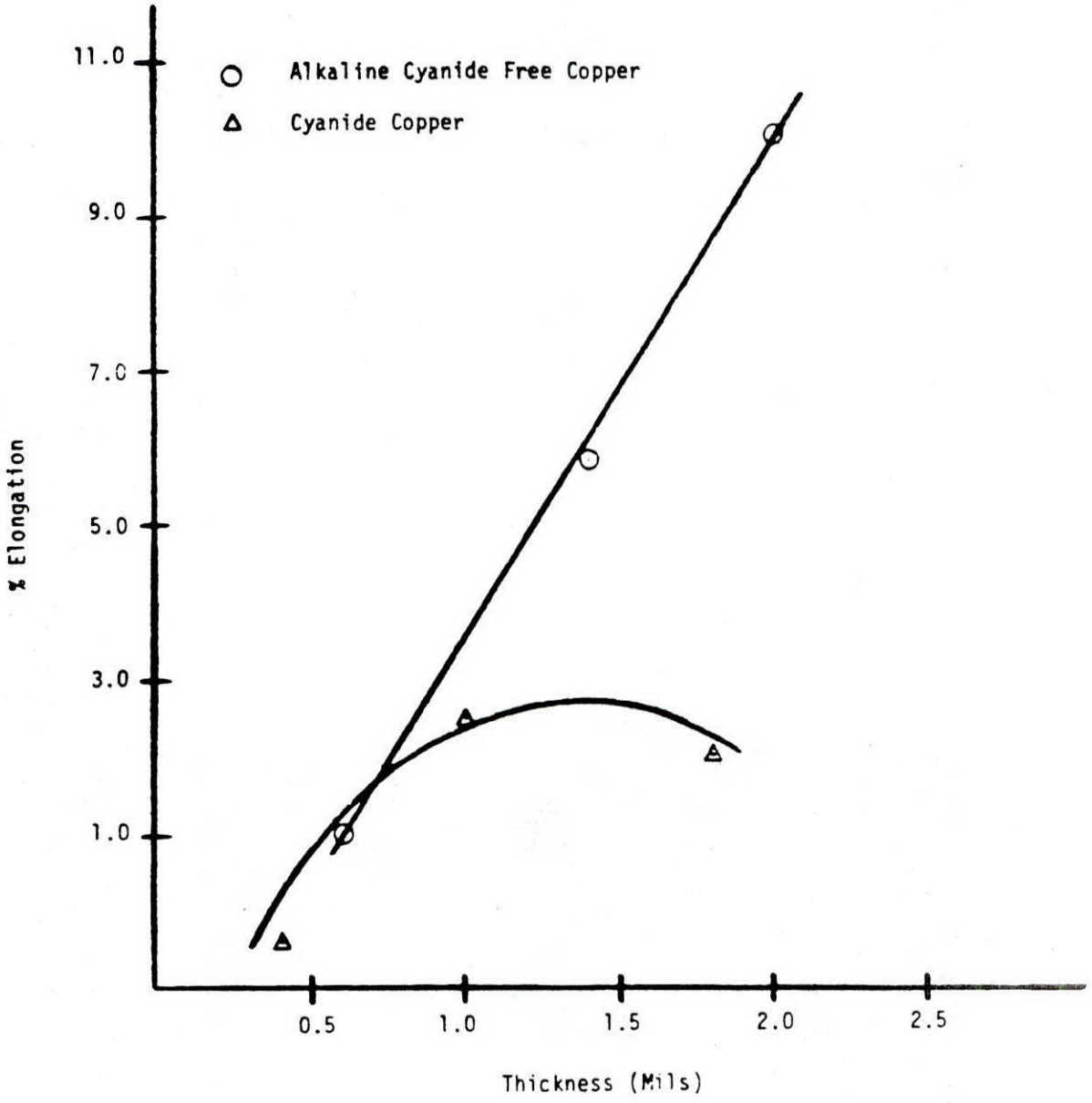

Fig. 4 Bulge Test results showing expressed as percent elongation vs. thickness.

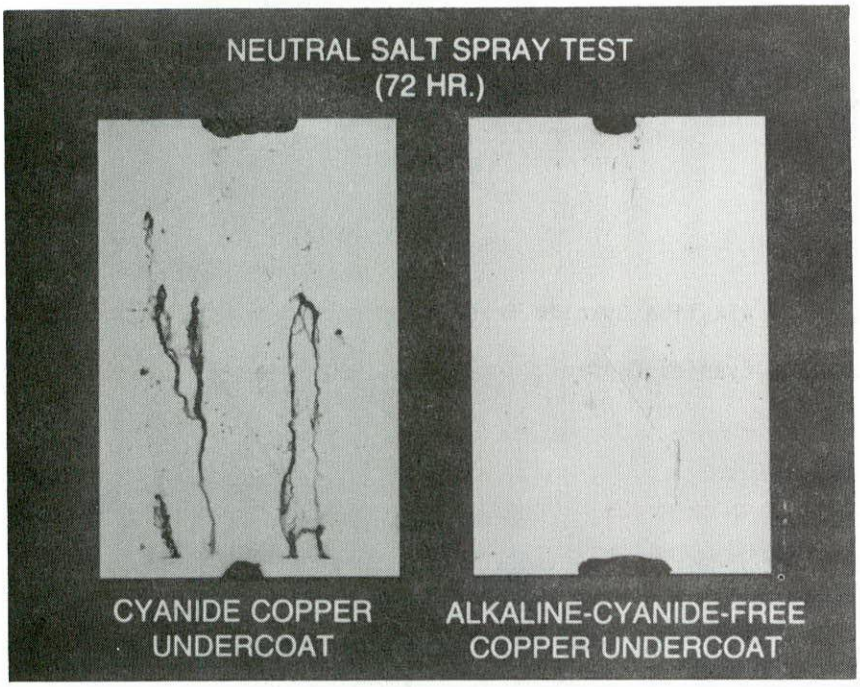

Fig. 5 Steel panels plated with 2.5 um (0.1 mils) of cyanide copper or alkaline cyanide free copper, 12.5 um (0.5 mils) of bright nickel and 0.25 um (0.01 mils) of conventional chromium and exposed in a neutral salt spray test cabinet.

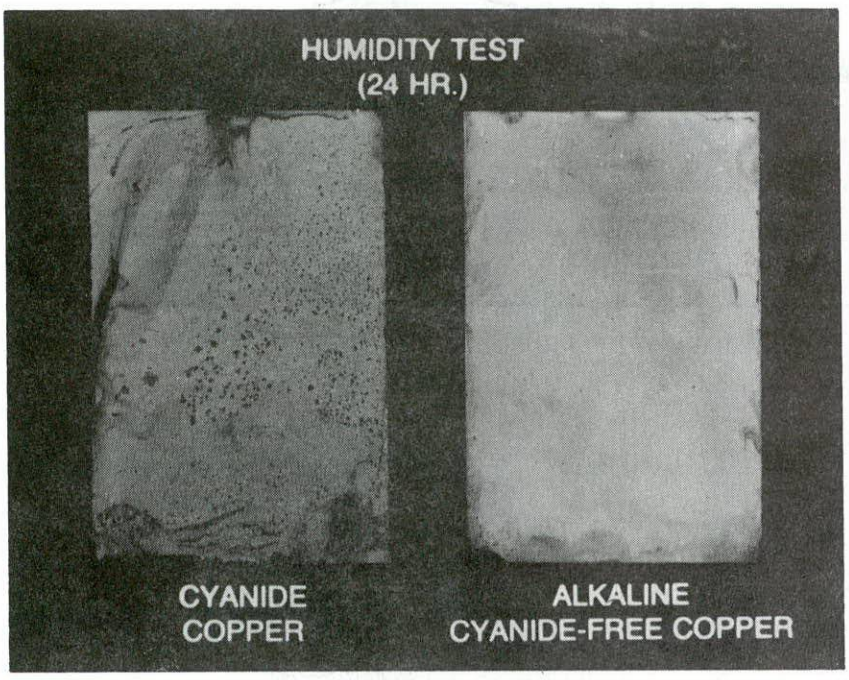

Fig. 6 Steel panels plated with 5.0 um (0.1 mils) of bright cyanide copper or bright alkaline cyanide free copper and exposed in a humidity test cabinet.

REFERENCES

1. H. N. Black, "Introductory Course In College Physics", New York, McMillian Co., 1937, p. 429.

United States Patents:

2. R. Pinner, "Copper & Copper - Alloy Plating", Copper Development Association, London, pp.19.74

3. W. B. Hollengshead, #427,513 (1890)

4. Ibid, #557,816 (1896)

5. Unpublished Research by R. Tremmel, 1970

6. W. Blum and G. B. Hogaboom, "Principles of Electroplating and Electroforming", Third Edition, New York, McGraw-Hill Book Co, 1949, p. 294.

7. E. Feno, W. Maloney, U.S. Patent #3,775,268 (1973).

8. N. J. Spiliates, "Acid Copper Plating", Guidebook & Directory, Metal Finishing, 1977, p. 206.

9. H. Creutz, et al, #4,110,176.

10. C. Strucyk and Carlson, "Copper Plating from Fluoroborate Solutions", Monthly Ren. Am. Electroplaters Soc., Vol. 33, 923 (1946)

11. J. E. Strucyk, #2,437,865 (1948).

12. E. Kern, #946,903 (1910).

13. I. L. Greenspan, "Electrodeposition of Bright Copper", Trans. Electrochem Soc. Vol 78, 303, (1940)

14. I. L. Greenspan, U.S. Patent #2,195,457 (1940).

15. X. Kowalski #3,706,634 (1972) & #3,706,635 (1972)

16. R. B. Kessler & F. I. Nobel, #3,928,147 (1975)

D-4

Decorative I
Session D

On The Role Of Additives In A Trivalent Chromium Plating Bath

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ON THE ROLE OF ADDITIVES IN A TRIVALENT CHROMIUM PLATING BATH

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ABSTRACT

By means of constant current and transient cyclic voltammetry, the electrochemical properties of a Pt cathode in aqueous $Cr_2(SO_4)_3$ solutions was studied as a function of the presence of various addition agents in solution. Guided by known successful bath compositions, $(NH_4)_2SO_4$, H_3BO_3 and Na_2HPO_3 were considered. When all three addition agents were present at a pH between 2 and 3, metallic Cr deposits were detected. It was found that boric acid is added chiefly as a buffer to control the pH of the bath in the range from 2 to 3. Ammonium sulfate may increase the conductivity of the bath but the NH_4^+ ion acts as a complexing agent (possibly as an inner sphere complex by replacing the complexed waters). The Na_2HPO_3 also complexes with the chromium probably in the outer sphere. Such a complex is dischargeable at the Pt cathode since a deposit of Cr is detected.

INTRODUCTION

There are a number of disadvantages in plating Cr from hexavalent chromium baths among which are the facts that Cr VI compounds are very poisonous, chromic acid solutions are highly corrosive, and the current efficiency for metal deposition is disappointingly low. If Cr could be deposited acceptably from baths other than those based on hexavalent Cr, the Cr VI baths would fall into disuse.

The advantages of plating Cr from trivalent Cr baths are attractive since such solutions are nonpoisonous, are much less corrosive and should give high metal deposition efficiencies because one is plating from a Cr-bearing cation instead of a Cr-containing anion. However, it is not possible to deposit Cr from a simple Cr III salt solution because of the formation of the very stable $[Cr(H_2O)_6]^{+3}$ complex ion.

Possible solutions to this problem rest in either the use of non-aqueous systems or the employment of destabilizing additives to an aqueous system. Success in the use of a non-aqueous system has been considerably limited because organic solvents and electrolytes are much more expensive with much lower conductivities and solubilities than water-based baths. Considerable success in decorative plating applications has been announced by Harshaw and Udilyte in this country and Canning Materials Lmtd. in England with aqueous trivalent Cr baths to which a number of additives have been added.

It is the purpose of this report to describe the initial efforts to determine the role of each additive in the trivalent bath in the Cr deposition mechanism by the use of steady-state and transient polarization studies.

EXPERIMENTAL

The test electrodes were made by melting small beads (1.3 mm in diam.) at the end of the Pt (99.99% pure) wires in an oxygen torch. Platinum was chosen as the basis metal because its electrochemical behavior is well known. These Pt test electrodes were cleaned by heating white hot in a burning H_2 jet followed by quenching in concentrated HNO_3. This procedure was repeated until the hydrogen flame was colorless when the bead was heated. Afterwards, the bead was

potted in molten polyethylene so that only a hemisphere was exposed and Teflon spaghetti was slipped over the lead wire.

Three of these prepared test electrodes for check runs were mounted in the test compartment of the dual-compartmented, Teflon cell described earlier (1). The two compartments are connected through a glass frit with a Pt gauze counter electrode in the test side and a saturated calomel reference electrode (SCE) in the reference side. Once the cell was filled with the solution of interest, the cell tops were sealed with molten polyethylene and the solution was saturated with purified N_2 gas flowing at a rate of about 200 cm^3/min for 30 min.

When the solution had become saturated with N_2, a steady state cyclic voltammogram was obtained as a function of the sweep rate and the potential limits of the recorded scan. Finally, the steady-state, galvanostatic polarization curve was determined.

All solutions were made with triply distilled water and the temperature of all experiments was ambient (25 ± 1°C). Potentials as quoted with respect the SCE unless stated otherwise.

RESULTS AND DISCUSSION

In the first set of runs, the polarization curves were obtained in N_2-saturated 0.1 M $Cr_2(SO_4)_3$. It required up to 20 cycles of polarization to arrive at a steady-state cyclic voltammogram as noted in Fig. 1. As in the case of Pt in 2M H_2SO_4(2) it has been concluded that this prepolarization required before the steady state is reached is due to the charging of Pt metal with dissolved oxygen at the high anodic potentials (above 800 mV).

The cyclic voltammogram obtained is a function of the sweep rate (17 mV/s to 100 mV/s) is recorded in Fig. 2. The hydrogen adsorption peaks (I'_H and II'_H) and desorption peaks (I_H, III_H, IV_H, and V_H), are the same as those described for Pt in H_2SO_4(2). Oxygen-precursor (oxygen or hydroxyl radicals), adsorption peaks, (I_O and II_O) are also present but the peak above 1000 mV and designated as III_O may be the interaction of the $[Cr(H_2O)_6]^{+3}$ ion with the oxidized Pt surface. Oxygen evolution takes place in peak IV_O. On the cathodic-going trace,

reduction of the oxidized Pt surface appears in I_0'. Since the peak heights are a linear function of the sweep rate, the electrochemical processes responsible for the peaks are surface reactions and do not involve diffusion of species to or from solution. Except for the region above 1000 mV, the voltammogram for Pt in $Cr_2(SO_4)_3$ is very similar to that in H_2SO_4.

The steady-state polarization curve obtained on the Pt electrode charged with dissolved oxygen is shown in Fig. 3. In this case the rest potential was recorded as 600 mV (845 mV vs Pt/H_2) which is close to the value of 880 mV vs. Pt/H_2 quoted (1) for the Pt/Pt-O couple in N_2-stirred 2N H_2SO_4. Therefore, the first plateau, A, in Fig. 3 is due to the reduction of the Pt-O layer. The steady state occurs when the rate of reduction of Pt-O by the demanded current density equals the rate of diffusion of dissolved oxygen in the bulk Pt to the surface. Above 10^{-6} A/cm^2 this process can no longer support the demanded current and the system shifts to more cathodic potentials where H_2-evolution can take place in plateau B.

A line with a slope of 0.03 which is the Tafel slope value for a Pt/H_2 electrode in acid solution is drawn for the sake of comparison. The slope of region B is larger, possibly, because this is H_2 evolution on a Pt-O alloy electrode and because the pH is high.

At high current densities (above 5 x 10^{-3} A/cm^2) the polarization curve shifts to plateau C. In this region the current is consumed not only in H_2 evolution, but likely in the reduction of Cr III to Cr II since a deposit of Cr metal was not detected on the Pt surface.

Enough H_2SO_4 was added to the solution in the cell to bring the pH down to about 2.0. The cyclic voltammogram was virtually the same as in Fig. 2. Next, the cell was opened and a weighed amount of boric acid was added to the 0.1M $Cr_2(SO_4)_3$ solution to make it 0.13M in H_3BO_3. As noted in Fig. 4, one observes virtually no change in the cyclic voltammogram from that shown in Fig. 2. Such behavior may support the conclusion (3) that the main role played by boric acid is that of a buffer.

Again, the cell was opened and a weighed amount of $(NH_4)_2\ SO_4$ was added to the solution to make it also 0.3M in $(NH_4)_2\ SO_4$. In this case, the cyclic voltammogram was changed as noted in Fig. 5. The hydrogen adsorption peaks on the cathodic-going curve have disappeared and the hydrogen desorption peaks on the anodic-going sweep are replaced by two equivalent peaks shifted to less noble values of potential. Also the complex peak III_0 has vanished, and the oxygen reduction peak I_0' has been shifted to less noble values. This behavior suggests that $(NH_4)_2SO_4$ plays a much more important role than as an addition agent to merely increase the conductivity of the solution (4). Apparently, the ammonium ion enters into a complex with the trivalent ion. In fact, the two peaks in the hydrogen region may result from the desorption of ammonium ions from weakly and strongly binding adsorption sites on the Pt surface.

The final addition agent was added to the solution as a weighed amount of Na_2HPO_3 to make it 0.1M in Na_2HPO_3. In this case a very large change in the voltammogram takes place as noted in Fig. 6. The hydrogen region is greatly reduced as well as peak I_0' and there is considerable structure in the so-called double layer region (between 0 and 500 mV). A very predominant peak appears at about 900 mV and the oxygen evolution region is greatly reduced.

To aid in determining the relationships between the peaks in Fig. 6, a family of voltammograms was generated by decreasing the upper limit of the trace in 50 mV steps as recorded in Fig. 7. As the upper limit was reduced from 1400 to 1150 mV, peak I_0' disappears but the oxidation peak II_0' remains until the potential of peak V_0 (900 mV) is passed.

Another family of voltammograms is obtained by increasing the lower limit of the potential scan in 50 mV steps (Fig. 8). With changes of the lower limit from -100 mV to 300 mV, the height of peak V_0 rapidly decreases. The height of the oxygen evolution peak (IV_0) progressively decreases as the lower limit is increased from 300 to 600 mV. From this data in Fig. 7 and 8, peak IV_0 is related to I_0' and V_0 to the region designated as III_H'. It is possible now to offer a interpretation of these findings.

In the region III'_H , there is strong adsorption of PO_3^{-3} ions which severely limits the amount of hydrogen that can be adsorbed. On the anodie-going sweep, the sparse amount of adsorbed hydrogen is desorbed in I_H. At higher positive potentials on the anodic-going trace, the large peak V_O appears which is associated with the desorption of the PO_3^{-3} ions. According to Fig. 8, as the lower limit is increased from -300 to 300 mV, V_O decreases in height. Such behavior indicates that as the lower limit becomes more positive less PO_3^{-3} ion is adsorbed. Once the PO_3^{-3} is desorbed, the Pt can be oxidized and O_2 evolution takes place in IV_O. Phosphite adsorption delays oxygen adsorption to potentials greater than 1100 mV.

At 1400 mV the sweep is reversed and the adsorbed oxygen is desorbed in the much diminished peak I'_O due to the smaller amount of oxygen adsorbed in Fig. 8 as compared to the phosphite-free solutions (Fig. 4 or 5). This is evident from Fig. 7 where I'_O disappears when the potential of the upper limit is not permitted to enter the oxidizing region above 1100 mV. Once the Pt surface is free of adsorbed oxygen, adsorbed PO_3^{-3} ions can be desorbed producing the oxidation peak II'_O. Even though the trace is cathodic-going, the potential is still in a region where PO_3^{-3} ions may be desorbed (the potential range of II'_O).

When the Pt electrode was scanned to -700 mV the current shifted rapidly to the high current density region designated IV'_H in Fig. 9 where evolution of hydrogen obscures the dependence of sweep rate due to the varying impedance of bubble formation. In the IV'_H region, the current is consumed in H_2 evolution and the reduction of Cr III to metallic Cr. A bead polarized at -700 mV for 5 min in the $Cr_2(SO_4)_3$ solution of the composition of Fig. 6 was removed from the cell, washed and dried. Analysis with AES (Auger Electron Spectroscopy) detected a thin layer (20 nm thick) of Cr containing oxygen (~40 a/o), phosphorous (~3 a/o) and some sulfur (~5 a/o).

The steady-state polarization curve obtained at constant current on Pt in the solution of Fig. 6 is plotted in Fig. 10. Because of the presence of adsorbed PO_3^{-3} ions, the reduction of the Pt-O partial layer produces a non-descript polarization curve up to about 10^{-6} A/cm^2 (A) where the system enters a Tafel region over three decades long (B). A line with a slope of 0.12 is drawn to show that the data are consistent with such a Tafel slope. In this Tafel

region the current is consumed in H_2 evolution and Cr III reduction to metallic Cr. At very high current densities (C), the curve shifts to higher potentials due to concentration polarization effects caused by inadequate agitation of the electrolyte.

When Cr III salts are dissolved in water, a complex with water is formed, $[Cr(H_2O)_6]^{+3}$, which is so strong that metallic Cr cannot be discharged even at very high cathodic current densities. The current is consumed in H_2 evolution. When NH_4^+ ions and PO_3^{-3} ions are added to the Cr III solution the H_2O molecules are replaced with NH_3 and PO_3^{-3} ions to form a complex. After this chromium-ammonium-phosphite complex is adsorbed on the Pt surface, metallic Cr can be discharged. That phosphite enters into the dischargeable complex is supported by detection of phosphorous in the Cr deposit.

It is concluded that it is possible to deposit thin layers of Cr from an aqueous trivalent chromium solution if the proper addition agents are present in solution. The presence of the NH_4^+ and PO_3^{-3} ions modify the $[Cr(H_2O)_6]^{+3}$ complex ion, probably by substituting the water molecules, to form a dischargeable chromium complex.

REFERENCES

1. J. P. Hoare, J. Electrochem. Soc., 109, 858 (1962).

2. J. P. Hoare, Electrochem. Acta., 27, 1751 (1982).

3. J. Gyllenspetz and S. Renton, U.S. Pat. 3,954,574, May 4, 1976; J. J. B. Ward and I.R.A. Christie, Trans. Inst. Metal Finish., 49, 148 (1971).

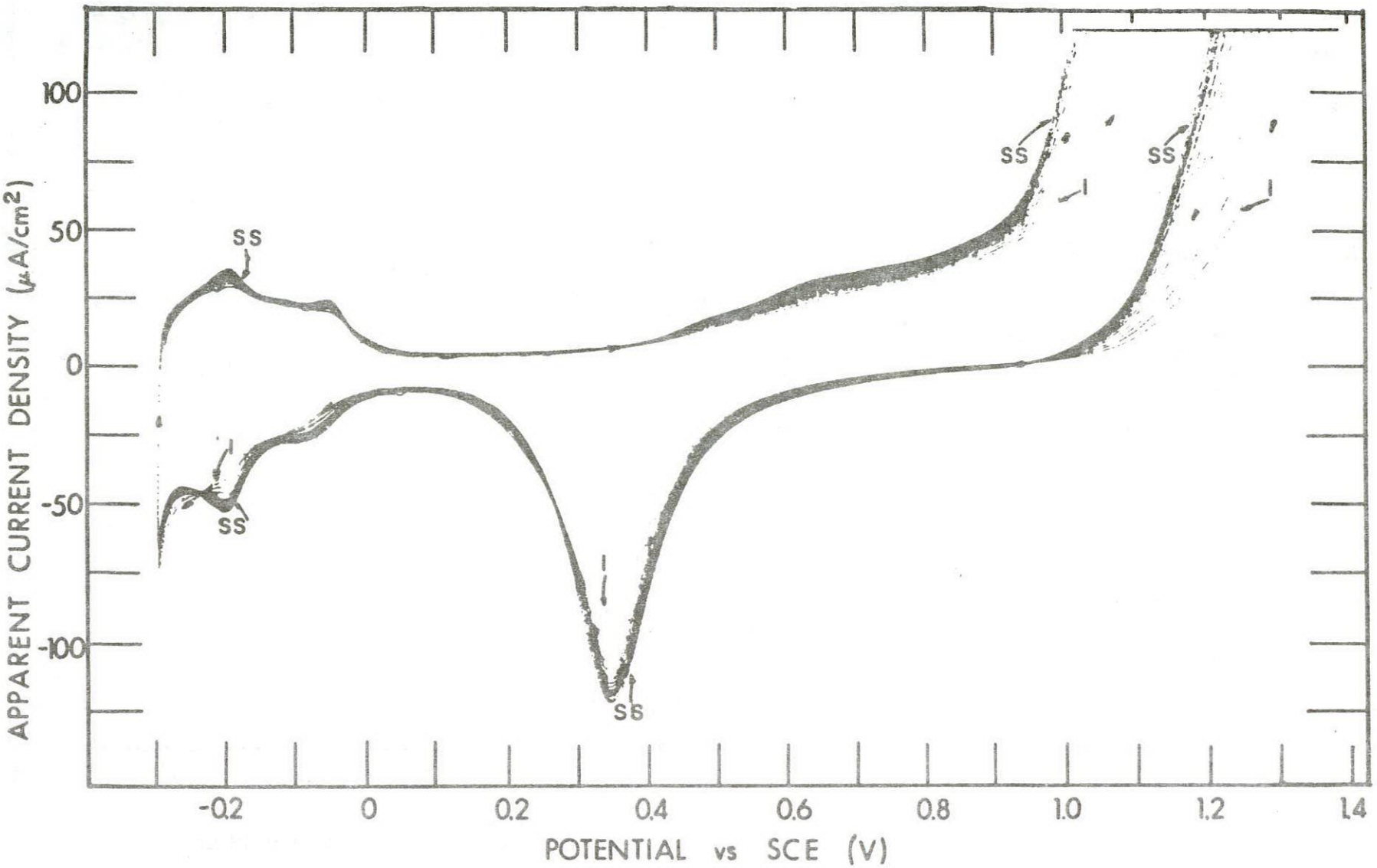

Fig. 1 The change in the cyclic voltammogram obtained at a sweep rate of 100 mV/s between -300 and 1400 mV on a Pt microelectrode in N_2-stirred 0.1M $Cr_2(SO_4)_3$ solution from the initial trace (1) to the steady state (SS); arrows indicate direction of polarization.

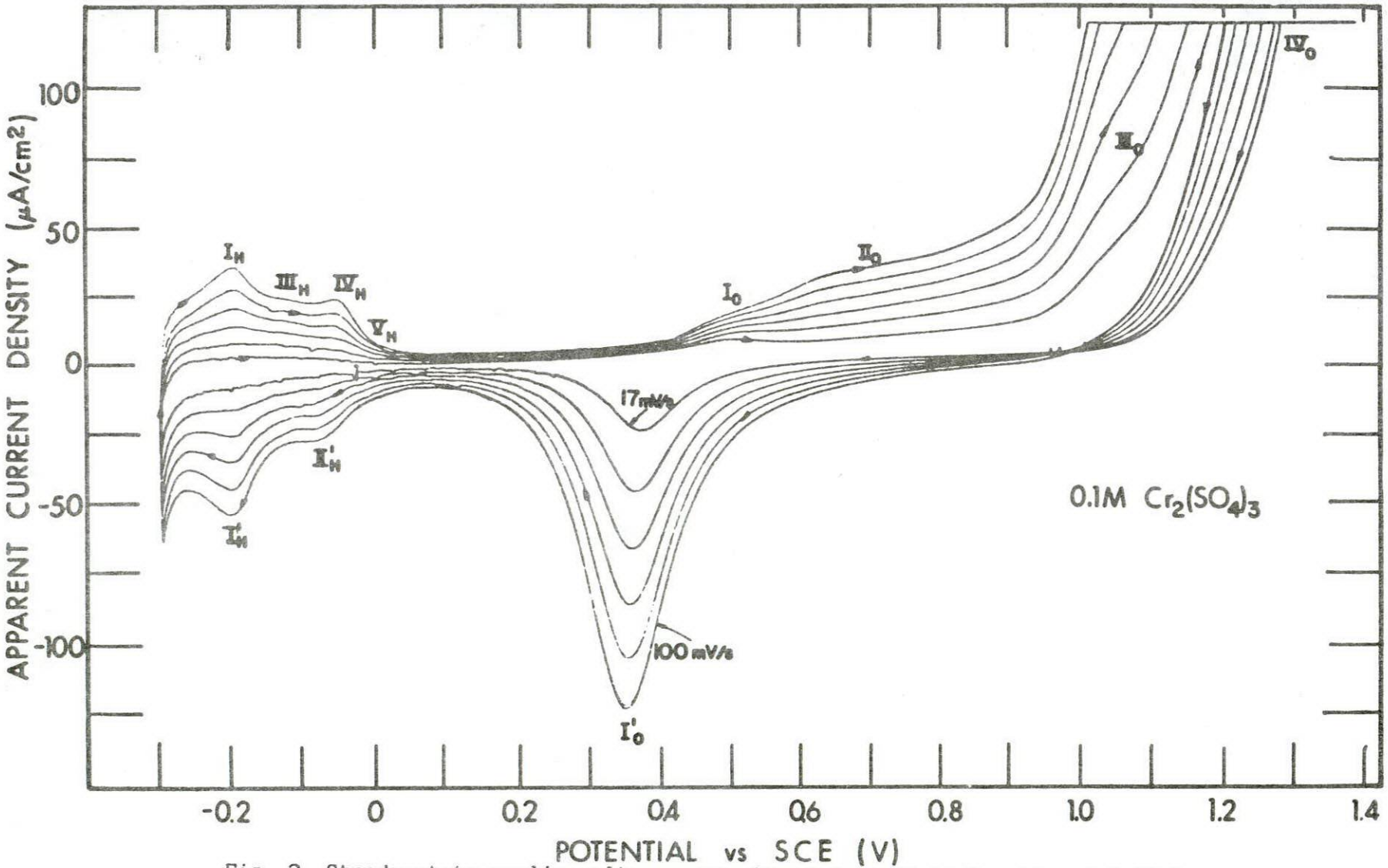

Fig. 2 Steady-state cyclic voltammogram obtained on Pt in N_2-stirred 0.1M $Cr_2(SO_4)_3$ from -300 to 1400 mV as a function of the sweep rate (17,33,50, 67,83,100 mV/s); major peaks are identified by Roman numerals with subscript H in hydrogen region and O in oxygen region; a prime is used to distinguish peak on cathodic-going trace from that on the anodic-going trace.

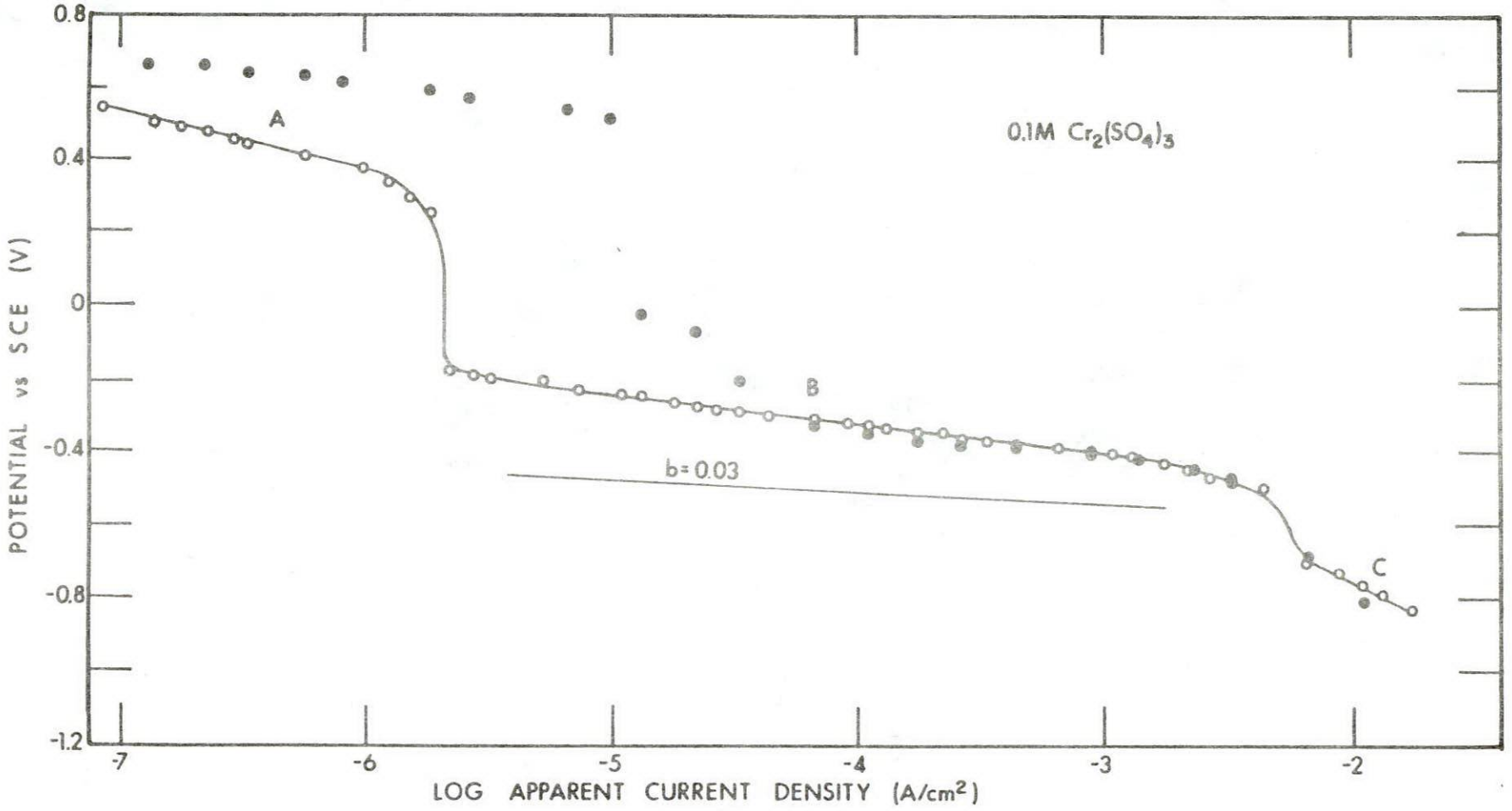

Fig. 3 Galvanostatic, steady-state polarization curve obtained on Pt in N_2-stirred 0.1M $Cr_2(SO_4)_3$; open symbols for increasing and filled for decreasing current density.

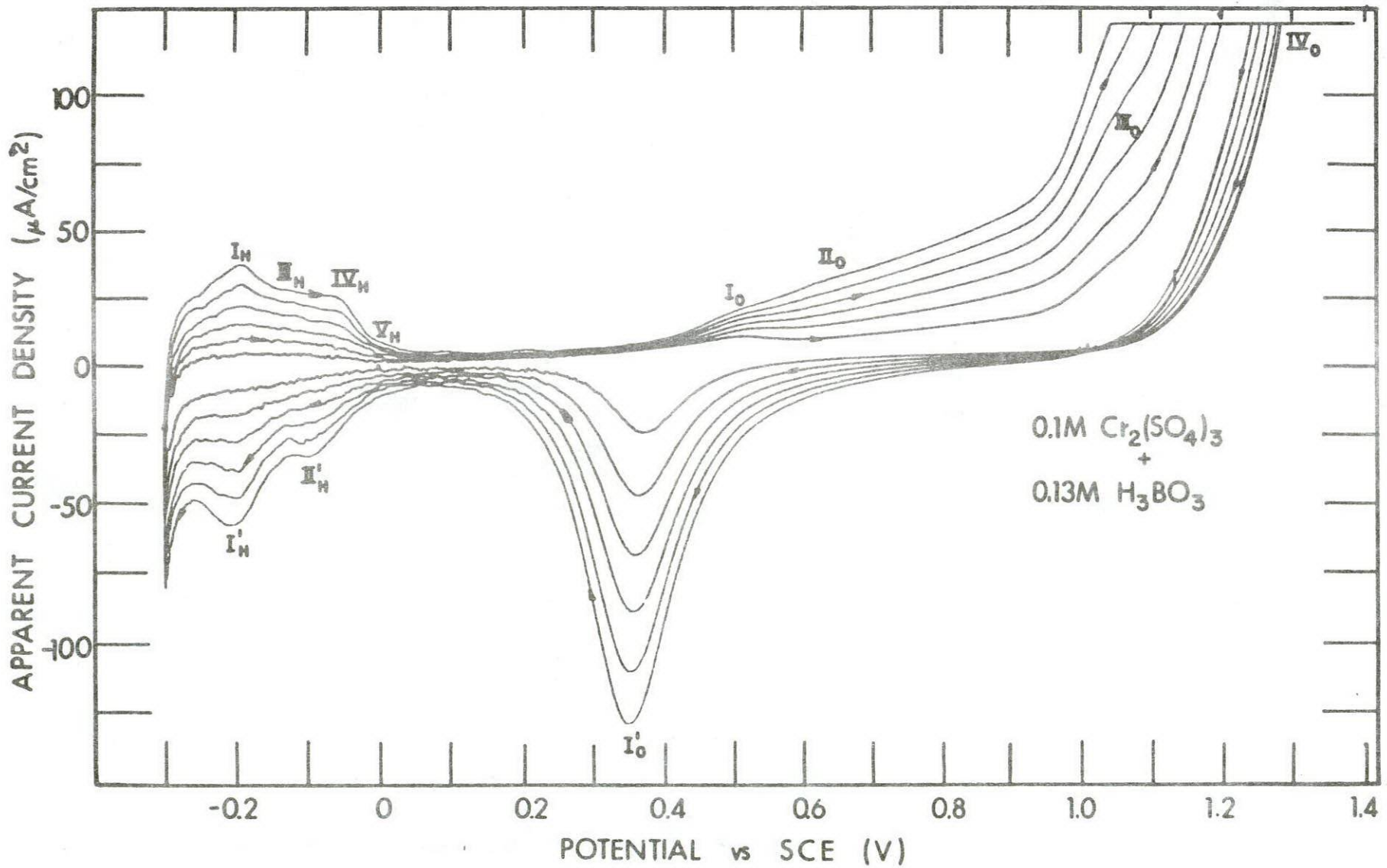

Fig. 4 Steady-state cyclic voltammogram obtained on Pt in the same solution as in Fig. 2 to which boric acid is; added (0.13M in H_3BO_3); notation is the same as in Fig. 2.

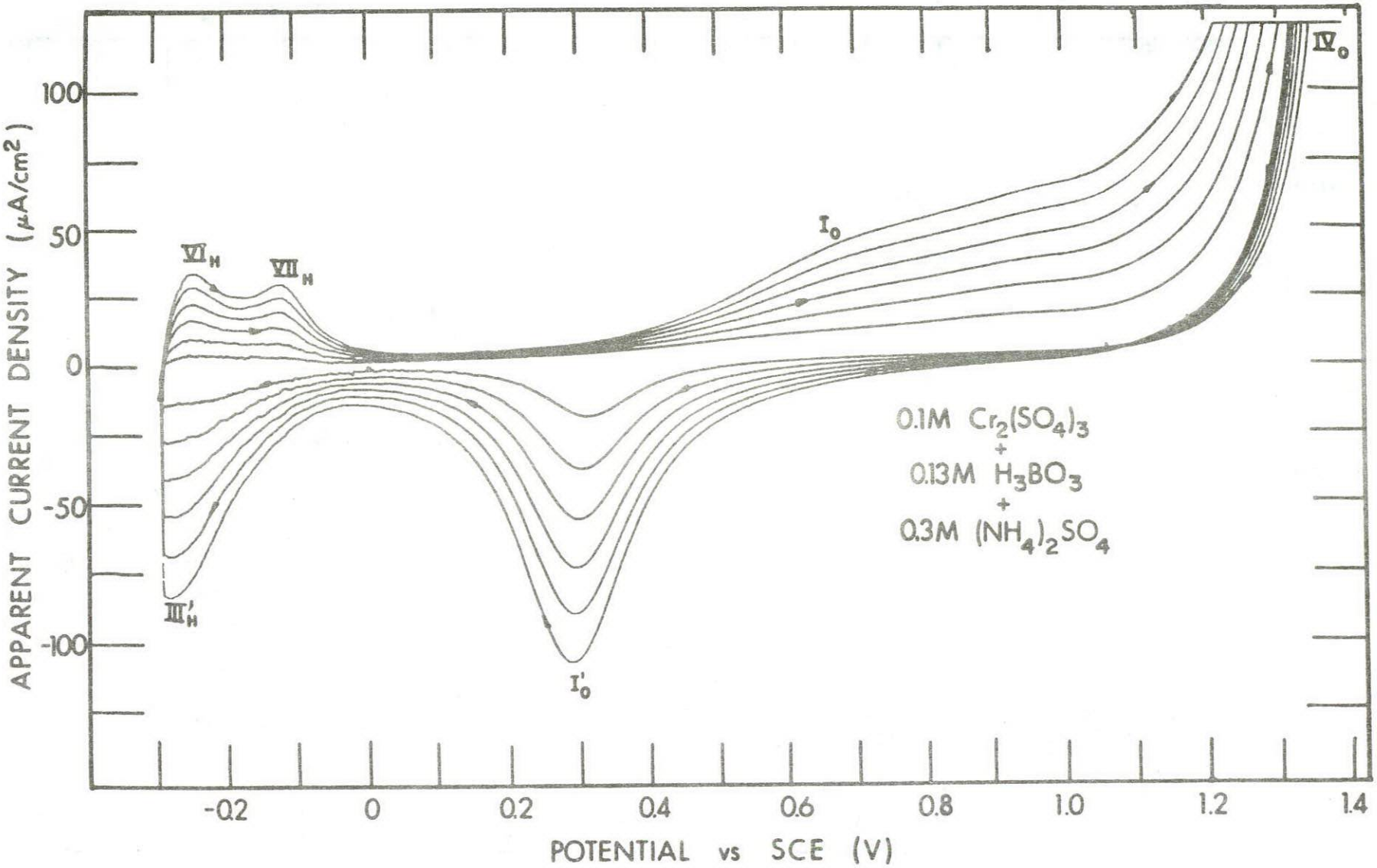

Fig. 5 Steady-state cyclic voltammogram obtained on Pt in the same solution as in Fig. 4 to which $(NH_4)_2SO_4$ was added (0.3M $(NH_4)_2SO_4$); notation same as in Fig. 2.

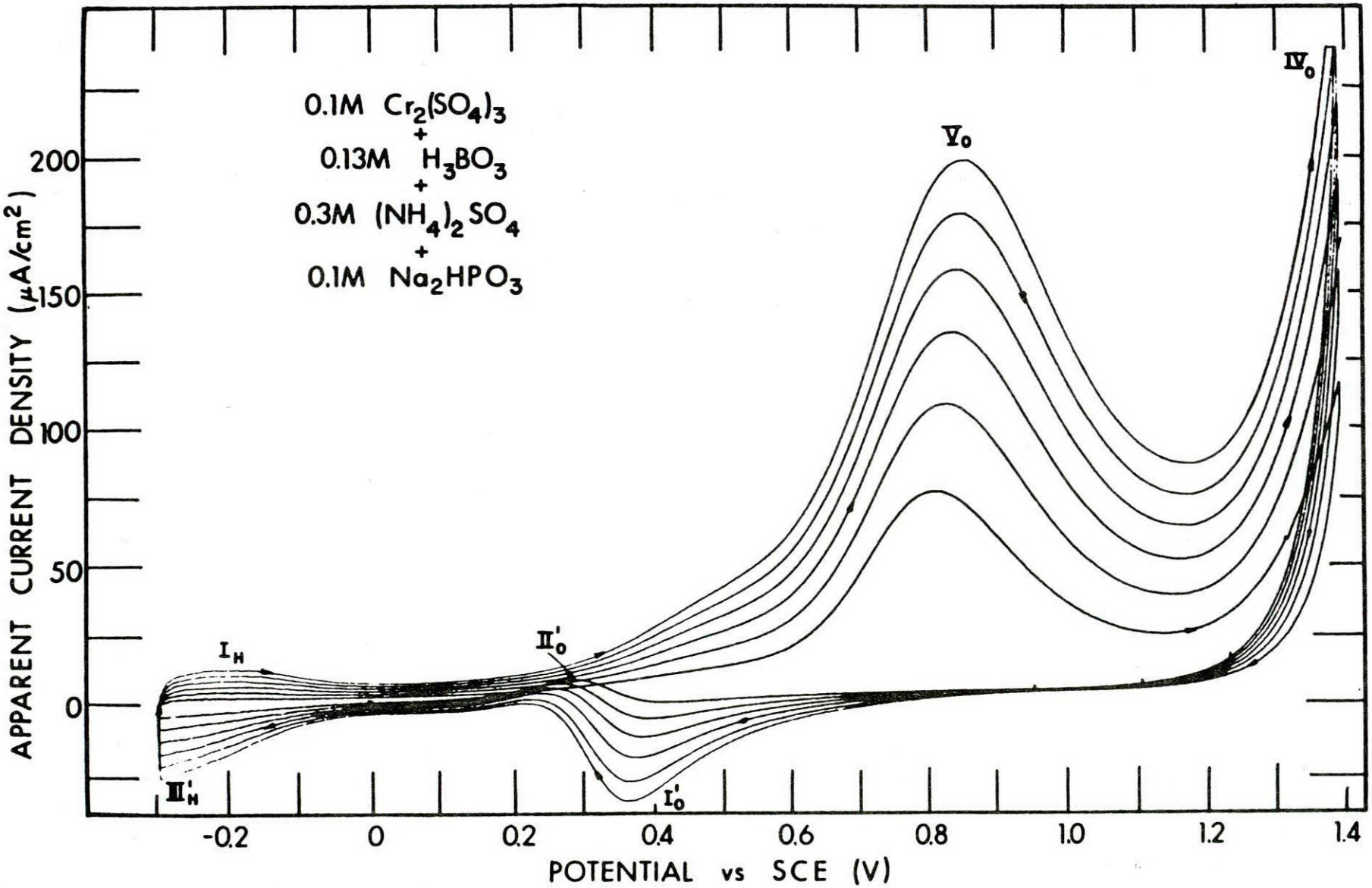

Fig. 6 Steady-state cyclic voltammogram obtained on Pt in the same solution as in Fig. 5 to which Na_2HPO_3 was added (0.1M Na_2HPO_3); notation same as in Fig. 2.

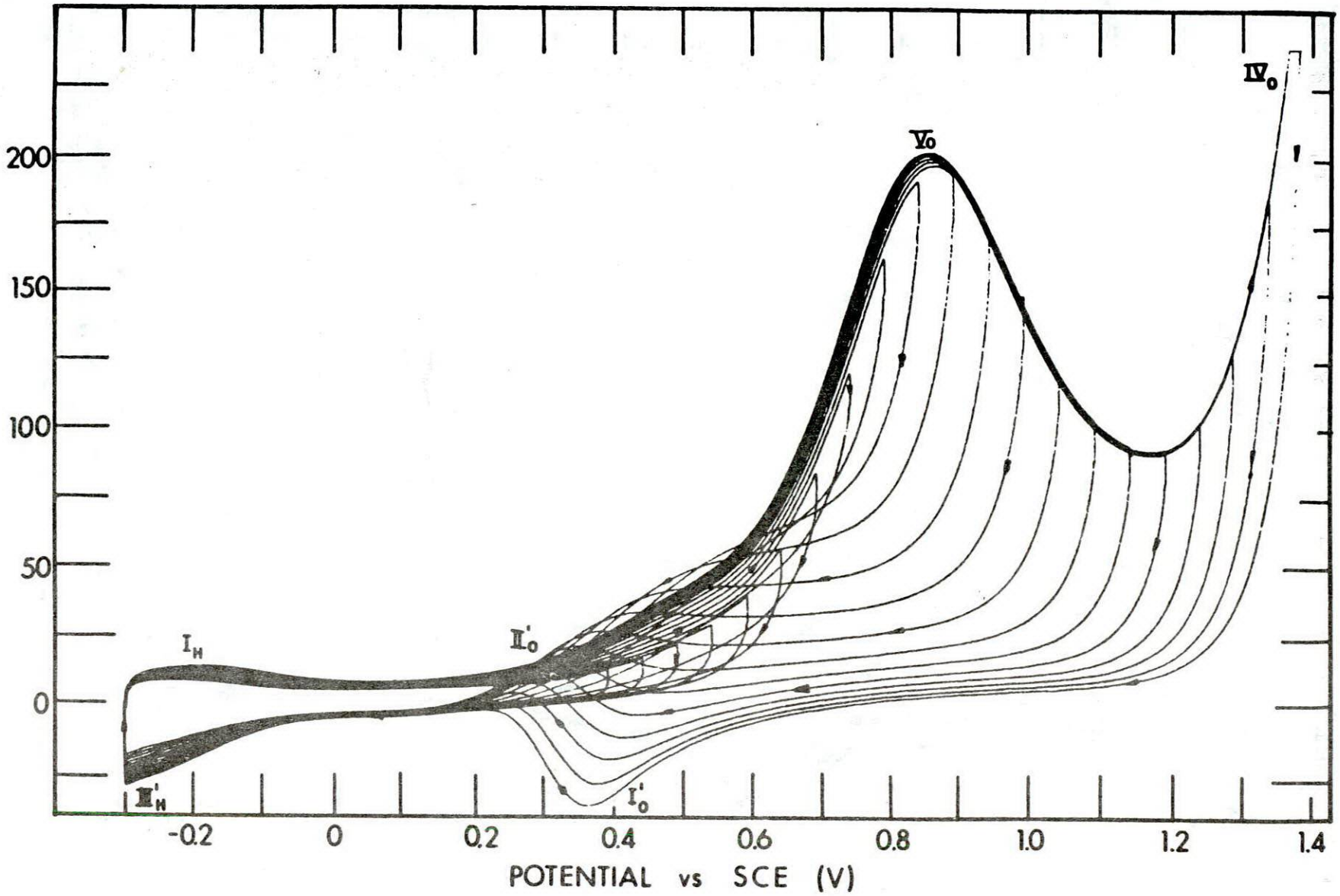

Fig. 7 Family of cyclic voltammograms obtained on Pt in the same solution as in Fig. 6, generated by decreasing the potential of the upper limit in 50 mV step; notation same as in Fig. 2.

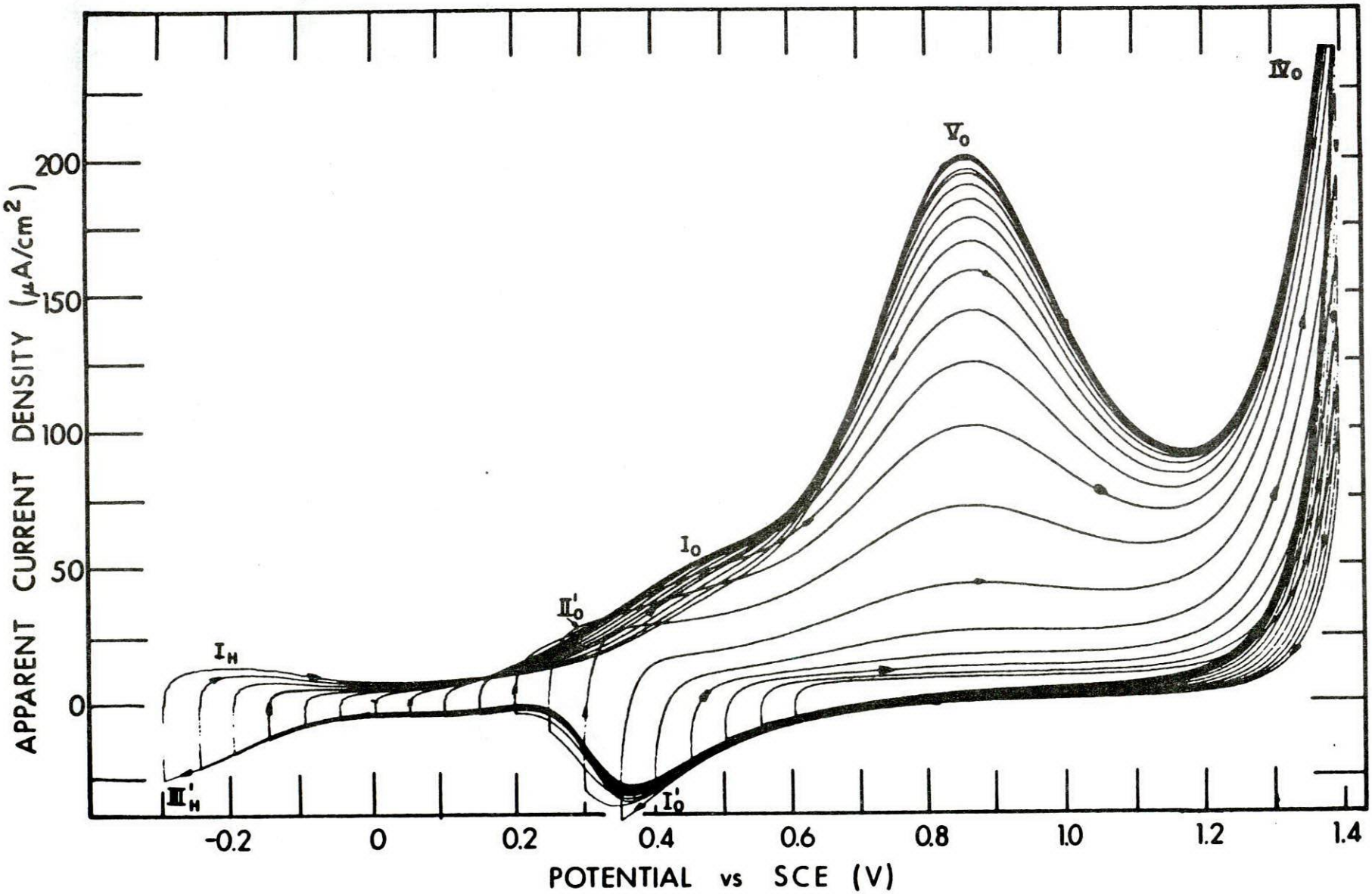

Fig. 8 Family of cyclic voltammograms obtained on Pt in the same solution as in Fig. 6, generated by increasing the potential of the lower limit in 50 mV steps; notation same as in Fig. 2.

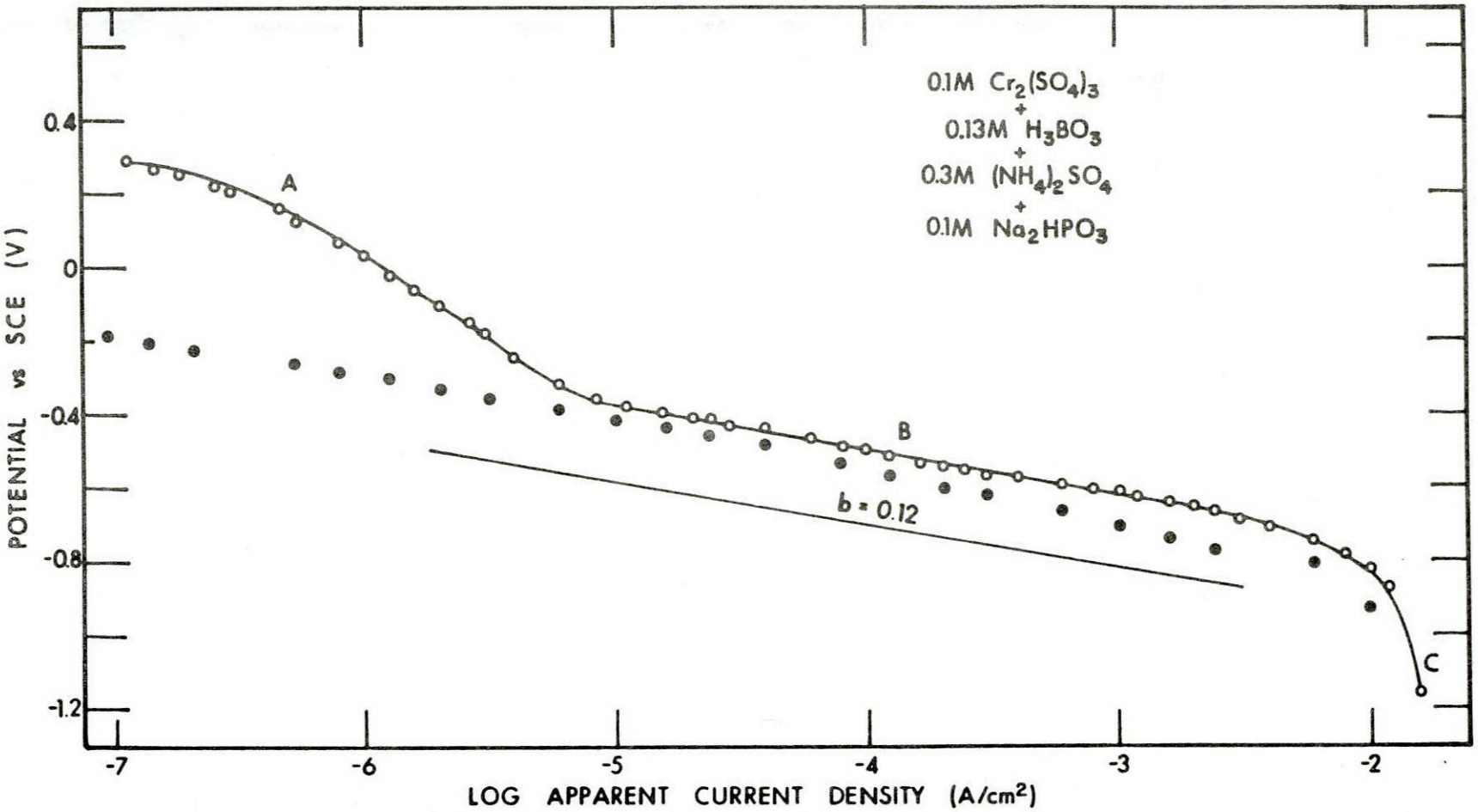

Fig. 9 Steady-state cyclic voltammograms obtained on Pt in the same solution as in Fig. 6 as a function of the sweep rate (17 to 100 mV/s) from -700 to 1100 mV; notation same as in Fig. 2.

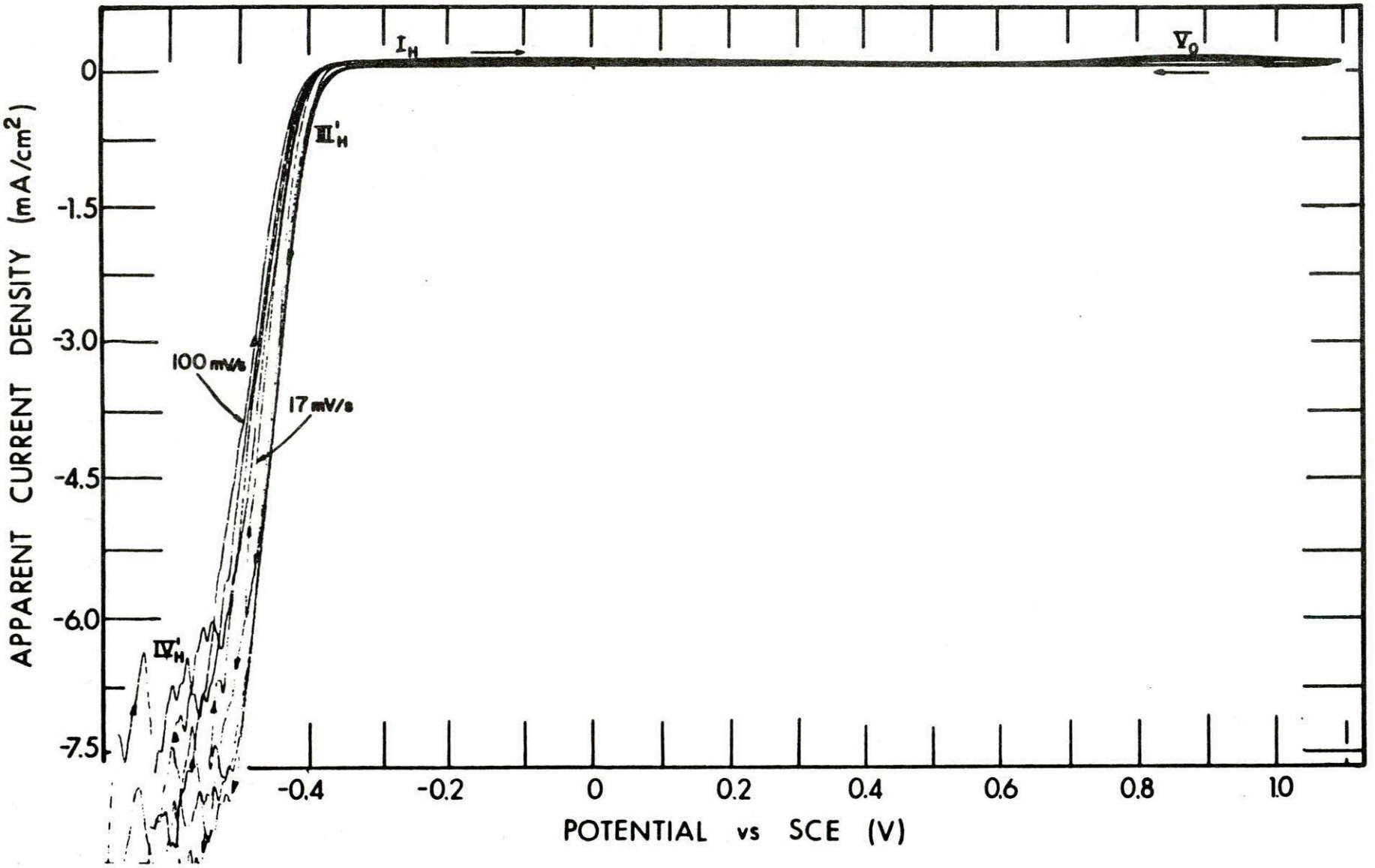

Fig. 10 Galvanostatic, steady-state polarization curve obtained on Pt in same solution as in Fig. 6; open symbols for increasing and filled for decreasing current density.

D-5

Decorative I
Session D

Decorative Trivalent Chromium Plating

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Chemistry of Trivalent Chromium

With all of the obvious advantages for plating chromium from the trivalent state, one must ask why it has not been done sooner. Part of the answer is simply because the chemistry of chromium, in general, is not easily understood. To begin with, chromium can exist in almost any positive valence state. The metal (valence = 0), trivalent (+3) and hexavalent (+6) are the most common valence states. To further complicate matters, trivalent chromium cations form complex cations in aqueous solutions. In aqueous solutions, almost any electron pair donor can form complexes with trivalent chromium causing literally thousands of compounds to exist. The most common aqueous complexes of trivalent chromium are octahedral, which require six ligands (associated ions or molecules) to bond with the trivalent chromium ion to form a complex cation, see Figure 1. The X's shown in the diagram may all be the same donating ion or all different; they may be neutral materials such as water; they may be inorganic anions such as halogens, sulfate or hydroxyl; or they may be organic anions such as carboxylates or many other donors.

To make it still more interesting, the equilibria between the various chromium complexes in aqueous solutions is often very slow and frequently dependent on parameters such as concentration. pH and temperature. For example, a solution of chromium trichloride ($CrCl_3$) in water will produce a violet colored solution when freshly made, probably due to complexing by six water molecules. As the solution ages, it may turn green in color, probably indicating that some of the coordinating water molecules have been replaced by chloride ions. Anywhere from one to six chloride ions can be associated with a single trivalent chromium ion in the complex. Depending on the pH of the solution, hydroxyl ions may also be coordinating with the trivalent chromium in addition to the chloride and water molecules. From this relatively simple example, it can be seen that a solution of chromium trichloride and water is not a simple easily understood chemical entity.

History

The balance of the answer to the original question lies in the difficulties early investigators ran into when trying to formulate suitable plating baths. Bunsen, in 1854, is credited with the first deposition of chromium, albeit from a trivalent chromium electrolyte. In 1856, the success of Geuther using a chromic acid without the need for Bunsen's double cell, probably resulted in directing most of the subsequent research toward the use of chromic acid. In 1933, Kaper[1] published a paper on the important variables involved in the deposition of chromium from trivalent electrolytes. As a result of his paper, research and development on the use of trivalent electrolytes significantly increased and resulted in many papers and patents on the subject. Unfortunately, most of the electrolytes that were developed were unsuitable for decorative chromium plating. Some of the disadvantages were:

1. The bath depended on a single chromium complex which was not stable.
2. The time required for complexing the trivalent chromium led to baths that depleted the complex by electrolysis faster than new chromium complex could be formed.
3. Noxious halogen gasses were often evolved from the anode.
4. Hexavalent chromium produced by anodic oxidation led to the cessation of plating. To overcome this, diaphragms were used to separate the anode and cathode.

During the period from 1950 to 1975, research on trivalent chromium electrolytes was stepped up considerably. Early in this period, Japanese investigators developed baths using urea. These baths had poor covering power as well as relatively low limiting current density and the current efficiency increased rapidly with increasing current density resulting in inferior metal distribution compared to hexavalent chromium.

Two other electrolytes developed during this period also deserve mention. One was based on the use of carboxylic acids as the complexing agent.[2,3,4] These baths also had the disadvantage of being unable to cope with hexavalent chromium generated at the anode, covering power was limited and unpredictable, deposit color was unacceptable and the bath required re-establishment of the chromium complex after a relatively short period of plating.

The other noteworthy solution developed during this period was the solvent bath based on the use of dimethyl formamide.[5] This bath also had its disadvantages such as poor coverage, poor conductivity, unacceptable color and bright nickel deposits required activation in order to insure satisfactory adhesion of the chromium to the nickel. In the mid-1970's, research in the United Kingdom resulted in a trivalent chromium electrolyte which was commerically introduced in England in 1975 and is the basis for this discussion. This electrolyte has been found to be stable, can be operated continuously, has acceptable color, can operate in most processing sequences used for hexavalent chromium, does not require anode compartments and operates without the evolution of noxious gasses at the anode. The important aspects of this trivalent chromium solution are as follows:

Trivalent Chromium Electrolyte

The nominal composition of this trivalent chomium plating bath is shown in Table I. The Additive provides the chromium and conducting salts necessary. Among other things, the additive contains the sulfate ion, chloride ion and borate ion. The similarity between the trivalent chromium electrolyte and a conventional nickel plating solution can readily be seen and, indeed, there are many similarities between trivalent chromium plating and nickel plating which will readily be noted in subsequent discussion. The Stabilizer provides the very mild complexing chemical to form the proper complex of chromium in situ. The Regulator is instrumental in providing good metal distribution over complex surfaces. The SA serves to assist the Stabilizer to maintain chromium solubility especially at the higher end of the operating pH. It will be noted that the total chromium content of the solution is only 20 g/L compared with 125 g/L in a chromic acid based bath.

Table II shows the material necessary to maintain the trivalent chromium plating solution. The means by which these materials are lost from the plating bath is also indicated and the technique for maintaining their concentration is also shown. The proper maintenance of the solution is quite simple. Some materials are lost by drag-out and some materials are lost by electrolysis. Once a drag-out rate is established for a certain installation, it is a simple matter to replace those items lost by drag-out, on the basis of time, and to replace those items lost by electrolysis on the basis of the total current passed through the solution during the same period of time. Additions of all materials

must be frequent enough to allow all of the materials sufficient time to complex with the chromium, usually about every eight hours of operation. Purifier is used to precipitate metallic impurities (copper, iron, nickel, zinc) and the amount is determined by the use of test paper. The amount of Purifier used will, of course, be dependent on many factors and will vary from installation to installation.

The normal operating conditions are shown in Table III. The pH of the solution is maintained by the addition of hydrochloric acid or ammonium hydroxide. The solution is usually operated in the range 2.7-3.5 pH. The lower pH values will tend to reduce covering power but also increase the rate of deposition. Higher pH values increase covering power but reduce the rate of deposition. The temperature of the solution should be maintained at approximately 23°C (70°F). The working temperature range can be between 15-30°C (60-85°F). The lower temperatures will tend to increase covering power but there is some risk of crystallizing the Additive material which will indirectly affect solution conductivity. The higher temperatures will tend to reduce covering power and also produce slightly darker deposits. Cathode current densities of approximately 1000 amps/m^2 (90 amp/ft^2)are usually used. Anode current densities of approximately 550 amps/m^2 (50 amps/ft^2) are required for conductivity and to ensure life of the anode material. The anodes are a special graphite. Mild air agitation of the solution is required to assist the Regulator material and provide good metal distribution over complex surfaces.

The equipment requirements for this trivalent chromium electrolyte are shown in Table IV. Only rubber or synthetic lined tanks may be used. Lead linings cannot be used due to attack of the lead by the trivalent chromium solution. Hexavalent chromium tanks using suitable linings must be thoroughly leached in order to remove all traces of lead salts which are present in the lining. Some type of cooling, either refrigeration or cold water, will be required in order to remove the wattage passing through the solution during operation and to maintain the solution at approximately 23°C (70°F). Heating may be required in wintertime in order to maintain the solution above 15°C (60°F). The trivalent chromium electrolyte is not as conductive as hexavalent chromium electrolytes and usually about 20% greater voltage is required above what is necessary for hexavalent chromium plating. The process uses special graphite anodes

which hang from titanium anode hangers. The anode has an indefinite life under normal operating conditions. Since the anodes do not need to be replaced there can be a considerable cost savings to the user compared to the periodic replacement of anodes for hexavalent chromium solutions. The anodes and solution chemicals interact in a fashion to prevent the liberation of noxious gasses from the solution. The only gasses evolved from the anode are nitrogen and carbon dioxide.

Advantages of Trivalent Chromium

There are numerous advantages to the trivalent chromium plating process in addition to the very important obvious advantage of complete removal of toxic and hazardous chromic acid from the plating bath. These advantages are best demonstrated by a comparative discussion of the two processes.

Plating Speed

From Faraday's Law, twice as much chromium should be deposited from trivalent chromium electrolytes as from hexavalent chromium electrolytes at the same current and time. However, hexavalent chromium baths usually operate at 1620 amps/m^2 (150 amps/ft^2) with an average cathode efficiency of 15% compared to trivalent chromium electrolytes operating at 1080 amps/m^2 (100 amps/ft^2) and an average 10% cathode effiency. The net effect of this comparison slightly favors greater deposition of trivalent chromium. However, in practice, the cathode efficiency of trivalent chromium decreases with increased current density. The comparison between the two baths is shown in Fig. 2 where increasing current density in hexavalent chromium results in increased thickness, however, increased current density in trivalent chromium results in minimum increase in thickness. Table V shows the plating rate for some of the more commonly used current densitites for both baths and clearly shows the decreased plating rate for the trivalent chromium plating solution at higher current densities. The net result of the decreased cathode efficiency with increased current density in the trivalent chromium plating solution is to produce fairly uniform thicknesses of chromium over complex surfaces.

Burning

Burning of the high current density areas on complex shaped parts is nearly impossible using the trivalent chromium process. This feature completely eliminates rejects due to chromium "burn". In addition, difficult to cover shapes may use a high current density "strike", to improve low current density coverage, without fear of burning high current density areas.

Coverage

The ability to cover the entire surface of complex shaped parts is remarkably better with trivalent chromium compared to hexavalent chromium. Chromium will deposit around holes, slots and recesses that were formerly considered impossible to cover with hexavalent chromium.

Racking

Because of the improved current density characteristics of the trivalent chromium electrolyte, racking of parts can often be considered in a new light. Heretofore, hexavalent chromium has usually been considered the weakest link in the plating operation often requiring precise location of parts and/or the use of auxiliary anodes in order to obtain a satisfactory chromium deposit. The features of trivalent chromium plating often result in the use of more parts per rack leading to improved production efficiencies. Table VI summarizes the racking requirements for trivalent vs. hexavalent chromium baths.

Deposit Structure

The new trivalent chromium plating solution satisfies a long-standing need of the plating industry. It produces a microporous chromium in normal chromium plating times at normal chromium plating thicknesses. The microporous chromium becomes microcracked when the chromium is plated above 0.5 µm thick (20 µin). Corrosion testing has shown that the trivalent chromium deposit behaves in a similar fashion as hexavalent microdiscontinuous chromium deposits. Table VII summarize the difference in methods used to obtain microdiscontinuous chromium deposits.

Anodes

Hexavalent chromium plating baths require the use of lead or preferably lead alloy anodes. The anode slowly erodes during operation requiring regular replacement. In addition,

it is necessary to have a lead peroxide film on the surface of the anode in order to oxidize some trivalent chromium which is formed during operation. With trivalent chromium plating solution, a special graphite anode is used which, under the operating conditions specified, have an indefinite life. No break-in or film formation is necessary.

Waste Treatment

Hexavalent chromium solutions require a two-stage treatment for the effluent, first, reduction of hexavalent chromium to trivalent chromium using suitable reducing agents and, secondly, precipitation by raising the pH with alkali. Hexavalent chromium baths contain from 75-200 g/L (10-26.7 oz/gal) of chromium as the metal. The amount of reducing agent and alkali required for the two-stage treatment is proportional to the concentration of hexavalent chromium in the original plating bath. With trivalent chromium elrolytes, only a single stage precipitation treatment is necessary which can be accomplished by raising the pH to approximately 9. The trivalent chromium electrolyte uses only 20 g/L (2.7 oz/gal) of chromium so that only minimal amounts of alkali are required to accomplish precipitation. Fig. 3 summarizes the chemicals required to treat trivalent and hexavalent baths as well as the comparative quantities of by-products produced when using sodium metabisulfite as the reducing agent and lime for neutralizing.

Impurities

Hexavalent chromium plating solutions are quite tolerant to the common heavy metals and contamination results in decreased solution conductivity and/or decreased plating range. On the other hand, these common heavy metals cannot be removed easily from the hexavalent chromium electrolyte. In addition, hexavalent chromium electrolytes have low tolerance to the drag-in of sulfate and chloride. Conversely, trivalent chromium electrolytes possess low tolerance to the common heavy metals. The effects of the impurities are to produce deposits with black streaks and/or reduce chromium coverage. As with nickel plating, however, the heavy metals may be removed by low current density electrolysis (dummy) or by precipitation with the use of the Purifier. The trivalent chromium electrolyte is tolerant to the drag-in of sulfate and chloride since the solution already contains these materials.

Current Interruptions

Hexavalent chromium plating baths will usually not tolerate current interruption frequently producing "whitewash" or dullness when this does occur. Current interruption has no effect on the trivalent chromium deposit. A rack may be partially plated, lifted from the solution for visual examination, and replaced on the cathode rail for additional plating with no deleterious effects. This eliminates many chromium rejects which were due to interruption of the current during chromium deposition.

Conclusions

Production experiences since 1975 at installations around the world have proven the many advantages of trivalent chromium. The process is easily operated and controlled in a variety of decorative situations. The unique characteristics of the trivalent process offers many advantages to the decorative chromium plater.

References

1. C. Kasper — "The Deposition of Chromium from Solutions of Chromic and Chromous Salts". U. S. Bureau of Standards Journal on Research 11, 515 (1933)

2. A. Deyrup — U. S. Patent 3,006,823
U. S. Patent 3,069,333

3. T. Berzins — U. S. Patent 3,021,267

4. J. E. Bride — U. S. Patents 3,706, 636-643

5. J. B. Ward and N. R. Bharucha (Brit. Non-Ferrous Metals Res. Assoc.) Brit Patent 1,144,913 (applied 10/9/67).

Table I

SOLUTION COMPOSITION

TC Additive	400 g/L	(53.3 oz/gal)
TC Stabilizer	80 ml/L	(8%/vol)
TC Regulator	1 ml/L	(0.1%/vol)
TC-SA	12 ml/L	(1.2 %/vol)

Table II

SOLUTION MAINTENANCE

Material	CONSUMED BY	CONTROLLED BY
TC Additive	Drag-Out	Specific Gravity
TC Chrome Adjuster	Electrolysis	Amp-Hours, Analysis
TC Stabilizer	Electrolysis	Amp-Hours, Analysis
TC Regulator	Electrolysis	Amp-Hours
TC Purifier	Metal Impurities	Test Paper

Table III

OPTIMUM OPERATING CONDITIONS

pH	3.2
Temperature	23°C (72°F)
Current Density	
Cathode	1080 A/m^2 (100 ASF)
Anode	540 A/m^2 (50 ASF)
Anodes	Special Graphite
Agitation	Mild Air Agitation
Specific Gravity	1.21

Table IV

EQUIPMENT REQUIREMENTS

Plating Tank - Rubber or synthetic lined (No Lead Linings)

Anodes - Special Graphite

Special Titanium Anode Hangers

Air Agitation- Mild uniform air agitation beneath cathode

Cooling/Heating-20-30°C (68-77°F). Refrigeration for high volume or continous production. Heating may be needed in winter.

Ampere Hour Meter - Recommended for easier bath maintenance.

Rectifiers - 6-9 volts suitable, 12 volt for maximum coverage (for typical installations).

Table V

Tri-chrome vs Hexchrome

CURRENT DENSITY/PLATING RATE

Hexchrome -

1080 A/m^2 (100 ASF)		= 0.1	μm/min (4 μ in/min)
1620 A/m^2 (150 ASF)	Normal	= 0.15	μm/min (6 μ in/min)
3240 A/m^2 (300 ASF)		= 0.3	μm/min(12 μ in/min)

Tri-Chrome-

1080 A/m^2 (100 ASF)	Normal	= 0.1	μm/min (4 μ in/min)
3240 A/m^2 (300 ASF)		= 0.1	μm/min (4 μ in/min)

Table VI

Tri-Chrome vs Hexchrome

RACKING

	Hexchrome	Tri-Chrome
Construction	Heavy (1620 A/m^2)	Medium (1080 A/m^2)
Throwing Power	Poor (part placement necessary)	Good
Covering Power	Poor (part placement necessary)	Good
Burning	Yes (part placement necessary)	No

Table VII

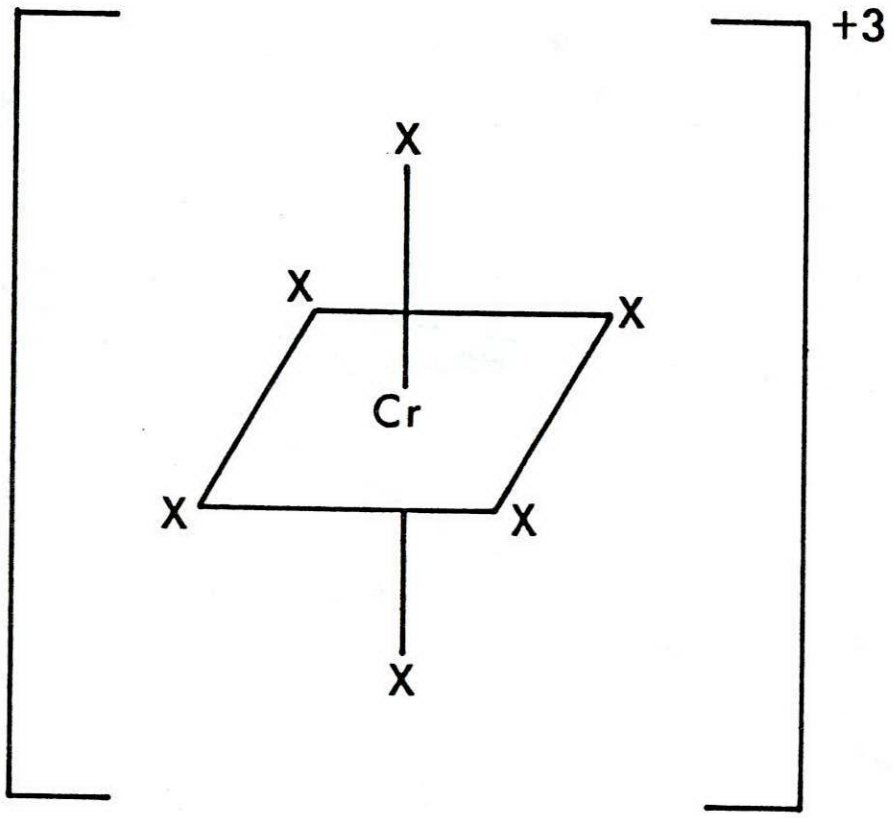
Tri-Chrome vs Hexchrome

DEPOSIT STRUCTURE

Hexchrome - relatively crack free, microcracking obtained with special Cr^{+6} bath at thickness >0.8 μm (30 μ in), microporous or microcracking obtained with special pretreatment.

Tri-Chrome -microporous below 0.5 μm (20 μ in)
microcracked over 0.5 μm (20 μ in)

Figure 1



AQUEOUS CHROMIC CHROMIUM COMPLEX

Figure 2

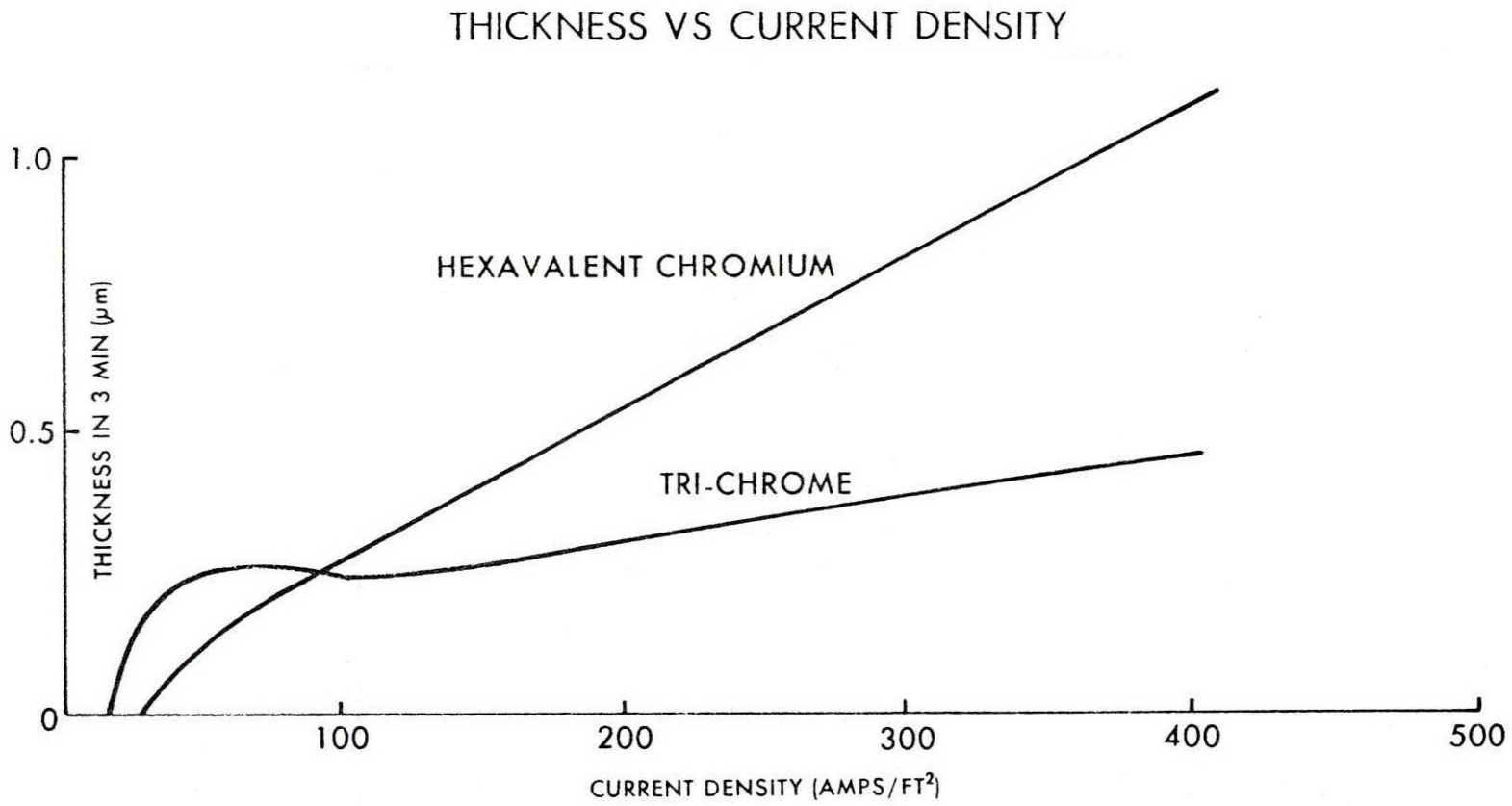

THICKNESS VS CURRENT DENSITY
1.0
0.5
0
THICKNESS IN 3 MIN (μm)
HEXAVALENT CHROMIUM
TRI-CHROME
100
200
300
400
500
CURRENT DENSITY (AMPS/FT²)

Figure 3

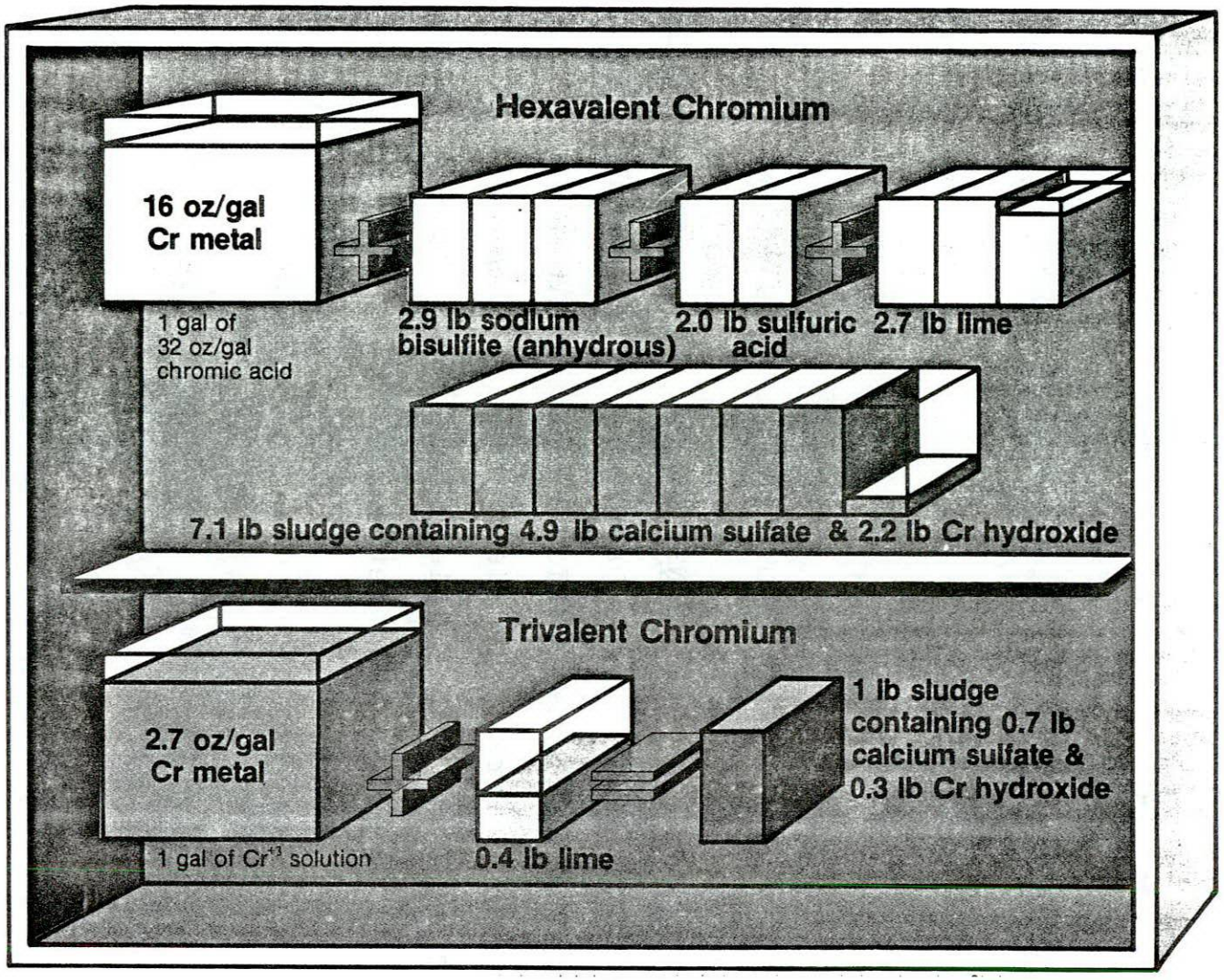

Hexavalent Chromium
16 oz/gal
Cr metal
1 gal of
32 oz/gal
chromic acid
2.9 lb sodium
bisulfite (anhydrous)
2.0 lb sulfuric
acid
2.7 lb lime
7.1 lb sludge containing 4.9 lb calcium sulfate & 2.2 lb Cr hydroxide
Trivalent Chromium
2.7 oz/gal
Cr metal
1 gal of Cr+3 solution
0.4 lb lime
1 lb sludge
containing 0.7 lb
calcium sulfate &
0.3 lb Cr hydroxide

Table I

SOLUTION COMPOSITION

TC Additive	400 g/L	(53.3 oz/gal)
TC Stabilizer	80 ml/L	(8%/vol)
TC Regulator	1 ml/L	(0.1%/vol)
TC-SA	12 ml/L	(1.2 %/vol)

Table II

SOLUTION MAINTENANCE

Material	CONSUMED BY	CONTROLLED BY
TC Additive	Drag-Out	Specific Gravity
TC Chrome Adjuster	Electrolysis	Amp-Hours, Analysis
TC Stabilizer	Electrolysis	Amp-Hours, Analysis
TC Regulator	Electrolysis	Amp-Hours
TC Purifier	Metal Impurities	Test Paper

Table III

OPTIMUM OPERATING CONDITIONS

pH	3.2
Temperature	23°C (72°F)
Current Density	
Cathode	1080 A/m^2 (100 ASF)
Anode	540 A/m^2 (50 ASF)
Anodes	Special Graphite
Agitation	Mild Air Agitation
Specific Gravity	1.21

Table IV

EQUIPMENT REQUIREMENTS

Plating Tank - Rubber or synthetic lined (No Lead Linings)

Anodes - Special Graphite

Special Titanium Anode Hangers

Air Agitation- Mild uniform air agitation beneath cathode

Cooling/Heating-20-30°C (68-77°F). Refrigeration for high volume or continous production. Heating may be needed in winter.

Ampere Hour Meter - Recommended for easier bath maintenance.

Rectifiers - 6-9 volts suitable, 12 volt for maximum coverage (for typical installations).

D-6

Decorative I
Session D

Precious Metals: Substitutes for the "High-Priced Spread"

Robert Duva
Catholyte, Inc.

PRECIOUS METALS: SUBSTITUES FOR THE "HIGH-PRICED SPREAD"

ROBERT DUVA, CATHOLYTE, INC.

(Extended abstract)

COLORS

Since 1968, when gold was decontrolled, price fluctuations have ranged from $50 to $850 per troy ounce. In the past 2 years the price has varied moderately between $400 and $500 per troy ounce. Gold "Hawks" predict cost levels of $1000 and up in the not too distant future. What will the reaction of manufacturers and consumers be to this occurrence?

Because gold is a colored metal with many hues from red thru pink, orange yellow to green, it is desired ornamentally as well as for its "value". If the cost of gold skyrockets as predicted, the affluent will not hesitate to continue purchasing solid gold (10 to 18 karat) items. (Estimated U.S. 1983 sales of solid gold articles were $4 billion -- 4,000,000 tr. oz.) There will still be a market for gold clad or electroplated objects -- estimated at 500,000 tr. oz. of gold consumed in 1983 and equivalent to $800 million in decorative sales dollars.

The less well-to-do may not be able to afford gold or gold-coated objects but instead may opt for look-alike substitutes to meet their need for a fashionable appearance.

An avenue that the manufacturer can use and still produce quality merchandise is in the use of electrodeposited low karat gold alloys in place of high karat coatings. Many 10 to 21 karat gold electroplating baths are commercially available as undercoats prior to the application of 22 to 23 karat electrodeposits. Such duplex systems have been known to outperform single systems in both corrosion and wear resistance.

There are any number of gold colored substitutes available -- bronze and brass electroplated items have always had their niche in commerce. These metals are being successfully electroplated to imitate gold in appearance, but because they are base metals, they require a sound laquer topcoat to impart corrosion resistance. This organic coating can cause changes in color and so must be carefully selected so that no apperance gradations are noted.

Simple electrolytes containing two metals, copper-zinc or copper-tin can produce a wide range of colors from pink thru orange to green with changes in electrolyte operating parameters. Temperature, pH, current density, operating voltage and component concentration variations can give different colored electrodeposits. Their apperance can match any gold tone desired. More complex systems containing up to 5 metals - copper, zinc, tin, lead, indium - are also available but are more difficult to control for consistent results.

WHITES

White finishes have always been needed to substitute for the "soft-white" appearance of silver without the detremental effect of tarnishing. Rhodium has long been used (since 1930) as a non-tarnishing coating in place of silver even though it has a "hard blue-white" appearance. The price of rhodium averaged about $600 per troy ounce or $20 per gram in 1983. The consumption of rhodium in the decorative market is decreasing (down from 500,000 grams in 1980 to 350,000 grams in 1983) due to the use of replacement lower cost substitutes. Palladium, palladium-nickel, ruthenium, tin and tin alloys are being used both as a direct substitute for rhodium as well as for different color variations for "white" finishes. Palladium deposits have been produced which almost match the "whiteness" of rhodium. Palladium-nickel and ruthenium are "greys" which are good color matches for stainless steels. Some tin alloys can almost match the "soft-white" appearance of silver, but color changes can occur (oxidation - much like tarnishing) and disturb their original shade.

Even though these details regarding substitutes or replacement of precious metal coatings are timely, quality in manufacture should not be disregarded. The consumer still wanst permanance and beauty in decorative items and the producer has many ways to achieve that end.

E-1

Environmental I
Session E

Pretreatment Requirements Implementation by General Motors

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PRETREATMENT REQUIREMENTS IMPLEMENTATION BY GENERAL MOTORS

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It is a pleasure to be here to review General Motors activities in implementing pretreatment requirements. My remarks will focus on GM's involvement in the pretreatment program from a historical perspective and the methods used to achieve compliance with electroplating pretreatment standards.

I wish to preface my remarks with a few comments about the pretreatment program, its implementation, and the resultant impact on industrial dischargers. The national pretreatment program has for over 6 years, experienced mixed levels of activity. Even today, the EPA, states and local authorities continue development of mechanisms to administer the program even though many of the standards, requiring compliance by industries by date certain, have existed for over two years. As a result, industrial dischargers have been subjected to changing regulations, have been unable to determine their exact requirements, and have received varying guidance from regulatory agencies in resolving compliance issues.

General Motors recognized the complexity of the pretreatment program and participated in the rulemaking process in the late 1970s. Our actions during the ensuing years focused on cost-effective, reasonable, practical, and technologically achievable pretreatment programs and standards. During this process, we were open and candid in bringing our problems to the attention of regulatory and legislative personnel in an attempt to resolve pretreatment issues affecting industry and the regulatory agencies. The compliance problems faced by industry, particularly those similar to GM with integrated plants, have been recognized by Congress during consideration of reauthorization of the Clean Water Act.

The Clean Water Act (CWA) requires the Environmental Protection Agency (EPA) to establish mandatory national pretreatment standards that regulate the discharge of pollutants by industry to publicly-owned treatment works. The statute specifies a time for compliance not to exceed three years from the promulgation date of a standard. The EPA has promulgated General Pretreatment Regulations which establish standards common to all industries, and industry-specific Categorical Pretreatment Standards for 26 industrial categories, including Electroplating and Metal Finishing. This approach requires an industrial discharger which combines wastestreams and is subject to multiple categorical pretreatment standards (i.e., integrated facility) to comply sequentially with each categorical standard as it is promulgated.

GM has over 140 plants that discharge to city treatment plants in twenty-six states. The Electroplating pretreatment standards are one of eleven pretreatment standards affecting 88 General Motors integrated facilities.

GM's compliance task was complicated by the fact that the Electroplating

standards are inextricably intertwined with the Metal Finishing pretreatment standards and the General Pretreatment Regulations. In order to place events in the proper perspective and gain a complete understanding of GM's compliance efforts, it is necessary to review the history of the General Pretreatment Regulations as well as the Electroplating and Metal Finishing rulemakings.

The first time the EPA addressed the issue of how categorical standards would affect facilities with combined wastestreams came on June 26, 1978, when EPA published final General Pretreatment Regulations. The regulations were silent on how EPA intended to handle these "integrated" facilities, but they were accompanied by a policy statement entitled "National Pretreatment Strategy" which included a formula for deriving combined wastestream standards. In comments submitted to EPA in July, 1978 General Motors and others pointed out that the formula resulted in standards for the combined wastestream that would be unattainable in the vast majority of cases.

In September 1979, EPA promulgated final categorical pretreatment standards that applied to all electroplating operations. While the regulations contained no method by which these categorical electroplating standards could be applied to facilities with combined wastestreams, EPA implied that such facilities were to be subjected to discharge limits computed under the formula included in the 1978 National Pretreatment Strategy.

This rulemaking triggered the interim reporting requirements and deadlines contained in the General Pretreatment Regulations. The most notable requirement was the submittal of baseline monitoring reports (BMRs) by all facilities subject to the electroplating standards. Notwithstanding our concerns regarding the validity of the combined wastestream formula, GM complied with the reporting requirements by submitting, in March, 1980, BMRs for 83 plants to the appropriate agencies. These BMRs indicated each plant's compliance status, even though the General pretreatment regulations did not specify the nature or frequency of sampling. Certain other plants were not in production with no reportable data.

Also in March, 1980, EPA suspended application of the Electroplating standards to integrated facilities until a combined wastestream formula was promulgated and provided specific sampling guidance for the preparation of BMRs. This action nullified GM's efforts to comply with the reporting requirements.

As a result of EPA's actions, GM facilities notified the EPA regional offices and the state and local agencies of EPA's actions and requested that they disregard the submitted BMRs. Additionally, GM facilities instituted interim actions, i.e., sampling, analyses, etc., to reevaluate compliance status consistent with EPA protocols and to ensure timely compliance with the Electroplating standards when they became effective to integrated facilities.

In June, 1980, EPA signalled their intent to pursue a new approach to regulating integrated electroplating facilites: development of effluent standards for a new category of industry identified as the "Metal

Finishing Category" (MFC). The MFC regulation would regulate facilities performing both electroplating and metal finishing operations, e.g. painting, machining, etc., by establishing one set of standards which would be applied at the point of combined process wastewater discharge. In addition to suggesting standards more restrictive than the 1979 electroplating standards, the report introduced a new parameter - total toxic organics - and proposed a corresponding limit on its dicharge.

The establishment of a single set of standards applicable to the combined process wastewater discharge was a sensible and straight-forward approach to regulating integrated electroplating facilities and would obviate the need to apply the combined wastestream formula. For our plants, it meant that all of a plant's wastewater discharges would be subject to one categorical pretreatment standard thus allowing the plant to more quickly identify its compliance oligations. While endorsing the approach in comments submitted to the Agency, GM questioned the attainability of the standards contemplated in the report and began to collect effluent data to assist EPA in developing achievable stadards for the MFC regulation. These data were ultimately shared with EPA in connection with that rulemaking.

On January 28, 1981, EPA promulgated final amendments to the Electroplating pretreatment standards. For integrated facilities, compliance was required within three years from the effective date of the combined wastestream formula.

Also on January 28, 1981, EPA promulgated a new combined wastestream formula different from the proposal that had preceded it. On March 27, three days before it was to become effective, EPA deferred indefinitely the effective date of the combined wastestream formula pending the results of a Regulatory Impact Analysis of the entire pretreatment program as required by Executive Order 12291.

The deferral of the combined wastestream formula again raised questions as to how and whether electroplating standards would be applied to integrated facilities. While such questions could not be answered with certainty until EPA had completed its re-evaluation, EPA's General Counsel, in a May, 1981 letter, assured General Motors that deferral of the formula caused a corresponding deferral in the compliance obligation. EPA announced that the Agency was studying various alternatives to the deferred formula. Therefore, until EPA finalized its thinking on the formula as well as the broader question of how to regulate integrated facilities, GM plants were unable to define their complince obligations.

In June, 1981, the Natural Resources Defense Council (NRDC) filed suit asserting that EPA's indefinite suspension was not consistent with the Administrative Procedures Act (APA). The Agency undertook two related administrative actions in late 1981 to remedy this deficiency. In February, 1982, EPA announced that the pretreatment amendments would be effective as scheduled except for the continued deferral of four amendments, including the combined wastestrem formula.

In July 1982, the Third Circuit Court of Appeals issued its opinion on the NRDC suit, ruling that EPA's indefinite suspension violated the notice and

comment provisions of the APA. As a remedy, the Court ordered the Agency to reinstate retroactively all the amendments effective March 30,1981 thereby establishing March 30, 1984 as the date by which integrated electroplating facilities had to comply with the Electroplating pretreatment standards, unless EPA took some further action. Effectively the court said to industry, "the clock has been running even though you didn't know it". GM was not litigating the standards up to this time.

The Court expressly noted that its decision did not forestall future Agency action to resuspend the regulations, provided that EPA did so in accordance with the APA. After the EPA took no action for 4 months, GM filed, on August 10, 1982, an administrative petition requesting EPA to reconsider and resuspend the combined wastestream formula. EPA eventually denied the petition in June 1983, and in September 1983, GM filed an appeal of this denial with the Third Circuit Court of Appeals.

Concurrent with these activities, EPA proceeded to develop the MFC regulations. In August, 1982, EPA issued proposed MFC regulations applicable to the same integrated facilities affected by Electroplating standards. In the proposal, EPA noted that the MFC standards were more stringent than, and in fact, superceded the Electroplating standards. Nevertheless, EPA maintained that the MFC standards could be achieved by the application of the same treatment technology required to meet the Electroplating standards. The proposed rules specified a June 30, 1984 compliance deadline; however, EPA solicted comments on whether facilities had sufficient time to comply by the proposed deadline.

Self-monitoring data from GM facilities employing well-operated precipitation/clarification treatment technologies indicated that these technologies would enable compliance with Electroplating standards; however, these same technologies would not be adequate to meet the proposed MFC standards for heavy metals. More importantly, our data revealed that new, more sophisticated treatment technology would be necessary to meet the proposed MFC standard for total toxic organics. GM expressed this concern in comments filed with EPA in June, 1983. GM also requested that the Agency provide sufficient time to install requisite treatment facilities where needed to achieve compliance.

In response to comments and data provided by GM and others, EPA issued final MFC rules in July, 1983 which relaxed somewhat the standards contained in the proposed rulemaking. Further, EPA extended the compliance deadline to February, 1986, and acknowledged that this extension was based on an Agency study which showed that 31 months is required to plan, design and install the requisite treatment technology. It is important to note that the relaxation of the MFC standards in the final rulemaking obviated the need for biological treatment and carbon absorption. In other words, the treatment technologies needed to meet the electroplating standards could also be used to meet the MFC standards. Regrettably, although the treatment technologies are identical, the deadlines for installing these technologies and achieving compliance are not. Thus, integrated electroplating facilities were first obliged to comply with Electroplating standards by June 30, 1984 and then comply with the MFC standards by February, 1986.

Although the Court ruling retroactively reinstating the combined wastestream formula to March 30, 1981 occurred in July 1982, EPA delayed until September 28, 1982 in responding to the Court's order. EPA then elected to reinstate the regulations without a subsequent resuspension. Therefore, operators of integrated facilities did not know, and in fact, could not have known, their exact compliance obligations prior to September 28, 1982.

EPA's September 1982 action was significant to GM's integrated electroplating facilities. First, it made the electroplating standards applicable to integrated facilities, thus retriggering the reporting requirements contained in the General Pretreatment Regulations. On October 4, 1982, the Court issued an order extending the deadline for submittal of BMRs and final compliance to June 25, 1983 and June 30, 1984 respectively. General Motors facilities resampled plant effluents to assess their compliance status and prepare BMRs. This sampling effort not only gathered data on inorganic constituents, but organic constituents as well in order to assess compliance with the as-yet-unpublished MFC regulations. On June 25, 1983, 88 GM facilities filed BMRs with the appropriate "Control Authority."

The second significance of this action was that it nullified 15 months of an original 36 month time for compliance. This meant that GM facilities that were noncompliant and needed to install treatment technologies to achieve compliance must plan, design and install these technologies in 21 months to meet the June 30, 1984 deadline. For 19 GM integrated plants requiring additional treatment facilities to comply with both the electroplating and metal finishig standards in a cost-effective manner, this was projected to be an impractical task and the BMRs for these plants provided compliance schedules extending beyond the June 30, 1984 deadline.

In subsequent meetings with EPA representatives, the Agency suggested that relief was available through Fundamentally Different Factors (FDF) variances and enforcement discretion. Accordingly, on June 27, 1983, GM filed requests for a compliance date extension, under the FDF variance procedure, for each of the noncompliant facilities. Unfortunately, four months later, the Third Circuit Court, in response to NRDC pleadings, ruled that the granting of FDF vriances for toxic pollutants was illegal under the CWA.

In view of this background relevant to the Electroplating, Metal Finishing and General Pretreatment standards, it is clear that GM was responding to conditions beyond its control which eliminated nearly one-half the compliance time Congress intended. GM highlighted this problem in testimony to Senator Chafee's subcommittee in early 1983. However, since the Court had withdrawn the FDF variance capability from EPA and since GM was not able to make up for the electroplating compliance time removed by government action, it was uncertain how these plants could operate in compliance with the Electroplating standards after June 30, 1984.

As a resolution to this problem, EPA directed GM to seek extensions to the compliance date through the use of administrative orders issued by the

control authority. To support this concept, enforcement policy guidance was to be issued by EPA in early 1984, which I might mention has not yet been finalized. GM contacted the applicable control authorities, but due to the lack of full implementation of the pretreatment program, the compliance date issue was not resolved.

During this same period, plants were directed to reassess their control strategies to determine if waste stream segregation and interim treatment could be accomplished by the June 30, 1984 deadline. This approach, although permitting compliance with electroplating standards, is not cost-effective and wasteful of resources when one considers these same plants must comply with metal finishing standards by February, 1986. Where deemed practical, plants began modification of existing wastewater treatment facilities to incorporate temporary controls pending completion of permanent facilities.

As the June 30 deadline approached it became apparent that installation of interim controls would not be completed in sufficient time to permit confirmation that consistent compliance could be achieved. These controls consisted of separating the phosphating wastestream, subject to electroplating standards, from the balance of the process wastewater and installing unitized precipitation/clarification equipment. The majority of this equipment will be obsolete upon completion of the permanent wastewater treatment facilities.

Since we were unable to ensure consistent compliance with the use of the interim controls at eight plants, GM actively sought enforcement actions to protect the Corporation. This has resulted in consent decrees which specify a schedule of penalties for noncompliant discharges, should they occur, by each of the eight plants. A brief comment about the consent decrees. During development of the consent decrees EPA personnel have been firm yet fair. We believe they conducted themselves in a highly professional manner.

In summary, due to delays in the implementation of the pretreatment program compounded by sequential promulgation of categorical pretreatment standards, it has been necessary for several of GM's integrated plants to separate process wastestreams for interim treatment pending completion of permanent facilites. These interim treatment systems will be obsolete upon completion of facilities designed to enable the combined wastestream to comply with the multiple pretreatment standards affecting the plants. Additionally, rather than endure the possibility of criminal sanctions, however remote, General Motors insisted upon the protection of consent decrees before continuing operation of its plants after June 30, 1984.

E-2

Environmental I
Session E

Pretreatment And Recovery At A Plating Shop

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PRETREATMENT AND RECOVERY AT A PLATING SHOP

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INTRODUCTION

New Method Plating Company is a job shop which performs a variety of electroplating operations on metal products for outside concerns. The processes include cadmium, chromium, copper, nickel, and zinc plating. Most of the plating lines are automated and are of the barrel or rack type. The metal bearing wastewaters from these processes are in three categories; cyanide, hexavalent chromium, and acid/alkali. Table 1 below shows 1980 flows and pollutant levels in the untreated effluent and the EPA pretreatment standards.

Table 1 Waste Characteristics and Discharge Limits

Parameter		1-Day Composite	EPA Limits 1-Day Max.	4-Day Average
pH		10	*	*
TSS,	mg/l	5	-	-
CN_A,	"	37	-	-
CN_T,	"	50	1.9	1.0
Cu_T,	"	4	4.5	2.7
Ni_T,	"	2	4.1	2.6
Cr_T,	"	18	7.0	4.0
Cr^{+6},	"	17	-	-
Zn,	"	5	4.2	2.6
Cd,	"	25	1.2	0.7
Fe,	"	6	-	-
Pb,	"	-	0.6	0.4
Total Metals,	mg/l	29	10.5	6.8
Flow **,	gpd	75,000	-	-

* Local Limit: 6.0 - 9.5
** One 10-hr. shift

New Method Plating began planning for their pretreatment facilities in 1980 in response to the proposed EPA regulations. A preliminary engineering study was completed in 1981. The company managers took an active part in the engineering studies.

DESIGN STUDIES

The preliminary engineering study considered both waste reduction at the source and end-of-pipe treatment.

First, the existing conditions were evaluated. The facility had eleven plating lines (departments) with a total of 55 running rinse tanks which discharged to a common drainage system. A floor plan of the facility was prepared which showed all the existing plating and rinse tanks, discharge points and drainage piping. Rinsewater flows were measured. The concentrations of critical pollutants in each rinsewater discharge were analyzed. As a result, cyanide, hexavalent chromium and acid/alkali streams were identified along with their relative pollutant strengths and flow rate from each rinse tank. Table 2 gives a summary of the flows in each category.

Table 2 Waste Characteristics (1980)

Waste Category	Flow, gpd	lb/day
Cyanide	25,000	$CN = 35$
Chromium	30,000	$Cr_T = 10$
Acid/Alkali	20,000	

Next, in plant process modifications for flow reduction and chemical recovery were investigated. Three general process modifications were considered: 1) rinsewater reduction, 2) plating bath dragout reduction, and 3) plating bath dragout recovery. The potential benefits of implementing these measures included cost reductions in plating chemicals used, water purchased for rinsing and sewer use fees, as well as the capital and operating costs of wastewater treatment facilities.

Rinsewater Reduction

The facility already employed countercurrent rinsing and flow restrictors in many lines. Since most of the plating/rinsing operations were continuous and automated, flow restrictors were particularly effective. Nevertheless, new measures reduced the flow from about 75,000 gallons per day (gpd) in 1980 to about 50,000 gpd in 1984. This was accomplished by a combination of measures including additional countercurrent rinses and carefully selected new restrictors and spray nozzles.

Plating Bath Dragout Reduction

One of the simplest methods of dragout reduction is to increase the dwell time of work pieces over the plating tanks to allow more of the plating chemicals to drip back into the plating tank. At New Method Plating, where the automated lines work at close to 100% capacity, an increase in dwell

times would mean a proportionate reduction in production capacity. Therefore, this measure was not applicable except for a few manual plating lines. Orienting workpieces for maximum drainage was also not feasible due to great variances in the shape of workpieces.

Plating Bath Dragout Recovery

The feasibility of recovering plating bath chemicals from rinse tanks through concentration techniques was evaluated. First, those plating tanks with high dragout were selected for evaluation of recovery methods. Five rinsing operations were identified as candidates. The cost of a closed loop system (evaporation) was compared with the annual chemical savings in these locations. (Evaporation was assumed as the recovery method only for initial economic screening.) From this evaluation, three rinsing operations were selected as candidates for total or partial recovery of nickel and cadmium. It was also determined that recovery equipment would not affect the need for or the size of the downstream treatment equipment. However reduction in treatment chemical costs was expected. Further study of recovery equipment was undertaken by New Method simultaneously with the design of the pretreatment system.

The recovery systems that were installed are discussed later in this paper.

TREATMENT OPTIONS

Two major treatment alternatives were evaluated: 1) the conventional methods of cyanide destruction, hexavalent chromium reduction, and metal hydroxide precipitation, 2) metal sulfide precipitation (with insoluble sulfide reagent) preceeded by cyanide destruction.

These methods have been discussed extensively in the literature and therefore only brief descriptions are provided below:

1) The metal hydroxide precipitation involves addition of an alkali such as lime or caustic to the waste stream to raise the pH to a level which provides minimum solubility of metals.

   The segregated hexavalent chromium stream is pretreated to reduce the hexavalent chromium to trivalent chrome so that chromium can be settled as a hydroxide. Also, the segregated cyanide stream is pretreated to destroy cyanide before addition to the other wastes for metals precipitation. This scheme, of course, requires three segregated waste collection systems.

   A disadvantage of hydroxide precipitation is that the pH which provides minimum solubility is different for each metal hydroxide. Therefore, more than one clarification step is required in some cases. At New Method we found that separate clarification of the chromium stream would be required to meet the discharge limits.

2) With insoluble sulfide precipitation (a patented process), metals are precipitated in one clarification step as metal sulfides. Metal

sulfides are much less soluble than corresponding hydroxides. In this process, it is not necessary to reduce the hexavalent chromium to trivalent chromium separately, as it is reduced by the sulfide reagent. Therefore a segregated chromium waste collection reduction system is not needed. A separate cyanide oxidation step is still necessary. Filtration of the effluent following clarification is advisable since the sulfide precipitate may give relatively fine floc.

A cost comparison of all the capital and annual operating costs favored the conventional methods. The treatment system is described below.

TREATMENT SYSTEM

Equipment

Figure 1 shows the process flow diagram for the system. Each segregated waste is received in a 20,000 gallon tank and then pumped to treatment units. The treatment capacity is 50 gpm for each wastestream, which corresponds to about 25,000 gallons per 8-hr. shift. The combined capacity is 75,000 gallons per shift. The design flows were determined by considering flow reduction plus future flows. (The current plant flow consists of 10,000 gpd of cyanide, 20,000 gpd of chromium and 20,000 gpd of acid/alkali wastewaters.)

The cyanide wastewaters are oxidized in two continuous stages. The treated cyanide wastewater is then combined with the acid/alkali wastes and the pH is raised to 10.5 with lime and caustic soda. Then the wastewater is flocculated with the aid of a polymer and settled in a parallel plate clarifier.

The hexavalent chromium wastewater is reduced with sodium metabisulfite at a pH between 2.0 and 3.0. The pH of the effluent from this tank is adjusted to 8.5 with alkali mixed through an inline static mixer. It is flocculated and then clarified in a parallel-plate clarifier separate from that for the other metal bearing wastewater.

The effluents from the two clarifiers are combined and the final pH is adjusted before discharge to the sewer. Acid is added upstream of a static mixer. This arrangement was selected to eliminate a mix tank. In spite of very short detention in the line, the final pH is kept very close to 7.5 well within the allowable range of 6.0 to 9.5.

The sludge from both clarifiers is wasted to a holding tank and then dewatered with a pressure filter. The dewatered sludge contains 40 to 45% solids and is hauled away by a licensed contractor.

The treatment processes are controlled by a programmable instrumentation system. All pH and ORP set points are controlled through feedback loops with flow compensation. Relay and interlock functions are performed by a programmable controller.

The treatment system, including storage tanks, is housed in a separate building adjacent to the production facility. The segregated wastewaters

are pumped from the production plant to the treatment plant.

The project cost for the pretreatment facility, including segregation of wastes, amounted to $1,000,000 in 1983. One fourth of this amount was for the treatment plant building.

Operation

The start-up period involved the usual debugging problems. One of them was indirectly caused by the success in flow reduction. The cyanide wastewater volume was greatly reduced but was considerably more concentrated than initial estimates. The hypochlorite pump could not always meet the reagent demand and therefore a larger pump was provided.

After startup, experiments were made to minimize the amount of sludge to reduce disposal costs. (The pressure filter had ample capacity.) As expected, when lime alone was used for pH adjustment, it provided the better floc for clarification compared to caustic soda. Lime also gave considerably higher volume of sludge in spite of its good dewaterability. Lime and caustic soda were blended in the chemical day tank at a ratio that gave good sludge settling at a minimum sludge volume.

The sludge provided during start-up passed the extraction procedure (EP) test but was still handled as hazardous waste due to its trace cyanide content.

RECOVERY SYSTEMS

Nickel Recovery

The first recovery system that was evaluated by New Method was an electrodialysis unit. The unit was initially tested for recovery of cadmium, but did not give satisfactory results.

The electrodialysis unit was successfully tested and installed for recovery of nickel. Figure 2 shows the schematics of the process employed. A reclaim rinse tank follows the plating tank. Rinsing is completed with a static rinse tank and a final rinse tank. This is an open loop recovery process where there is still a rinsewater discharge. The discharge has very low concentration of nickel. The reclaim rinse is recirculated through the electrodialysis unit at 20 gpm. The concentrate from the unit is collected at about 2.5 gallons per hour and periodically is returned to the plating tank. The nickel concentration in the process streams are shown in Figure 2 based on one set of grab samples. The long term experience shows savings of about 100 pounds of nickel sulfate salt per week (equal to about $9,000 per year). The installed cost of the system was about $35,000 in 1983 dollars. The power requirement is 6 amp at 100 volts. The membranes, which are the most critical parts, have lasted over a year. Their actual life is not yet known. (The present membrane replacement cost is estimated at $10,000 - $15,000.)

Cadmium Recovery

Two cadmium plating operations offered the opportunity to recover substantial amounts of cadmium. One electrochemical recovery unit was installed to serve both locations. The unit also incorporated an electrochemical cyanide destruction module. The flow scheme for cadmium recovery, as shown in Figure 3, is similar to the one used for the electrodialysis recovery system. The reclaim rinse is recirculated through the recovery/destruct system at a high rate. The cadmium recovery module is incorporated into a separate recirculation loop. The unit features a high surface area carbon fiber cathode where the cadmium deposits. When the cathode is loaded, the cadmium is stripped with the plating solution. As shown in Figure 3, the discharge from the recovery unit is also recirculated through a separate loop incorporating an electrochemical unit for oxidation of cyanide. The start-up problems were generally related to the automation features of the recovery module. The controls were relaced with a simpler system by the manufacturer and the related problems were eventually eliminated. The nominal power requirement for the unit is 400 amps at 23 volts D.C., both for recovery and cyanide destruction. The installed cost is about $105,000 in 1983 dollars. The unit recovers 200 pounds of cadmium (as Cd) per week (equivalent to $15,000 per year). Cadmium recovery also reduces the volume of treatment plant sludge. The savings in sludge disposal are estimated at $4,000 per year.

About 25 pounds of cyanide (as CN) is destroyed daily in the electrochemical process, reducing hydrochlorite consumption at the treatment plant. This is equivalent to savings of about $75 per day or $20,000 per year in chemical costs. This saving may be offset by the replacement cost of anodes used in the cyanide destruct module. The frequency and cost of replacement has not yet been established.

CONCLUSIONS

The experience at New Method Plating shows that recovery processes can compliment conventional wastewater treatment methods. At this time, there is not sufficient operational data to establish long term cost effectiveness. The operation of the recovery units during the first year can only be regarded as experimental. Downtime was frequent and several improvements were made by the manufacturers after one installation. However, now the units are more reliable than immediately after purchase. There is clear, long term environmental benefit: the net discharge of hazardous chemicals to the environment, either through the effluent or the sludge, will be reduced.

It was demonstrated that significant reduction in water consumption can be achieved with carefully selected, simple equipment such as flow restrictors and rinse spray nozzles.

The treatment plant is currently meeting the discharge limits. The required operator time is about 3 man hours during one 10-hr. daily shift.

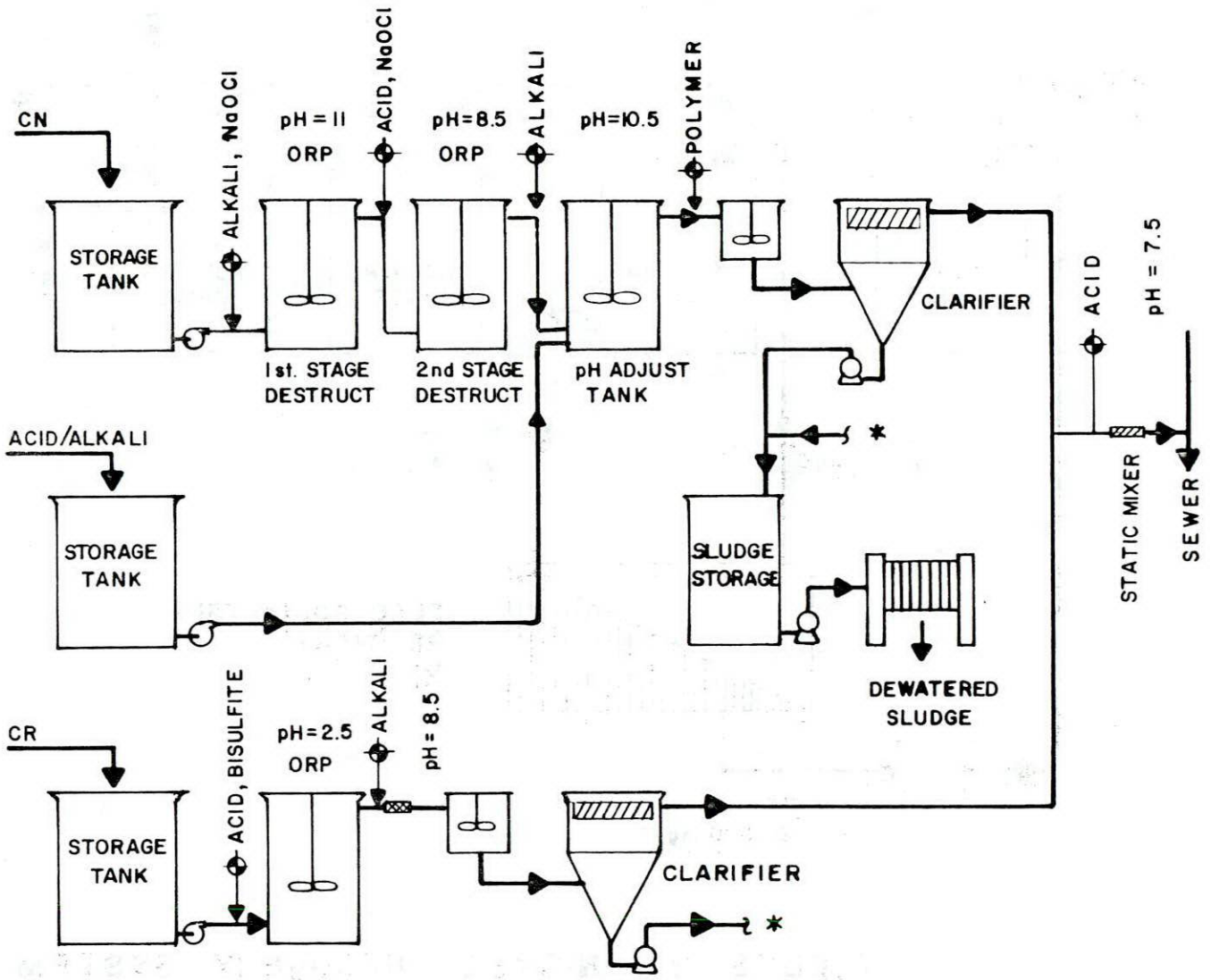


FIGURE 1 — TREATMENT SYSTEM

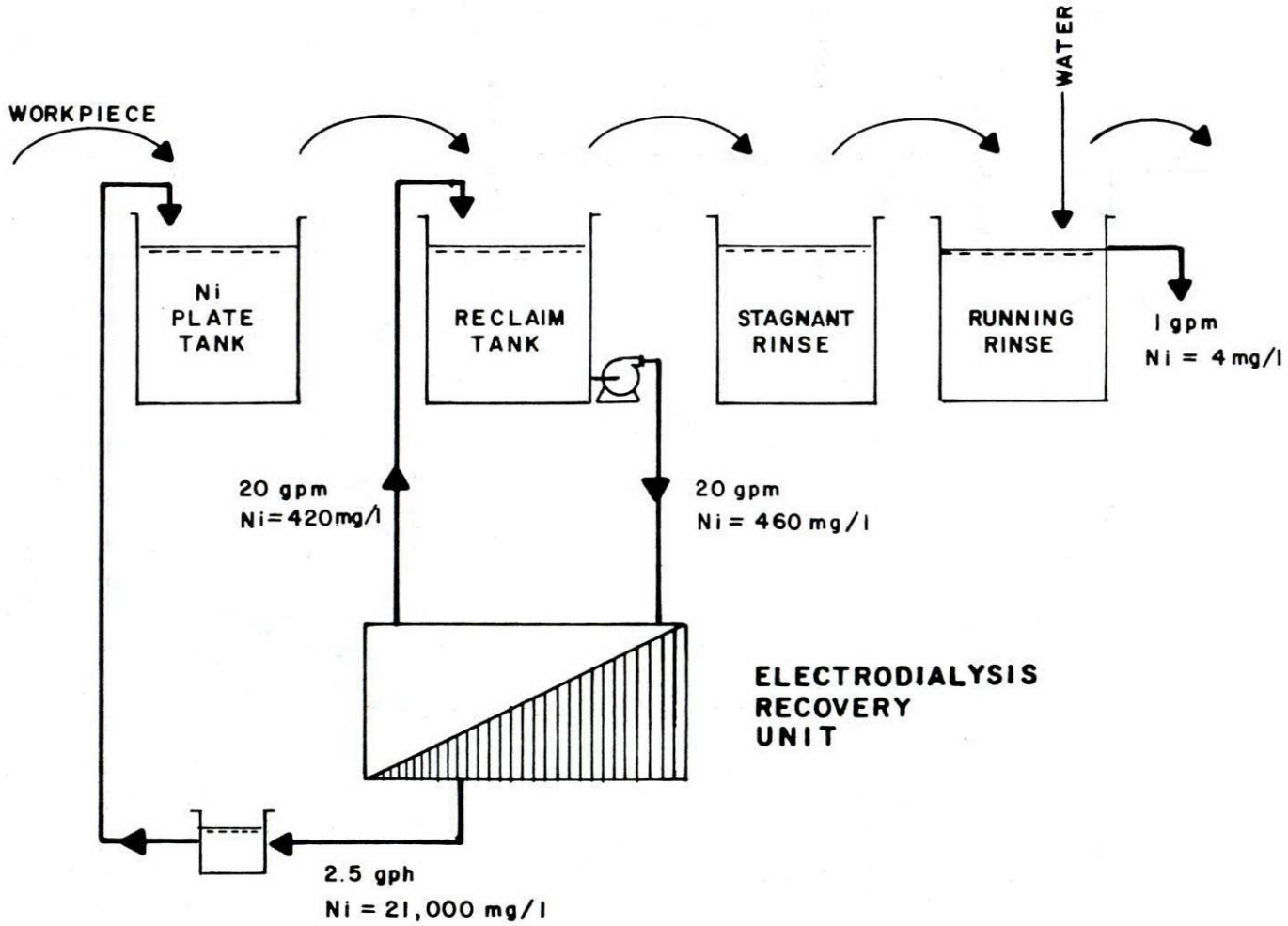
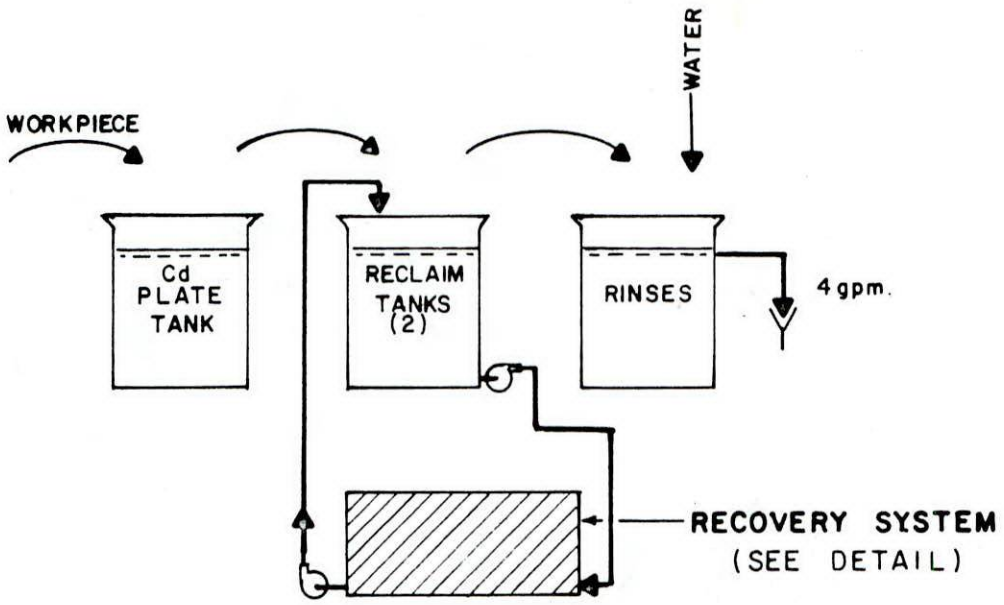
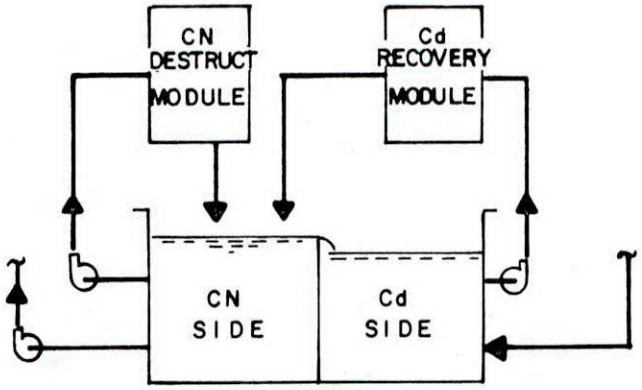


FIGURE 2 – NICKEL RECOVERY SYSTEM



GENERAL FLOW SCHEMATIC



RECOVERY SYSTEM DETAIL

FIGURE 3 - ELECTROCHEMICAL CADMIUM RECOVERY/CYANIDE DESTRUCT SYSTEM

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Environmental I
Session E

Electrodialysis For The Recovery Of Nickel Salts

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ELECTRODIALYSIS FOR THE RECOVERY OF NICKEL SALTS

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The process of bright nickel electroplating is an attractive candidate for development of a minimum-waste approach to operation since it is so widely used, and the value of the nickel is significant. To the contrary, it is a difficult candidate because the process chemistry is complex, and control is already a formidable challenge without the introduction of waste-minimization techniques. Nevertheless, the need to reduce wastage and sludge generation is acute, and recent developments have begun to show promise that a close approach can be made to total elimination of the non-productive consumption of nickel.

Historically, most efforts to recover losses from a bright nickel operation have focused on the drag-out to rinsewaters. Technologies such as evaporation and reverse osmosis have been considered for concentration of the nickel salts from the rinsewaters for return to the plating tank. However, practical experience has indicated that the nickel in the drag-out is only a portion of the total amount of nickel lost from the process.[1) 2)] A very significant loss occurs as the result of purification operations performed to restore desirable metallurgical properties to the electrodeposit after prolonged operation has caused an accumulation of organic impurities. In the authors' experience, such losses are a small fraction only in those cases where little or no effort is made to minimize and/or return drag-out losses. In effect, excessive drag-out provides a purification vehicle of its own. This seems to be a classic case of diminishing returns, since increasing efforts to eliminate drag-out losses simply exaggerate the problem of harmful organic accumulation, producing a need for more purification of the bath, and thus increasing the losses that are unavoidable during an effective purification operation.

In addition to the problems created by accumulation of undesirable organic compounds, a close approach to zero nickel losses will be complicated by the fact that the anodic dissolution process is more electrolytically efficient than the cathodic deposition reaction.[3)] If one could totally eliminate nickel losses to both drag-out and purification operations, there would be a progressive increase in the nickel concentration of the plating bath.[4)] Commonplace evidence of this phenomenon is the need for routine additions of acid to a nickel plating bath. Each quart of concentrated sulfuric acid consumed in pH control of the solution corresponds to a theoretical gain of 2.3 pounds of nickel in the solution. Normally, drag-out and purification losses more than offset this gain, so it does not become a practical problem. An apparent expedient for this problem would be the use of insoluble anodes, but is undesirable because of additional oxidative degradation of organics.[5)] Thus, an optimized recovery scheme should provide for return of nickel salts rather than nickel metal due to their higher commercial value, but

should also provide a means for converting the excess amounts of salt into metallic nickel that can be recycled as anodes. The amount which would need to be recycled as metallic nickel would be equivalent to the differential electrolytic efficiency of the anodic and cathodic reactions--typically considered to be in the range of 3%-5%.[3) 6)]

Organic Compounds

A published report on research work in West Germany[6)] has provided documentation of the impact of organic materials accumulating in a bright nickel bath. This work has also provided a material balance indicating the significance of the losses during periodic batch purifications for organic removal and demonstrating that return of all nickel losses as salts is impractical. This work also demonstrated the ineffectiveness of activated carbon for removal of many organic constituents present in the operating bath. Further reinforcement that treatment with activated carbon alone will not adequately remove organics is found in a paper by Immel and Gaethke.[7)] As indicated by both authors, effective purification requires massive dosages of strong oxidants such as potassium permanganate, in combination with the use of activated carbon. Our practical experience agrees with the findings of Fischer[6)] in that 10-15% of the plating bath is lost during each such purification operation. This is due to the fact that the last step in the process is allowing suspended solids to settle and then decanting purified plating bath back to the operating tank. The "heel" which is left behind consists of a slurry of plating bath together with precipitated manganese, iron, nickel, and activated carbon. Losses of this magnitude are very significant when compared to typical drag-out losses.

The work reported on by Fischer[6)] concludes that an alternative scheme is more desirable than the conventional approach of returning drag-out and batch purifying the plating tank. The proposed scheme involves precipitating nickel from the drag-out, concentrating the resultant sludge, and redissolving the nickel in a liquor circulated through an electrolytic recovery cell. This allows a portion of the nickel sulfate formed to be recycled to the plating tank as salt, while another portion is recovered as nickel metal. Furthermore, this scheme allows a steady bleed of plating solution from the plating tank into the recovery process. This provides a constant purge of organics, eliminating the need for batch purification. The end result is a more stable plating process since the lower overall organic concentration gives improved mechanical properties in the deposit at lower dosage rates of the internal stress control agent (saccharin). The scheme features complete recovery of all nickel losses and improved plating performance at lower consumption rates for the organic brighteners; but the biggest advantage is in the elimination of batch purifications with their associated down-time, loss of nickel and desirable organics, and the obvious discontinuity in the performance of the plating bath before and after the purification treatment. On the negative side of the trade-off, the scheme is relatively complex and involves considerable labor and operating control requirements.

An additional consideration for organic compounds is necessary in large-scale, multi-layer nickel plating plants. The return of organic brightener constituents to the semi-bright bath is undesirable, so evaporation and reverse osmosis are not attractive as candidates. Ion exchange has been tried, but the regenerant stream from the process is too dilute for return in almost all cases, necessitating an additional energy-intensive step for further concentration. In addition, careful control is necessary to control excess acid in the regenerant stream and to ensure that adequate removal of organics has occurred.

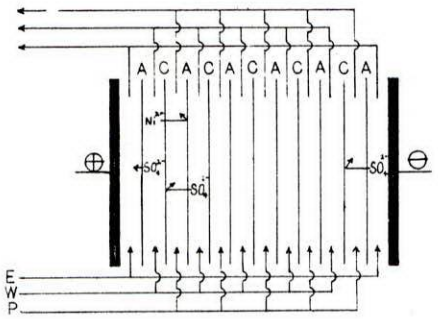
Electrodialysis

A number of authors have discussed the principles of electrodialysis and its potential applicability for recovery of nickel salts from bright nickel plating operations.[8) 9) 10)] Two important characteristics of the technique are that various soluble constituents are concentrated at different rates and that some organic materials appear to be highly rejected. The authors have undertaken a study to quantify the transport of organic compounds. The initial emphasis was on the total quantity of organics as indicated by an analysis for total organic carbon (TOC). In addition, because of the widespread use of saccharin as a Class I brightener, and for control of internal stress in an electrodeposit, and because of the undesirable impact of accumulation of one of its reaction products (O-Toluenesulfonamide) [5) 11)], they have been selected for quantification in the study.

Experimental Procedure

A bench-scale electrodialysis unit was constructed using one-inch-thick PVC end blocks ported with manifolds to accommodate the inflow and the outflow of the solutions involved, the product, electrolyte wash, and simulated drag-out solution, hence referred to as waste solution. Mounted between these blocks are twelve solution compartments, or cells, separated by alternating cationic and anionic membranes. The membranes used are typical, commercially available ion-exchange membranes. There are a total of five depleting and five concentrating compartments in the unit, with one end cell at each electrode used to recirculate electrolyte solution (see Figure 1).

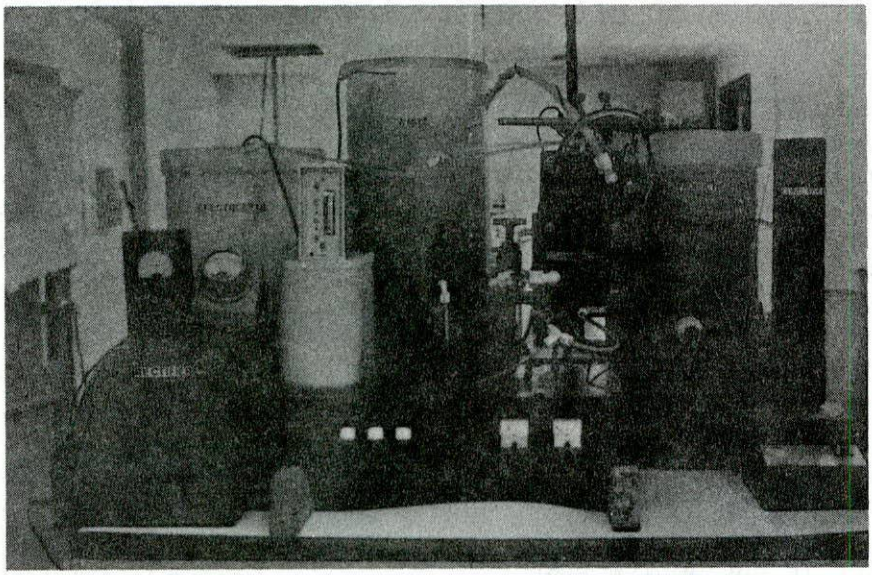
FIG. 1 - STACK CONFIGURATION



E = ELECTROLYTE
P = PRODUCT
W = WASTE

This arrangement creates five cell pairs, each pair having an active membrane surface (cationic) of 96.25 cm^2. Inside each cell is a polypropylene woven grid that serves as a spacer. These spacers serve two functions. The primary function is to promote mixing of the solution as it passes through the cell, in turn creating a reduction in the boundary layer at the membrane surface. This improves mass transport of ionic species and prevents precipitation of nickel hydroxides and fouling of the membrane. Secondarily, the spacer provides internal support for the membranes. A stainless steel cathode and platinized titanium anode serve as the electrodes. The stack assembly was compression bolted together and was mounted in an upright position with the inflow ports at the bottom and outflow ports at the top to prevent gas accumulation in the electrolyte chambers.

Prior to start-up of the bench-top system, consideration was given to the desired operating conditions with respect to solution make-up. The system is equipped with 25-liter reservoirs to afford: 1) a gradual change in the solution concentrations; 2) ease of monitoring; and 3) accommodation of fluid loss or gain. The schematic of the system is shown in Figure 2.



The solutions were made up as follows:

1) The product solution consisted of 10 liters of 5 g/l H_2SO_4.

2) The waste solution consisted of 20 liters of deionized water spiked with a proprietary bright nickel plating bath to a total accumulated nickel concentration of 3.25 g/l.

3) The electrolyte consisted of 10 liters of 25 g/l H_2SO_4.

A photograph of the experimental set-up is given in Figure 2A.

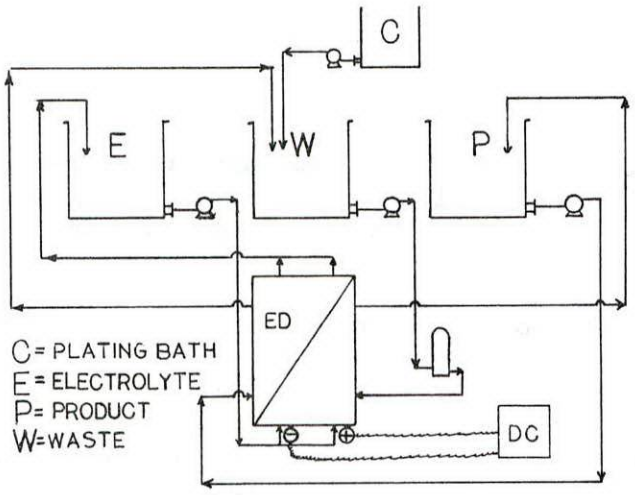


FIG. 2
FLOW SCHEMATIC

Figure 2A - Experimental Apparatus

Throughout the work, a current of 21.5 A/cm^2 was applied to the stack. Solutions were recycled at 470 ml/min/cell. After two hours of running, the product was analyzed for nickel concentration. From this number, an approximation of the nickel transfer per hour was determined, and a precision metering pump was set up to feed the plating bath into the waste solution to maintain a nickel concentration of 3.0-3.5 g/l. The system was run 24 hours per day, 7 days per week to a desired termination time, depending on either product concentration or total hours run.

The system was sampled twice per 24-hour period to closely monitor desired chemical parameters. Temperature and volume of solution and the voltage on the stack were also recorded at each sampling. One set of samples was analyzed daily and the second set was used as a back-up to detail any unexpected changes in the system between sampling times. The rate of the metering pump was adjusted daily to keep the nickel concentration in the desired range.

The results of two discrete experimental campaigns are described in this paper. The first, preliminary campaign was primarily devoted to debugging the experimental methodology. This run was done at room temperature (27° C) and the pH of the waste solution was held in the range of 1.5-2.0.

As a result of the experience from the first campaign, minor changes were made in the operating procedures so as to allow tighter control over operating variables and more accurate tracking of materials in and out. This second run was done at a slightly elevated temperature (38° C) to more closely model the typical operating conditions in the field. The pH of the waste solution was held carefully between 3.0 and 3.5. Again, this was to more closely model the conditions anticipated in the field, and represents a much narrower window of variability in hydrogen ion concentration.

Analytical Procedures

Nickel and boric acid were analyzed using titration methods as outlined in the Metal Finishing Guidebook - 1983 edition. The pH was measured with the conventional electrometric approach using calibration before each set of measurements.

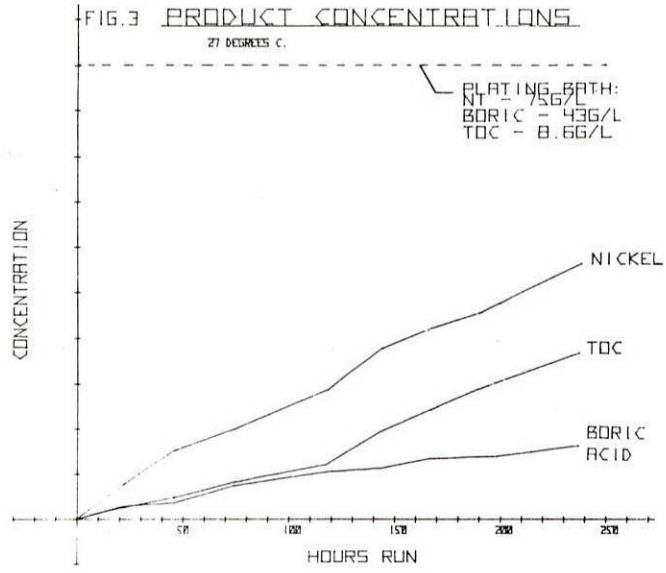
The technique used for total organic carbon determination was the ultraviolet/acid persulfate oxidation method using infrared detection on a Dohrman Total Carbon Analyzer.

During the second experimental campaign, additional analyses were conducted for saccharin and O-Toluenesulfonamide. The routine saccharin determinations for process control were done using a standard solvent extraction/titration method.[12] In addition, selected samples were taken for analysis by High Performance Liquid Chromatography (HPLC) with ultraviolet detection. This method was chosen because of its ability to detect and reproducibly quantitate both saccharin and O-Toluenesulfonamide

and because it allows direct injection of the various solutions, containing a wide range of component concentrations. This is an advantage since it eliminates the need to dilute or extract the samples. Several combinations of columns and eluents were evaluated to arrive at the selected method. The most accurate and reproducible system was found to be a Supelco LC-8-DB column with an eluent solvent/water ratio of 30% methanol and 70% water. An eluent flow rate of 1 ml/minute was found to be optimum.

Results and Discussion

Results of the first campaign are presented in Figure 3. The concentration of nickel, TOC, and boric acid are plotted on three separate scales on the Y-axis. The horizontal line gives the concentrations in the plating bath which was fed into the waste solution during the campaign. By establishing the scale separately for each of the three plots, the slope of the lines is a visual indication of the rate of transport in the electrodialysis process. During this first campaign, pH control was not as rigorous as in the second campaign, and this undoubtedly contributes to the variability of the slope of the curve. In addition, the relatively low pH maintained in the waste solution (1.5-2.0) undoubtedly suppressed the transport of boric acid.



Based on the experience gained in the first campaign, slightly different control techniques were used in the second campaign, giving tighter control over variables and a better overall material balance. The results for nickel, TOC, and boric acid are presented in Figure 4. As can be readily seen, the TOC and boric acid transported at approximately one-half of the efficiency of the nickel.

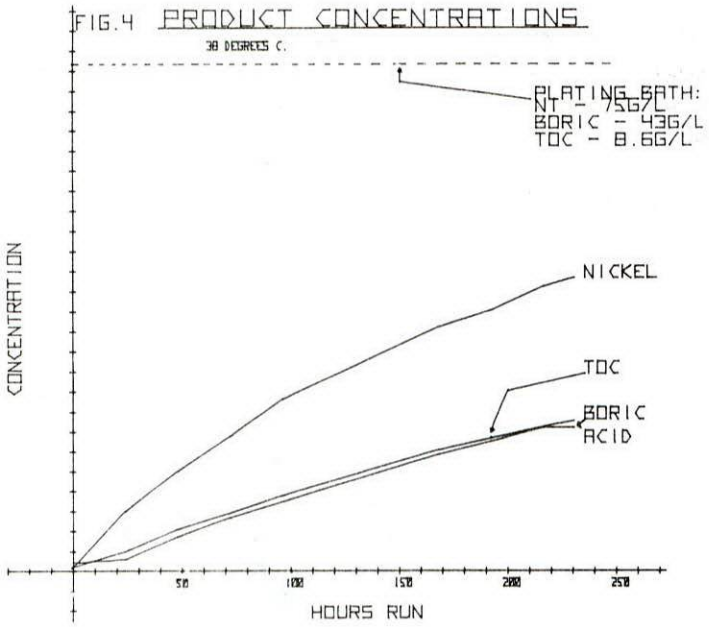
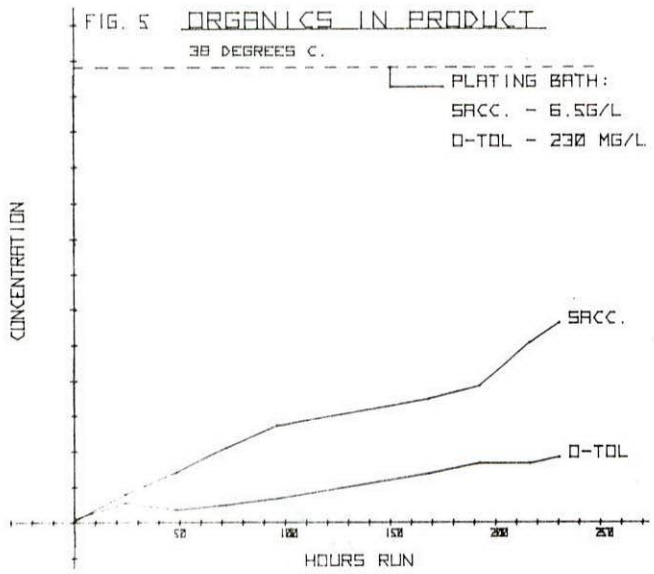


Figure 5 shows similar plots for saccharin and O-Toluenesulfonamide in the product. The saccharin results are from the routine process control titrations, which correlated well with periodic checks by the HPLC method, except at the higher end of the concentration range. Further method development on the HPLC technique is needed to get complete recovery at the higher concentrations. As can be seen, the O-Toluenesulfonamide is significantly retarded in transport as compared to the saccharin.



In order to confirm the validity of the analytical methods, a material balance was done on the entire system at the end of the second campaign. Table 1 shows the inputs of nickel, TOC, and saccharin as fed into the system by the metering pump introducing plating bath into the waste loop.

Quantities of these materials reporting at the end of the run in the Product, Waste, and Electrolyte Loops are also indicated and compared as a percentage of the input. All of these quantities are based on analysis of the various solutions with corrections for any volumetric changes during the campaign.

TABLE 1

MATERIAL BALANCE FOR CAMPAIGN 2

	System Input	In Product	In Waste	In Electrolyte	Total Reporting	% of Input
Nickel	1120.65g	1043.6g	54.74g	0 g	1098.3g	98%
TOC	133.3 g	61.6g	53.1 g	7.1g	121.8g	91%
Saccharin	100.75g	64.5g	8.4 g	22.4 g	96.2g	95%

Table 2 uses a similar approach to indicate the quantity of saccharin and TOC transported during the second campaign. A significant portion of the TOC found in the product is due to the saccharin content. Saccharin standards run through the TOC procedure gave good correlation throughout the range of concentrations involved in this work. On this basis, approximately 21 grams (34%) of the TOC in the product at the end of the campaign may be attributed to saccharin. The ultimate fate of saccharin transported into the electrolyte loop is questionable, and might be considered a loss as far as recovery from the process is concerned. However, in this experimental stack, one of the five membranes transporting anions connects with the electrolyte solution so that 20% of the anions will be found in the electrolyte. In a practical operating stack in a plating shop, the stack would be a minimum of 20 cell pairs, so that 5% or less of the anions would report to the electrolyte loop. It is assumed that some degradation of organics would occur in that loop due to oxidation at the anode surface.

TABLE 2

TRANSPORT EFFICIENCIES OF SACCHARIN AND TOC

	Input	Recovered in Product	Recovered in Electrolyte	Total Recovered	% of Input
Saccharin	100.75g	65.4g	22.4g	87.8g	87%
TOC	133.3 g	61.6g	7.1g	68.7g	51%

Some of the HPLC chromatograms are presented since they give a good visual depiction of the transport of certain organics through the electrodialysis process. Figure 6 is a section from the chromatogram on the plating bath used as feedstock for the work. The peaks are labeled to indicate saccharin, an unknown compound, and O-Toluenesulfonamide. While unidentified, the unknown material was found at corresponding concentrations in one of the proprietary addition agents for the bath. We presume it is a wetting agent. Figure 7 is a corresponding section of the chromatogram on product solution at the end of Campaign No. 2. As is visually obvious, the relative transport of O-Toluenesulfonamide and the unknown compound is very low as compared to saccharin.

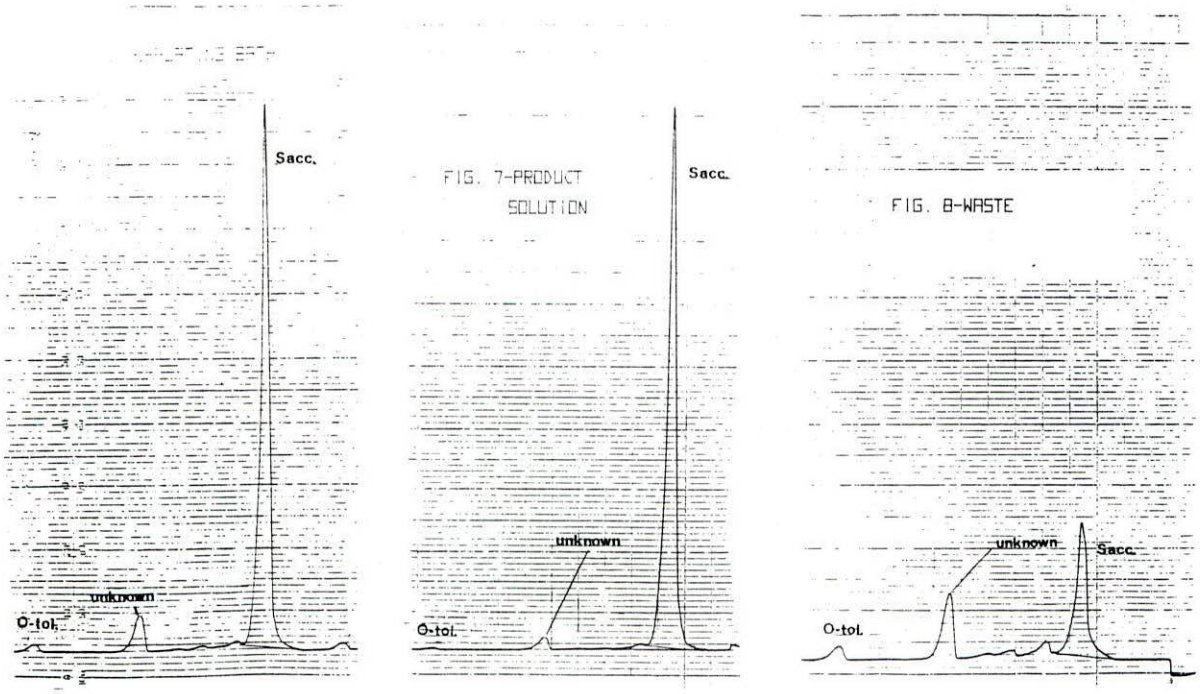
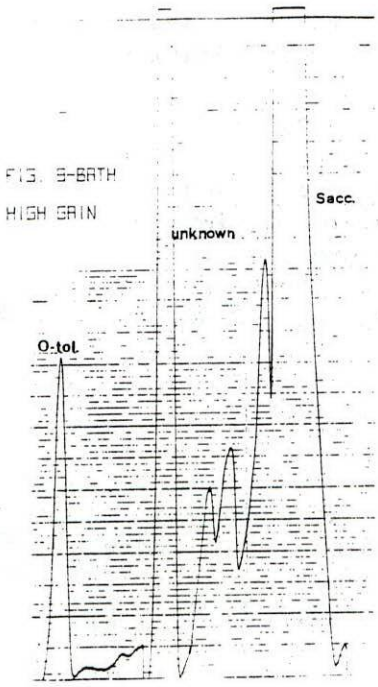
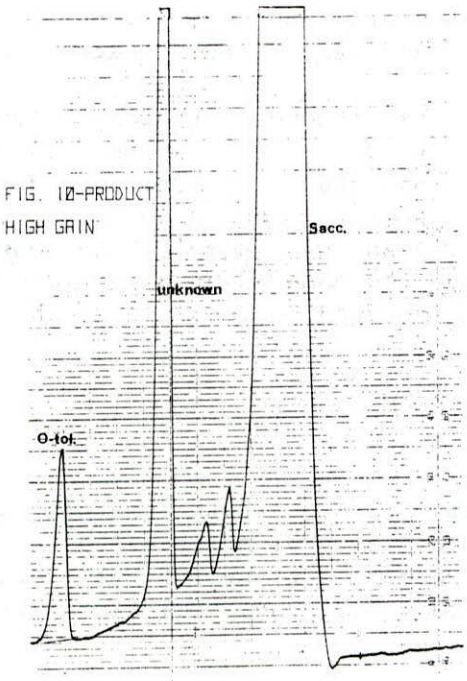


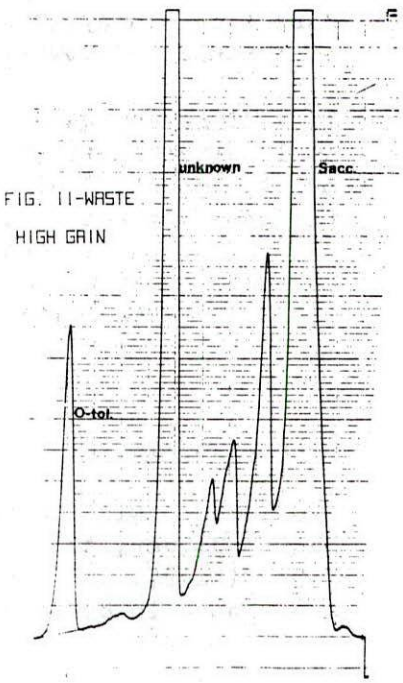
Figure No. 8 is the corresponding section for the waste solution at the end of Campaign No. 2. The relatively low saccharin concentration indicates that it was transported into the product and the relatively high peaks for the unknown and O-Toluenesulfonamide indicate their retention by the membranes.

Figures 9 , 10, and 11 represent the same sections of chromatogram for the plating bath, product, and waste solution respectively. The gain on the detector was turned up considerably to allow reasonable quantitation of the O-Toluenesulfonamide peaks. However, the graphs are reproduced here because the numerous peaks located between the large ones for saccharin and the unknown are indicative of variousother organic compounds not found in the virgin chemicals used for bath make-up. Thus, they represent reaction products which accumulate during operation of the plating bath. As can be seen in Figure 10, they are considerably reduced

in the product indicating retardation by the membranes.







Conclusions

The ability of electrodialysis to concentrate nickel salts to high levels has been documented previously and confirmed in this work. As compared to reverse osmosis and ion exchange, this characteristic increases the likelihood that product from an electrodialysis unit can be accommodated volumetrically in the plating tank due to natural evaporative losses.

This work has given a clear indication that organic materials (TOC) in the nickel plating rinsewater will be selectively retarded as compared with the desirable nickel salts. Furthermore, saccharin makes up a significant portion of the organic which does transport. This is very advantageous for recovery operations on single bright nickel plating lines or electroforming operations, since the saccharin is a valuable and needed constituent. In multi-layer nickel plating operations, both saccharin and O-Toluenesulfonamide can be readily and completely removed by activated carbon without the need for expensive and time-consuming chemical oxidation.[5) 11)] Thus, a simple filtration through activated carbon can remove a major component of the TOC from the electrodialysis product.

Bleed-off of a small stream of plating solution to the electrodialysis process can allow a consistently low level of TOC to be maintained in the plating bath. This scheme will drastically reduce, and quite likely eliminate, the need for periodic batch purification. The net result will be the obvious savings in nickel and organic addition agents, but more importantly, a more stable and consistent plating operation and elimination of down-time and labor for the batch purification treatment.

If a close approach to total recovery of nickel losses is desired, a small electrolytic metal recovery cell can be used to convert the appropriate amount of nickel into chunks of metal which can be recycled to the anode basket. It is believed that such a scheme would be simpler and less labor intensive than the precipitation scheme proposed by Fischer,[4] but would give the same advantage of complete recovery of all nickel together with an improved performance of the plating operation itself.

Acknowledgements

The authors wish to thank Dr. R. G. Luthy and his staff at Carnegie Mellon University for their counsel and assistance, and Dr. L. E. Lancy, John Ritzert, and Gary Hapach of Lancy International, Inc., for their assistance in experimental design and analytical methodology.

REFERENCES

1. Steward, F., and Lancy, L., Transactions IMF, 1978; Vol. 56, 113.

2. Steward, F., "Conservation and Recovery of Materials and Treatment of Wastes," IMF Guidebook Directory, 1981

3. Pinner, R., Electroplating and Metal Finishing, October, 1967.

4. Lancy, L., "Accumulation of Organic Impurities from Recovery of Nickel Plating Dragout," Metal Finishing, April, p 27 (1983)

5. Bocker, J.W., "Voraussetzungen zur automatischen Badsteuerung," Galvanotechnik 75, p 150 (1984)

6. Huss, R., Fischer, G., and Peters, W., "Process for the Removal of Organic Addition Agent Breakdown Products from Bright Nickel Solutions, Coupled with Complete Nickel Recovery," Galvanotechnik 71, No. 7 (1980)

7. Immel, W., and Gaethke, T., "Effect, Decomposition, and Separation of Organic Inhibitors in Bright Nickel Plating Solutions," Proc. Interfinish 80, p 66 (1980)

8. Eisenmann, J., "Recovery of Nickel from Plating Bath Rinse Waters by Electrodialysis,," Plating and Surface Finishing, 64 (11):34, (1977)

9. Markovac, V., and Heller, H. C., "Principles of Electrodialysis for Nickel Plating Rinsewaters," P&SF, 60, 66 (Dec. 1981)

10. Markovac, V., and Heller, H.C., "Engineering Aspects of Electrodialysis for Nickel Plating Rinsewaters," P&SF, 60, 67 (Jan. 1982)

11. Zerweck, K., Bocker, J., and Bolch, "Determination of Organic Agents in Watts Nickel Solutions for Electroforming," Interfinish 8, Kyoto, Japan (1980)

12. Langford, K., and Parker, J., "Analysis of Electroplating and Related Solutions," 4th Ed. (1971)

E-4

Environmental I
Session E

Environmental Design Considerations for Metal Finishing, Electroplating and Printed Circuit Board Manufacturing Facilities

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ENVIRONMENTAL DESIGN CONSIDERATIONS FOR METAL FINISHING, ELECTROPLATING AND PRINTED CIRCUIT BOARD MANUFACTURING FACILITIES

by
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I. General

In the initial planning phase for construction of a new facility to perform metal finishing and/or electroplating operations, many factors have to be taken into account. The planner must, obviously, first determine, based on the market anticipated, the type of product to be manufactured and how to implement its production. Production rate goals for both initial as well as for future growth patterns should be carefully defined. Deversification from single or double sided boards to multilayer and flex film circuitry or employing the newer substrate materials (i.e. teflon) in the printed circuit board manufacturing process, for instance, might also be anticipated to keep the facility abreast of rapidly changing technology. The planner must next determine the optimum location for the facility considering the availability of a skilled labor force, zoning restrictions, the possibility of Industrial Revenue Bond (IRB) financing and easy access to transportation routes, among others.

Environmentally, the political atmosphere of the target area must also be surveyed so that the planner can assess the level of regulation he is likely to be required to meet and the impact the regulations will have on his overall construction budget. Issues such as the availability of sewerage systems and whether local or municipal effluent discharge requirements will be more stringent than Federal statutes must be known prior to the commitment for location in any particular community. Once the location for the plant has been selected, the planner must next define and lay-out the process to be employed within the new facility.

II. Process Definition

The layout of the manufacturing plant, in general, should be determined, primarily, on material work flow patterns or facilitization. Efficient use of space can minimize delays between process operation steps which can contribute to the long range success of the facility.

The layout and definition of wet processing operations is equally important. Process bath chemistries should be evaluated for their potential impacts upon waste treatment requirements, air pollution control technology, hazardous waste storage and/or treatment needs and OSHA acceptability, among others. Provisions for segregation of incompatible materials, spill control and passive secondary containment

trenching must be employed without having an impact on product facilitization. Contingency planning for line-growth due to production rate expansion, implementation of integrated waste treatment technologies, source reduction techniques and product staging should be part of the process layout. Beyond the wet process itself, the layout must accomodate environmental and process support services.

III. Process Water Pretreatment

Water is one of the most critical raw materials used in electroplating/metal finishing operations. Rinsing operations following certain wet chemistry cleaning, developing, stripping, plating and etching processes as well as bath makeup may require water of a better quality than that available from the local municipality or the facility's private source. In the design phase of the project, the facility's source water quality and possible seasonal variations of same should be thoroughly investigated.

Depending upon the extent of need for higher purity water within the manufacturing process, based on limited water quality data in critical and non-critical rinses, the facility planner should determine whether total facility process water conditioning/treatment with on-site regeneration capabilities are warranted or whether point-of-use water treatment via service contract to an outside vendor will suffice. This decision should not be made lightly and should consider factors such as floor space availability, initial capital versus longterm operations and maintenance (O&M) costs, system life expectancy and susceptibility to adverse impacts caused by the characteristics of the facility's influent plant water.

IV. Local Exhaust Ventilation/Air Pollution (LEV/AP) Control

The primary function of an industrial exhaust system is to protect workers against potentially toxic airborne contaminants generated in the workroom. Additionally, a properly functioning exhaust system will also prolong the life of corrosion susceptible plant components and production equipment. The design of the exhaust ventilation system should be predicated upon the maximum levels mandated by the US Occupational Safety and Health Administration (OSHA) or according to the guidelines recommended by the American Conference of Governmental Industrial Hygienists (ACGIH).

Air pollution control for new or substantially modified plating and metal finishing exhaust systems is regulated by the individual states. Some states mandate and enforce specific emission limitations while others require the design to be in accordance with "standards of good engineering practice. Accordingly, applicable regulations and/or restrictions should be well defined prior to the initiation of design activities.

Gases, vapors and mists from the work area are captured at the point-of-generation, most efficiently, by tank/station mounted ventilation

hoods. Typically, each open surface tank is provided with an individual hood, however, the exhausts from most, if not all, of the process baths can usually be combined into a common duct network leading to a single scrubber/exhaust fan combination. Information on chemical fume compatibility prepared during the process inventory/definition phase of the project is used to define central or segregated system requirements.

The exhaust ductwork system should be designed to efficiently transport the pollutant laden mists/gases from the connected workstations to the Air Pollution Control Device. Since corrosive fumes are being transported, the systems are usually constructed of PVC, FRP or polypropylene. These materials are combustible to varying degrees and certain insurance underwriters may impose restrictions upon their designs including internal sprinkler systems or collapse rated PVC to inhibit flame spread caused by an electric immersion heater in a tank gone dry or some other similar mishap. The planner should be aware of these possible restrictions at the outset of the project to avoid costly redesign at a later date.

Packed bed, counter-current wet air scrubbers are the most efficient type of air pollution control device for the electroplating/metal finishing PCB industry. Their design provides a large surface area for gas-liquid contact which enables nearly complete capture of both mists and soluble gases. These systems normally employ a scrubber liquid recirculation system which neutralizes airborne acid mists and absorbs metal contaminants. Due to the eventual build-up of contaminants, a portion of the recirculating fluid is bled to in-house Industrial Wastewater Treatment (IWWT) facilities.

As with the purchase of any piece of major equipment, the initial cost should be only one of a number of factors to be considered when purchasing and/or designing air pollution control equipment. Matching the nature of the pollution problem with the most suitable technology is critical. Expected operation and maintenance costs, service life and performance are other important factors.

V. Make-up Air

The air removed from a workplace by the exhaust ventilation system must be replaced. This can occur either passively through infiltration or actively via a make-up air supply system. Since infiltration is almost never sufficient in providing the needed replacement air, well designed and energy efficient make-up air systems providing tempered air to the facility are typically employed to work in cooperation with exhaust ventilation systems.

Make-up air is usually supplied by a roof mounted supply fan equipped with air filters and some method of heating the air. Direct fired heating of the influent air with natural gas is usually the method of choice due to its relative efficiency and lower cost in comparison to other fuels. Steam can be employed as a heat source but winter freeze-

up problems and relative slow response to changing air temperatures present significant disadvantages to it use.

The distribution of make-up air in the workplace is important from the stand point of worker comfort but equally important for the proper operation of the exhaust ventilation system. Cross-drafts over the tops of vented process tanks can significantly affect the efficiency of the exhaust system and should be avoided through the use of adjustable louver arrangements at the injection points of the duct diffuser system.

Heat recovery from exhaust air and the recirculation of interior air to the make-up air system are generally not recommended for the metal finishing/electroplating industry. This is due to the corrosive nature of exhaust fumes and mists upon heat exchangers and the risk of reintroduction of air bourne contaminants into occupied areas. In facilities where heat recovery and/or recirculation systems have been employed, maintenance and equipment replacement costs associated with corrosion usually convert initial economic feasibility into a long term headache.

VI. Electrical Considerations

As previously mentioned, the use of corrosion resistant materials within all wet manufacturing areas of the electroplating/metal finishing facility can be an important factor in the useful life of both capital equipment and support services. This is especially true of electrical devices. PVC or other thermoplastic conduit should be used for raceways. Local disconnects should be housed in Fiberglass or other NEMA 4X rated enclosures and lighting fixtures should be specially selected for use in wet and possibly corrosive or explosive atmospheres.

A worst case design approach, in spite of the attention given to exhaust ventilation and make-up air systems, may result in higher initial construction costs but long term operation and maintenance costs for equipment replacement will be minimized.

VII. Spill Protection

With the current concern and attention given to groundwater quality and environmental protection in general, more and more new facilities employing wet processes are incorporating passive spill control/ secondary containment provisions into the building designs. Though capital appropriations for these controls may be difficult to extract from the facility budget, recent experiences are showing that the initial expense is minor when compared to the cost of a remedial groundwater cleanup project made necessary as a result of an uncontrolled release of chemicals through the facility infrastructure.

Wet processing areas should be contained by bermed exterior walls or by a network of subslab drainage trenches for spill collection.

Service walkways or other pedestrian areas should be pitched to low point collection systems. Specially designed FRP or epoxy protective floor coatings should be employed throughout the wet manufacturing areas and the type of material selected for use should be specific to the service conditions anticipated (i.e., spills, immersion, or drippage). Though floors should be designed to be operated in a dry condition, contingency planning is the best insurance against future liability.

Beyond passive containment control, active spill response measures may be employed for additional protection. Automatic spill detection alarms can be incorporated into the facility design to alert a trained emergency response team that an event has occured and that expeditious clean up activities are required. Providing the proper clean up materials are always on hand, the impacts of an event can be minimized.

VIII. Chemical and Hazardous Waste Storage

Areas for storage of process support chemicals as well as waste by-product storage should be designed into the facility layout during the planning phase. Too often, these considerations are pushed off to a low priority in comparison to the primary goals of the manufacturing operation. Segregation of incompatible chemistries (i.e., acids and alkalis) should be carefully planned with each designated area given OSHA, safety, spill control and secondary containment considerations. Bulk chemical storage versus drum chemical storage should be decided early in the planning phase since the chemical storage area layout and material movement within the area will be affected accordingly.

Storage of organics must be considered separately since red label flammable storage will require special structural/architectural and fire protection system designs. Outdoor, underground, organics spill containment vaults, used in conjunction with exterior wall or roof mounted blowout panels and high density sprinkler systems may be implemented as state-ofthe-art design. The facility insurance underwriter should be closely involved with any decision for on-site flammable organics storage from the initiation of the project planning stage.

IX. IWWT Requirements

Effective August 28, 1983, the industrial wastewater effluent from a newly constructed metal finishing/electroplating facility is required, at a minimum, to meet Federal Pretreatment Standards for New Sources (PSNS) or New Source Performance Standards (NSPS) depending upon whether the discharge is made indirectly to a locally owned municipal treatment plant (POTW) or directly to a receiving surface water via a NPDES permit, respectively. The regulations require that compliance within either of these subcategories of the Metal Finishing Guidelines (40 CFR 433) be attained upon the commencement of the discharge. In addition to the minimum Federal requirements, the local municipality

may impose more stringent limitations upon an industry which may impact the type and extent of industrial wastewater pretreatment (IWWT) technology employed or may even dictate the selection of an alternate site.

Knowing the regulations which will apply to the new facility, the planner should conduct a thorough inventory of all process manufacturing operations which will contribute to the influent wastewater stream. The typical flowrates for all continuously running rinses and volumes with associated dump frequencies for intermittent batch discharges as well as the chemical composition/characteristics of either source must be initially known so as to define the optimum type of pollution abatement technology to use to meet end-of-pipe effluent restrictions. Remember that the proper design of an IWWT system should begin with in-process controls to minimize the volume of waste generated. Source reduction considerations should be implemented in the process definition phase and benefit/cost justification for implementing point-of-generation pollution abatement or recovery technologies should be completed to assess their economic feasibility.

Treatment can be categorized as either integrated, using source reduction or in-line recovery methods, or end-of-pipe technology such as physical-chemical precipitation of the mixed metal influent with caustic soda, lime or soda ash. Whether or not end-of-pipe complexing agent bond destruction/ metal valence reduction chemistries are employed (ferrous sulfate, sodium hydrosulfite, sodium borohydride, etc.) as a precursor to or in conjunction with hydroxide precipitation is largely dependent upon the results of the process inventory and information gathered from chemical suppliers. Some electroplating metal finishing operations utilize process chemistries which contain common complexing agents such as EDTA, Quadrol, ammonia and citrates, among others, and it is fairly common to employ dual train IWWT chemistries as part of end-of-pipe pollution abatement facilities in these cases.

The best way to approach wastewater pretreatment requirements for the facility is to prepare a comprehensive data base of process operations and chemical characteristics, as previously discussed, and to work in constructive cooperation with local, state and Federal regulatory officials. Treat these officials as a part of your project team, rather than as adversaries, in implementing your plans. Be forthright and discuss your problems openly and honestly with them and negotiate solutions as required. Follow-up on a periodic basis and keep them informed throughout the course of the project of any changes to the construction/start-up schedule. Cooperate and encourage their participation, where appropriate, in commissioning activities subsequent to construction. Such an approach, initially, will pay for itself many times over in the course of the facility's residence in the community.

X. Budget Impacts - Case Studies

To illustrate the impact of proper planning for environmental controls relative to wet manufacturing operations, Table 4 shows, on a percentage of the total construction basis, the cost of implementing the various elements discussed in this presentation. The figures presented were developed from actual projects recently completed. The table does not include, however, the costs associated with the actual building construction (walls, slab, roof) since architectural features vary so greatly from job to job.

The higher cost of process water pretreatment at Company A can be attributed to its location in the Southwest section of the United States where the influent plant water contained between 350 and 400 mg/l ($CaCo_3$) of hardness. Accordingly, the pretreatment system was comprised of filtration, carbon adsorption, reverse osmosis and ion-exchange softening with on-site regeneration capabilities. The second facility employed only cannister type point-of-use ion-exchange water pretreatment under a service contract to a local vendor.

The second point of interest between the two projects is the cost of LEV/AP control systems. Capital and installation costs for the systems employed at either facility were essentially equivalent. However, since the scope of the second project was about on-half that of the first, the comparable costs for the air pollution control system at the second facility consumed more than twice of the percentage of the overall construction budget.

In either case, only above 1/5 of the total construction budget allocated for wet manufacturing related operations was expended for process related hardware. The remainder of the budget was distributed to environmental control support services and installation.

XI. Summary

I have only briefly touched upon some of the more critical but sometimes overlooked environmentally related aspects of a new electroplating/metal finishing facility project. I hope that some of the topics presented here will be useful to those of you who are anticipating renovations of your existing facilities or construction of a new plant.

TABLE 1

SOURCE REDUCTION TECHNIQUES

1. Minimize bath chemical concentrations to low end of recommended operating range.

2. Maximize bath operating temperature to minimize solution viscosity.

3. Maintain racking orientation to maximize drainage.

4. Minimize board withdrawal rates and allow time for drainage above the process tank prior to rinsing.

5. Install drain boards between process and rinse tanks to reroute drippage back to process tanks.

6. Utilize air knives over process tanks to minimize dragout loss due to poor drainage.

7. Employ multistage counter-current rinsing with low pressure oil-free air agitation to minimize rinsewater flowrates.

8. Reuse chemically compatible rinsewaters in non-critical areas (i.e. acid rinse to alkali rinse).

9. Employ flow restriction valves, conductivity controls or demand actuated solenoid valves on process water supply lines to minimize water consumption.

10. Reuse uncontaminated cooling water as process rinsewater feed as appropriate.

11. Utilize bath chemistry substitutions to minimize impacts on associated environmental systems.

TABLE 2

RINSEWATER QUALITY GUIDELINES

Location/Operation	Recommended Contaminant Concentration
inse following CuCl etch and prior to trip	140 mg/l Cu
inse following alkaline clean and rior to pickle	750 mg/l - Total contaminants
inse following acid pickle and prior o acid plate	750 mg/l - Total contaminants
inse following alkaline clean and ior to drying	375 mg/l - Total contaminants
ximum copper contamination of resist rip	110 mg/l
lowable fluoride contamination of drochloric pickle	1 mg/l
nse following alkaline etch plenisher rinse	15 mg/l - Copper
lowable Caustic (NaOH) in rinse(s) llowing resist strip	350 mg/l - 1st stage 5 mg/l - 2nd stage
nal rinse following electroless pper plating	25 mg/l
nal rinses - general	2-400 mg/l - Total contaminants
nse after nickel (or copper or any her heavy metal)	40 mg/l - Total
nse after cyanide	40 mg/l - Total
nse after alkaline clean and prior alkaline tin plating	7,500 mg/l - Total

TABLE 3

COMMON CHELATING AGENTS

Ammonium Chloride
Ammonium Hydroxide
Ammonium Bifluoride
Acetylacetone
Citric Acid
Chromotropic Acid (DNS)
Cyanide
Diethylenetrinitrilopentaacetic Acid (DTPA)
Dihydroxyethylglycine
Dimeracaptopropanol
Dimethylglyoxime
Dipyridyl (2,2-Bipyridine)
Disalicylalpropylenedimine
Diphenylthioformic Acid
Ethylenediamine
Ethylenediaminetetraacetic Acid (EDTA)
Glyceric Acid (Dihydroxypropanoic Acid)
Glycolic Acid (Hydroxyacetic Acid)
Hydroxyethylethylenediamine
Hydroxyethylethylenediaminetriacetic Acid
Hydroxyethylidenediphosphonic Acid
Hydroxyquinoline
Hydroxyquinoline Sulfate
Lactic Acid
Malic Acid
Monosodium Phosphate
Nitrilotriacetic Acid (NTA)
Phenanthroline
Phosphoric Acid
Phthalocyanine
Polyethyleneimine
Polymethacryloylacetone
Potassium Xanthate
Rochelle Salts (potassium sodium tartrate)
Salicylaldehyde
Salicylaldoxime
Sodium Citrate
Sodium Fluoride
Sodium Gluconate
Sodium Pyrophosphate
Sodium Tripolyphosphate
Succinic Acid
Sulfosalicylic Acid
Tartaric Acid
Thioglycolic Acid
Thiourea
Toluene Dithiol
Triethanolamine
Triethylenetetramine
Trisodium Phosphate (TSP)
Quadrol

TABLE NO. 4

CASE STUDIES - BUDGET DISTRIBUTION

		Percent of Construction Budget	
		Company A	Company B
1.	Process Equipment & Fit-up	19.0	18.9
2.	Process Water Pretreatment	14.0	1.3
3.	LEV/AP Systems	9.2	18.6
4.	Make-up Air Systems	5.5	7.4
5.	Electrical Power Distribution and corrosion resistant lighting	9.9	10.7
6.	Floor Coatings and Gratings	7.0	5.7
7.	Segregated Drainage to IWWT	7.9	8.6
8.	IWWT System (PSNS)	27.5	28.8
	TOTAL	100.0	100.0

E-5

Environmental I
Session E

Environmental and Safety Consequences - The Hidden Value in New Metal Finishing Processes

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ENVIRONMENTAL AND SAFETY CONSEQUENCES - THE HIDDEN VALUE IN NEW METAL FINISHING PROCESSES

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INTRODUCTION

Concern for the environment and safety of employees by the public and public interest groups has resulted in an upsurge of legislation affecting the selection of process chemicals in the Metal Finishing Industry. Traditionally, performance has been the basis of selection; new restrictions, however, require that other factors dealing with the toxicological, safety in use and handling, and the environmental properties of the chemicals must be considered and balanced to yield an acceptable product. To meet this challenge, the chemical manufacturer and the metal finisher continue to work in concert to develop processes which meet the required performance criteria while, and at the same time, deal with the issues of toxicology, safety and the environment. Significant positive impact has been achieved in the last ten years in each of these areas with benefits for both the manufacturer and the user. Results are presented to illustrate the benefits and point the way for future developments.

TOXICOLOGY AND SAFETY

The Chemical Manufacturer is concerned both with synthesized products and those that it purchases. Responsibility for the products within its own facility and those of the end users is of primary importance. This responsibility is controlled by the requirements for toxic substance control, hazardous communication, shipping, and safety in the work place.

Toxic Substance Control Act (TSCA) Requirements

Before a chemical is first synthesized by the researcher with a particular end use in mind, the chemical is reviewed for any potential health and safety problems. A suspected carcinogen can often be identified by looking at its structure. Another aspect is to see if the chemical could be explosive by nature. If the chemical passes this precursory stage and is to be a manufactured product, the Toxic Substance Control Act (TSCA) requires that the Manufacturer file a Premanufacture Notification, if the chemical is not on the TSCA Inventory. Acute Toxicity data, which is the basic set of information is usually run on new chemicals, takes from three to six months, at an approximate cost of $5,000.00. This program looks at the effect of the chemical on swallowing, irritation to the eyes, and to the skin of animals, which is related to humans. These tests are conducted on the pure substance and, since the substance is diluted during use (usually > 100:1) in the Metal Finishing application, this is taken into account during the review process. It is not required by law to do the above testing; but if it is done the test results must be reported. There is a 90-day review process and the clock can be stopped on the review process at anytime.

Though not usually required of Metal Finishing Chemicals, a longer testing program can be initiated, if the substance is a suspected carcinogen, to investigate potential carcinogenic effects. This can take up to three years, at a cost of up to 3/4 million dollars. During this time, the "review clock" would be stopped.

Material Safety Data

Once the product has been approved for manufacture, the Manufacturer must provide a Material Safety Data Sheet (MSDS) for each product containing the substance if it is hazardous. This is now required due to "Right-To-Know" rules currently being enacted in each state[1]. The OSHA ruling as published in the Hazard Communication Standard 29 CFR 1910.1200 is effective November 1985, for all chemical manufacturers, importers and distributors and is effective May 1986 for all employers. This standard is shown in Figure 1. The MSDS (Figure 2) contains the manufacturer's name with an emergency phone number, chemical name, chemical formula and tradename, and physical and chemical data needed for its safe use and disposal.

Shipping Requirements

Once the material has been approved for manufacture, and the MSDS has been prepared, the product then must be shipped to the end user. Shipping is either regulated by the Department of Transportation (DOT), the International Marine Dangerous Goods (IMDG) or the International Air Transportation Association (IATA). Each of these sets of regulations specifies certain items that must be clearly identified on the container during shipment. The EPA also requires that reportable quantities be identified. This is specifically in case of an accidental spill. The range of the reportable quantity is 10 to 5000 lbs. For example, a package of less than 5,000 lbs. of nickel sulfate must have a reportable quantity on it, as well as a package of more than 10 lbs. of cupric sulfate or sodium or potassium cyanide. However, a 5 lb package of sodium cyanide only has to have a poison label and no reportable quantity.

Safety in the Workplace Requirements

After the chemical has been shipped and is in use, it is covered by a variety of regulations such as those for ventilation and labelling. The American National Standards Institute (ANSI) publishes a standard for the labelling of Hazardous Industrial Chemicals[2] and a standard for Ventilation and Operation of Open-Surface Tanks[3]. It is recommended that these are followed by the user. The MSDS for each chemical in use in a plant must be available to the workers and special training programs should be developed for the workers. These programs should cover operating safety, exposure prevention and emergency procedures.

In cases of spills or other accidents, the DOT has provided an Emergency Response Guidebook[4] for use by firefighters, police and other emergency services personnel. This book can be used as a guide for initial actions to be taken by the Emergency response personnel to protect themselves and the public when they are called to handle incidents involving hazardous materials. To obtain additional assistance for the most effective handling of an incident, a call can also be made to the Chemical Transportation Emergency Center (CHEMTREC). CHEMTREC provides information and/or assistance to those involved in or responding to chemical or hazardous material emergencies. CHEMTREC is a public service of the Chemical Manufacturers Association in Washington, D.C. and was established in 1971. It operates in two stages. First, on receipt of information regarding the name of a chemical, it provides immediate advice on the nature of the product and steps to be taken in handling the early stages of a problem. Secondly, CHEMTREC promptly contacts the shipper of the material involved for more detailed information and appropriate follow-up, including on-the-scene assistance when feasible. Some manufacturers also operate their own 24-hour response teams for such emergencies.

FEDERAL OSHA

Effective Date(s): November 1985 chemical manufacturers, importers, distributors; May 1986, employers

Sunset Clause: None

HAZARDOUS SUBSTANCES	All chemicals, normal conditions of use, foreseeable emergency, one positive study with statistically significant evidence; 29 CFR 1910 Subpart Z, ACGIH, TLVS; NTP, IARC lists.
REQUIREMENTS	Written hazard communication program, hazard evaluation procedures, hazardous chemicals list, inform contract employers; container label, chemical or common name; MSDS; information and training; review potential hazards for all chemical substances and mixtures; chemical manufacturers or importers provide MSDS to distributors and manu- facturing purchases before or at time of shipment.
RESPONSIBILITY	Federal OSHA, state preemption; manufacturing sector SIC codes 20-39; manufacturers, importers, distributors, manufacturing purchasers, employers.
EMPLOYER-EMPLOYEE RESPONSE	MSDS, readily accessible during each work shift.
EXEMPTIONS	Labeling FIFRA, FDA regulated substances and components, distilled spirits, consumer products, immediate use containers; RCRA hazardous waste; tobacco; wood; articles; food, drugs, cosmetics for personal consumption; less than 1.0% of a mixture; less than 0.1% carcinogens.
TRADE SECRETS	Chemical manufacturers, importers, employers; may withhold all specific chemical identities under certain conditions; upfront substantiation not required.
OUTSTANDING REQUIREMENTS	Covers all chemical substances and mixtures; state preemption; only one positive statistically significant study for hazard determination; covers only SIC codes 20-39; may claim chemical name for any substance as trade secret; written hazard communication program.
COMMUNITY/ EMERGENCY RESPONSE	None.
RECORD-KEEPING	Most current MSDS.
EMPLOYEE RIGHTS	Request information.
RESEARCH LABORA-TORIES	Labels on incoming containers not removed or defaced; maintain and make available received MSDS; training.

FIGURE 1. Hazard Communication Standard 29CFR1910.1200

MATERIAL SAFETY DATA SHEET

SECTION I

MANUFACTURER'S NAME	EMERGENCY TELEPHONE NO.
ADDRESS	
CHEMICAL NAME AND SYNONYMS	TRADE NAME AND SYNONYMS
CHEMICAL FAMILY	FORMULA

SECTION II. HAZARDOUS INGREDIENTS

SECTION III. PHYSICAL DATA

SECTION IV. FIRE AND EXPLOSION HAZARD DATA

SECTION V. HEALTH HAZARD DATA

SECTION VI. REACTIVITY DATA

SECTION VII. SPILL OR LEAK PROCEDURES

SECTION VIII. SPECIAL PROTECTION INFORMATION

SECTION IX. SPECIAL PRECAUTIONS

FIGURE 2. Material Safety Data Sheet

ENVIRONMENTALLY ACCEPTABLE PROCESSES

The manufacturer not only has to deal with the above regulations concerning the research, manufacturing, shipping and operation of a particular Metal Finishing process, but also they must try to find substitutes for chemicals currently used in the workplace, when these chemicals are unfavorably viewed. Such chemicals include hexavalent chrome, cyanide, cadmium, as well as certain immersion strippers and etching baths. The emphasis in many research organizations is to find processes that may be substituted for these chemicals. Substitution is not that easy. The new finishing process not only must eliminate the offending chemical, but it must also operate as economically as the traditional process and the results must be equal or superior. Without this market edge, the old process will not be replaced. Some examples of environmentally acceptable processes will now be described.

Trivalent Chromium for Decorative Plating Processes

In the early 1970s, various government agencies encouraged the Metal Finishing Industry to find a substitute for hexavalent chromium, which is usually used in the form of chromic acid. Chromic acid is known to have undesirable health characteristics. It is toxic and corrosive to the skin, causing ulcers; inhalation causes damage to the respiratory system, and it is a suspected carcinogen. In anticipation of further government regulations, research programs were initiated to commercialize a trivalent chromium plating process.[5] This research area was not new. In the 1800s, chromium was deposited from trivalent electrolytes, but over the years there was no process produced that could match the dependability of hexavalent chromium baths. Since the late 1970s, chromium deposition from electrolytes containing trivalent chromium salts has been in commercial use.

A process had to be developed that had as good plating characteristics as hexavalent chromium, i.e., good covering power, color and hardness and good corrosion performance. Such a process has been developed[5] and reported at SUR/FIN '83[6].

As a result of recent improvement in trivalent chromium plating processes, it was found that the trivalent chromium baths do exhibit comparable plating characteristics. In fact, because of increased covering power, the absence of sensitivity to nickel brightener levels, lack of whitewash due to current interruption, and the absence of high current density burning, it meant that productivity could be increased through a trivalent chromium bath as compared to an hexavalent chromium bath. This led to increased productivity and reduced rejects on lines using the trivalent chromium plating process.

Another advantage of the trivalent chromium bath is that it contains an average of 25 gm/liter total chromium as compared to a conventional hexavalent chromium bath which may contain between 120 to 140 gm/liter total chromium. This factor leads to reduced waste treatment costs not only due to the fact that reduction of the chromium is not necessary but also due to the fact that the total metal loading is reduced. Table I compares the average plating costs per square foot processed and the waste treatment cost per gallon of dragout for a working trivalent chromium process solution with a working hexavalent chromium process solution.

TABLE I

TYPICAL PLATING AND WASTE TREATMENT COSTS

TRIVALENT VS. HEXAVALENT CHROMIUM

Process	Metal Content (gm/L)	Cr Thickness (mil)	Plating Cost (a) ($/Ft^2)	Effluent Treatment Cost (b) ($/gal dragout)	Sludge Produced (c) (Ft^3/gal-dragout)
Trivalent Chromium	26.5	0.01	0.03-0.06	0.14	0.021
Hexavalent Chromium	126	0.01	0.01-0.02	1.45	0.075

(a) Basis: 2 gal./1000 ft.^{2} dragout.

(b) Hexavalent chromium treatment included reduction with sodium bisulfite at a pH of 2.5 and precipitation with lime and a flocculant at a pH of 9.0. Trivalent chromium treatment included precipitation with lime and a flocculant at a pH of 9.0 only.

(c) Sludge produced was air dried. Volume calculation is based on 35% DWS at 80 lbs/cu. ft.

It can be seen in Table I that even though the plating costs are generally more for the trivalent bath, the associated waste treatment costs and sludge produced are far less, thus making the process more attractive.

As with any new process, the process bath control and operation are always different than for a conventional process, and for the trivalent chromium bath this is also true.

Trivalent chromium solutions are more sensitive to heavy metal contamination than hexavalent chromium solutions. Cation contaminants, such as, copper, iron, lead, nickel and zinc affect the operation of the bath. Tolerance levels of which are compared in Table II. Tolerance levels for chloride are also shown below.

TABLE II

A COMPARISON OF ANION AND CATION CONTAMINANTS FOR CHROMIUM PLATING PROCESSES

CONTAMINANT	TOLERANCE UNDER OPTIMUM CONDITIONS	
	Trivalent Chromium Process	Hexavalent Chromium Process
Chromium (+3)	N/A	<1/2 oz/gal
Chromium (+6)	<10 mg/L	N/A
Lead	<20 mg/L	N/A
Copper	<20 mg/L	
Iron	<500 mg/L	
Nickel	<200 mg/L	<10 gm/L Total
Zinc	<50 mg/L	
Chloride	N/A	<100 mg/L Total

These tolerance levels for heavy metal contamination are at maximum conditions, and in practice will generally be lower, since more than one contaminant normally will be present in the bath. The effect of impurities in trivalent chromium deposits is to produce hazy-white to very dark, streaked thin deposits having poor coverage. Nickel contamination is due to improper rinsing between the nickel and chromium and parts left on the bottom of the chromium tank. This problem can generally be corrected by an efficient rinse cycle.

Lead contamination in trivalent chromium baths is the result of leaching of lead salts from liners previously used for hexavalent chromium baths. In spite of thorough cleaning, some lead and chromium salts can remain in the lining. Lead contamination can be removed by low current density electrolysis as well as by precipitation.

Copper, iron and zinc contamination in trivalent chromium baths results from parts dropped in the process bath or attack on unplated areas, as for example, blind holes and open tubing. Fortunately, these impurities can be removed either by precipitation and filtration or by low current density electrolysis. Precipitation techniques using nonhazardous materials have broadened the operation of trivalent chromium plating.

The frequency of chromium bath purification will depend on the efficiency of the rinsing between nickel and chromium, the type of work being plated, the number of parts falling into the tank and the plating time.

Trivalent chromium baths also contain between 70 to 80 gm/L of ammonia. This is necessary because of the chemistry of the bath matrix. These ions are lost via dragout and can enter an effluent treatment system. In areas where there are strict effluent limits for heavy metals or where there are limits for ammonia nitrogen or ammonia, the trivalent chromium dragout can be successfully treated by oxidation with sodium hypochlorite or chlorine to reduce the ammonia to an acceptable level. In practice, this has not been a problem.

The recovery of the trivalent chromium bath is best effected by the use of a direct dragout recovery tank and forced evaporation of the bath to make room for the recovered solution.

The trivalent chromium process has now been field tested and is a proven process. The benefits of this process are: significantly improved chromium coverage which allows more parts per rack, reduced reject rate, improved quality, while waste treatment costs are reduced and the use of toxic chromic acid is eliminated.

Alkaline Cyanide-Free Copper for Copper Plating Applications

In terms of tonnage, probably more copper is plated or etched per year than any other metal. Copper is easily plated from an aqueous solution containing copper ions, so much so, in fact, that if the activity of the copper is not reduced, the deposit occurs as an immersion plate and is nonadherent. An agent is necessary to complex the copper ion sufficiently so that the plating process can be controlled to give a uniform, adherent deposit. The most common complexing agent used for this purpose was, until recently, cyanide. In the last 10 years, however, various government agencies have encouraged the Metal Finishing Industry to find an alternative to cyanide plating systems, by the enforcement of stricter effluent limits and the concern for the use of cyanide in the workplace. In order to meet this new challenge, technology was directed towards: (1) The reduction of cyanide concentrations, and (2) the substitution of cyanide with new, nontoxic complexing agents.[7]

To date, at least four different types of commercial electrolytes have been developed. These are the:

Micro Cyanide Bath
Copper Pyrophosphate Bath
Acid Copper Sulfate Bath
Copper Fluoroborate Bath

The Micro Cyanide Bath contains 11.7 gm/L of copper metal and 2.5 gm/L of free KCN, as well as other agents. This is a very low cyanide formulation bath which was not fully acceptable to the plating industry because it had limited cathode efficiency and still required the handling, storage and waste treatment of cyanide materials.

The Copper Pyrophosphate baths exhibit high efficiency and good throwing power, but also had some inherent limitations. A copper strike was required prior to plating on steel and zinc die cast substrates and the baths have limited solution life due to the hydrolysis of pyrophosphate to orthophosphate.

The Acid Copper Bath contains 210 gm/L of copper sulfate pentahydrate and sulfuric acid. While acid copper plating baths can provide excellent plating speed and outstanding leveling and brightness, they have certain limitations which include the need for a copper strike prior to plating on steel and zinc die cast parts and on an acid resistant ventilation system to remove "acid mist".

The Copper Fluoroborate Bath contains 224-448 gm/L of copper fluoroborate and fluoroboric acid. Other cyanide-free baths also have been developed but were never commercially successful.

The four baths described were not a viable alternative to cyanide copper plating baths for industrial applications. In many cases, although cyanide had been eliminated, alternate complexing materials posed serious waste treatment problems and reduced deposit quality. Following the development of the above baths, further research culminated in the recent introduction of an alkaline cyanide-free copper plating process[7], shown in Table III.

TABLE III

TYPICAL ALKALINE CYANIDE-FREE COPPER SOLUTION COMPOSITION

Copper Sulfate Pentahydrate	37.5 g/L (5.0 oz/gal)
Organic Complexing Agent	162.5 g/L (21.7 oz/gal)
Buffer Salts	20.0 g/L (2.7 oz/gal)
Proprietary Anode Depolarizer	0.40 g/L (0.05 oz/gal)
Proprietary Addition Agents*	

*Optional - Added to provide additional brightness to the deposit.

The copper deposits plated from the new process, under optimum solution concentrations and operating conditions, are fine-grained, ductile and adhere to steel, brass and bronze base metals. Research is still continuing to improve adhesion on zinc and aluminum substrates. The anodes used for this process are specific to the process and both high cathode effficiency and high throwing power are inherent as compared to conventional copper systems. Ductility and corrosion resistance of the deposit were found to be comparable, if not better, than cyanide based copper deposits.

This alkaline cyanide-free copper process has been used successfully in both rack and barrel applications. The process can be used in both copper strike and copper plate applications. Typical plating and waste treatment costs for working baths are compared in Tables IV and V.

TABLE IV

TYPICAL PLATING AND WASTE TREATMENT COSTS

CYANIDE-FREE COPPER VS. CONVENTIONAL CYANIDE COPPER BATH, STRIKE APPLICATION

Process	Metal Content (gm/L)	Total Cyanide (gm/L)	Copper Thickness (mil)	Plating Cost (a) ($/Ft^2)	Effluent Treatment Cost (b) ($/gal dragout)	Sludge Produced(c) (Ft^3/gal-dragout)
Cyanide-Free	8.3	N.A.	0.25	0.03	0.17	0.022
Cyanide Copper Strike	26.9	32.0	0.25	0.03	1.47	0.019

(a) Basis: 1 gal./1000 ft^2 dragout.

(b) Cyanide treatment included two stage oxidation of the cyanide with sodium hypochlorite at a pH of 11.0 and 8.0, with precipitation of the copper metal ion at a pH of 9.5 with lime and a flocculant.

(c) Sludge produced was air dried. Volume calculation assumed 35% DWS and a density of 80 lb./cubic foot.

It can be seen from Table IV that the plating costs for the two baths are comparable, however, the costs associated with waste treatment are far less. Due to buffering agents in the process solution it was found that there is no significant difference in the sludge generation per gallon of dragout between the two processes even though copper metal content of the bath was less for the cyanide-free bath.

It can be seen from Table V that acid copper is clearly less costly to operate and waste treat; however, it cannot be used for every application. A true comparison should be made between the cyanide-free and cyanide copper data. The operating costs and sludge produced by the cyanide-free bath are slightly more than for the cyanide copper bath, however, the waste treatment cost for the cyanide copper bath is eight times that for the cyanide-free bath.

TABLE V

TYPICAL PLATING AND WASTE TREATMENT COSTS

CYANIDE-FREE COPPER VS. CONVENTIONAL COPPER BATH, PLATE APPLICATION

Process	Metal Content (gm/L)	Total Cyanide (gm/L)	Copper Thickness mil	Plating Cost (a) ($/Ft^2)	Effluent Treatment Cost(b) ($/gal dragout)	Sludge Produced(c) (Ft^3/gal-dragout)
Cyanide-Free	8.3	N.A.	0.5	0.059	0.17	0.022
Cyanide Copper	26.8	32.0	0.5	0.041	1.47	0.019
Acid Copper	58.45	N.A.	0.5	0.028	0.103	0.0125

(a) Basis: 1 gal./1000 ft^2 dragout.

(b) Cyanide treatment included two stage oxidation of the cyanide with sodium hypochlorite at a pH of 11.0 and 8.0, with precipitation of the copper metal ion at a pH of 9.5 with lime and a flocculant.

(c) Sludge produced was air dried. Volume calculation assumed 35% DWS and a density of 80 lb./cubic foot.

Unlike the trivalent chromium process the alkaline cyanide-free copper plating bath is more tolerant to contaminants which are introduced into the system via drag-in and dropped parts.

The cyanide-free copper process is an alkaline solution process which contains a relatively strong complexing agent. The copper may be removed from rinse waters by displacement with calcium ions through the use of either lime or a calcium chloride/sodium hydroxide mix. Recovery of the cyanide-free copper process is best effected by the use of a direct return drag-out tank or electrolytic recovery of the copper.

As a practical alternative to cyanide based copper processes, this novel alkaline cyanide-free process does indeed compare favorably with cyanide copper systems but without the treatment problems associated with cyanide.

Zinc Coatings for Increased Corrosion Resistance

Zinc is principally used as a coating to protect iron and steel from rusting. Because of the low cost of the zinc metal, and with a relatively long maintenance free protective life, zinc coatings are recognized as the most economical method of protecting iron and steel products against atmospheric corrosion.

Zinc coatings have been traditionally electroplated from two types of solutions - acid and alkaline. Cyanide zinc solutions were selected for general purpose zinc electroplating because of their excellent throwing power but with the advent of stricter effluent limits and the concern for the use of cyanide in the workplace, addition agents were developed to improve the throwing power of acid zinc solutions and these solutions have rapidly gained in popularity for general purpose use. Acid baths have also been found to have higher cathode efficiency and brightness than alkaline baths. The higher cathode efficiency lowers the risk of hydrogen embrittlement.

In the late 1970s and early 1980s, there was an increased demand for improved corrosion resistance driven by the Automotive and Fastener Industries. Cadmium offered the required increase in corrosion resistance but had two adverse environmental contaminants, cadmium and cyanide. It was found at that time that zinc plated onto a part when combined with a small amount of cobalt increased the corrosion resistance by a factor of two or greater.

The original zinc cobalt plating process was developed in the Netherlands[8] and is presently being evaluated and used in Europe by the Automotive and Fastener Industries. The process is now being introduced into the United States. The zinc solution contains 26 gm/L of zinc and 2.6 gm/L of cobalt and the zinc alloy plated during the process has been found to be predominately a 99.4% zinc alloy with 0.6% cobalt. Typical plating and waste treatment costs for the zinc/cobalt process as compared to the conventional working zinc baths amd a cadmium cyanide bath are shown in Table VI.

It can be seen from Table VI that the waste treatment costs are not significantly different from the various noncyanide zinc baths. However, with cyanide baths, the cost for treatment is more by a factor of 20. Sludge production is also greater for the cyanide baths.

The cost of plating is slightly more for the alloy bath but this is offset by the increased corrosion resistance of the parts.

The equipment, solution composition and maintenance of the zinc/cobalt bath are similar to that for existing acid zinc processes, based on sodium chloride electrolysis.

Recovery of the zinc/cobalt alloy bath is best effected by the use of a direct return dragout tank and forced evaporation of the bath to make room for the recovered solution. Alternately, the solution lost to the rinse via dragout can be recovered similarly by techniques currently employed for acid baths.

The zinc/cobalt plating process is an example of a process developed by a demand for increased corrosion resistance and reduced environmental impact.

TABLE VI

TYPICAL PLATING AND WASTE TREATMENT COSTS

ZINC/COBALT VS. CONVENTIONAL ZINC PROCESS

Process	Total Metal Content (gm/L)	Total Cyanide (gm/L)	Zinc Thickness (mil)	Plating Cost (a) ($/Ft^2)	Effluent Treatment Cost(b) ($/gal dragout)	Sludge Produced(c) (Ft^3/gal-dragout)
Zinc/Cobalt	29.4	--	0.1	.0097	0.066	0.016
Zinc Cyanide (1/2 bath)	16.5	38.0	0.1	.0067	1.60	0.030
KCl Zinc	36.0	--	0.1	.0075	0.072	0.016
Cadmium Cyanide	28.0	54.0	0.1	.0156	2.65	0.066

(a) Basis: 4 gal./1000 ft^2 dragout.

(b) Cyanide treatment included two stage oxidation of the cyanide with sodium hypochlorite at a pH of 11.0 and 8.0, with precipitation of the metal ion at a pH of 10.0 with lime and a flocculant. In the case where no cyanide was present the metal ion was precipitated at a pH of 10.0 with lime and a flocculant only.

(c) Sludge produced was dried in the oven at 60°C for one hour. Volume calculation assumed 35% DWS and a density of 80 lb/cubic foot.

Electrolytic Strippers for Metal Removal

During the plating process deposits of metals build on the racks that hold the parts. These deposits can cause loss of productivity mainly due to poor plating contact, resulting in parts being rejected due to poor plating quality, such as pitting and roughness. Today, because of the high cost of labor and materials, it is no longer economically feasible to either scrap the parts or remove the deposits on the racks by hand. This removal of unwanted metallic coatings has been usually accomplished by chemical immersion stripping or, in some cases, buffing. Electrolytic stripping[9] can also be used to remove the unwanted metallic coating, and the same principle applies to both the parts and rack stripping processes.

The metallic deposits are removed by stripping electrons, thus, oxidizing the metal to the ionic form which then goes into solution as shown in Equation 1.

$$M^{\circ} \longrightarrow M^{+2} + 2e^{-} \qquad [1]$$

For this reaction to occur, the oxidation potential of the metal must be attained, and for effective stripping of metal overlays, it is necessary to maintain this potential and this process must occur without affecting the properties of the basis metal.

A variety of chemical and electrolytic stripping processes have been used for removing metal from metal substrates, the most common of which are chemical immersion processes. These processes use nitric acid, ethylene diamine and cyanide based stripping solutions. These solutions, though still in use, are inadequate for consistent stripping quality and their limitations are as follows:

(a) The solutions are often metal specific.

(b) The solutions become saturated with the stripped metal and need to be disposed of, which means high treatment or haulage costs. Often, the only option is haulage due to the high metal or the organic content of the spent bath.

(c) The solutions cannot be regenerated economically.

(d) The stripping rates are slow and nonuniform due to the gradual build-up of metal ions in solution and, thus, stripping must be controlled continuously.

(e) The cyanide-based strippers are being phased out due to their workplace impact and high waste treatment costs.

Electrolytic stripping baths are generally based on aqueous solutions of ammonia, and/or alkali metal salts of nitric acid. However, some formulations have contained sulfuric acid or phosphoric acid. Some of the old electrolytic strippers also show slow stripping rates and sometimes attacked the base metal.

The new electrolytic stripping processes exhibit almost unlimited solution life. By the use of special buffer and chelator systems, it is possible to run the bath at a steady state metal ion concentration. Above this metal ion concentration, the metal stripped precipitates out of solution as a complex hydroxide sludge. This sludge settles to the bottom of the stripping tank and can be removed periodically by desludging using a settling tank or by filtration. In some instances the bath may be continuously filtered. After desludging, the solution can be adjusted to its original volume with additional new stripping solution. The new electrolytic strippers also exhibit constant stripping rate, do not give off NO_x fumes as nitric acid does and do not contain amines.

Most electrolytic strippers contain ammonia ions. These are lost via dragout and can enter a waste treatment system. In areas where there are strict effluent limits for heavy metals or where there are effluent limitations for total nitrogen or ammonia, the stripper dragout has been successfully treated by oxidation with sodium hypochlorite or chlorine to reduce the ammonia to an acceptable level.

Recovery of the stripper dragout can be considered to reduce waste treatment requirements and conserve operating costs. Recovery is best effected by the use of a direct return dragout tank and a fog spray. The recovered solution can be returned to the bath to substitute for bath evaporative losses, for example, in processes that operate above 120°F. In processes that operate at less than 120°F, there may not be sufficient bath evaporation and forced evaporation of the bath may be necessary in order to allow the return of the recovered dragout.

Following their introduction in Germany, electrolytic stripping processes have been in operation in the U.S. for several years, and have been used to remove a wide variety of unwanted metallic deposits. These processes not only offer maximum protection of the metal substrate, but also are capable of meeting the new environmental restrictions that have been established by recent legislation.

Hydrogen Peroxide/Sulfuric Acid Etch

Copper etching is an important step in the manufacture of printed circuit boards. The etch is used to remove excess copper from the printed circuit board in order to leave the electrical circuit required. The copper that is to remain as the circuit is protected from the etch by a resist layer, such as tin/lead.

Typical etching chemicals are cupric chloride, ferric chloride and a variety of proprietary ammoniacal solutions. The etching reaction is shown in Equation 2,

$$Cu + E^{x+} \longrightarrow Cu^{2+} + E^{(x-2)+} \qquad [2]$$

where E is the etchant ion present in the etching solution. As the reaction proceeds, the concentration of dissolved copper in the etching solution increases while more ions of the etchant E^{+} are converted from the oxidized to the reduced state. If this condition is allowed to continue, the etchant will not remove the copper fast enough and the spent etchant, which now contains considerable quantities of dissolved copper and a mixture of the oxidized and reduced states of the etchant ion, E, will have to be discarded. Generally this does not happen and the etchant can be either chemically or electrolytically regenerated. This can be done either on site or off-site. Many etchants traditionally were returned to the supplier where they were regenerated and the user given a credit. However, this process has lost favor due to stricter shipping regulations. Electrolytic regeneration of the etch on site is possible but somewhat difficult to operate and a close watch must be kept on the etchant chemistry.

The effect of increased environmental pressure on the circuit board industry to improve effluent quality has spurred the need to develop an etch that can be regenerated easily and also provides an etching process that is consistent in operation. The result of this focus has been the development of stabilized peroxide/sulfuric acid processes.

The effective and economical use of hydrogen peroxide lies solely in the use of stabilizers and the copper concentration of the etch solution. High levels of copper in the solution affect the stability of hydrogen peroxide in the etching solution. Stabilizers are used to reduce the catalytic decomposition of the hydrogen peroxide in the presence of copper.

Recovering the copper from the etch not only covers part of the etching cost but also aids in keeping the losses of peroxide through catalytic decomposition to a minimum.

The recovery equipment for the peroxide/sulfuric system is very simple. When the etch contains approximately five ounces per gallon of copper metal at the operating temperature of 128°F it can be cooled to 70°F. At this temperature, the copper will precipitate from the solution as copper sulfate. These crystals can be sold, or could be used for copper plating operations in a shop, or the metal can be plated onto electrolytic copper cathodes.

A comparison of alkaline etchants and peroxide etchants[10] is shown in Table VII.

TABLE VII

ETCHANT COMPARISON

	Process	
	Alkaline	Peroxide
Spent Etchant Disposal	store and haul away	never dump.
Control of Etchant	Automatic feed and bleed	Automatic metering
Ventilation	Extensive	Minimal
Waste Treatment of Rinse Water	Extensive (contains Copper and Ammonia)	Simple (precipitation only)

Three simple tests are carried out periodically (depending on the amount of work being processed) for the control and maintenance of the peroxide/sulfuric system. These are wet chemistry tests, used to determine the relative amounts of: copper, sulfuric acid and hydrogen peroxide in the etch solution. All three tests may be completed in approximately twenty minutes.

The etch system may be controlled either manually or with automatic metering and is adaptable to most existing equipment. Other advantages offered by the use of hydrogen peroxide/sulfuric acid etch are:

(a) A constant, predictable etch rate.
(b) Infinite etchant bath life with closed loop operation.
(c) An extremely clean, oxide free surface.
(d) Easy recovery of copper either as copper sulfate or metal.
(e) Elimination of waste treatment and disposal problems.

Peroxide/sulfuric systems offer complete control of the etching bath and reduced waste treatment costs without sacrificing board quality. These advantages plus lower cost makes the hydrogen peroxide/sulfuric acid process extremely attractive.

SUMMARY

Under the pressure of legislation, the Metal Finishing Industry was challenged to implement chemical processes which are safe to employees and the environment. Some chemical manufacturers have met this challenge and developed superior plating processes which provide improved plating properties and reduced operating costs, yet minimize environmental impact, reduce the toxicological effects, and meet the safety in handling and use requirements mandated by Federal and Local Regulations. In the years ahead, we can expect similar new developments as a result of increased concern for the environmental and safety consequences of metal finishing processes. Such developments represent real benefits to industry and society.

REFERENCES

1. "A Guide to State and Federal 'Right-To-Know'", Hazards Communication Exchange, Thompson Publishing Group (1-800-424-2959).

2. "American National Standard for Hazardous Industrial Chemicals - Precautionary Labeling", American National Standards Institute, Inc. ANSI® Z 129.1-1982. Revision of ANSI Z 129.1-1971.

3. "American National Standard Practices for Ventilation and Operation of Open-Surfaced Tanks", American National Standards Institute, Inc., ANSI® Z 9.1-1977. Revision of ANSI Z9.1-1971.

4. "1984 Emergency Response Guidebook, Guidebook for Hazardous Materials Incidents", U.S. Department of Transportation. DOT P 5800.3.

5. "Trivalent Chromium Electrolyte and Process Employing Vanadium Reducing Agent." U.S. Patent No. 4,392,922. July 12, 1983.

6. "Trivalent Chromium: A commercially Viable Alternative", Paper presented at SUR/FIN '83, T. W. Tomaszewski and R. E. Fischer.

7. "New Alkaline Copper Process: A Novel Alternative to Cyanide Copper", Paper to be presented at SUR/FIN '85, L. C. Tomaszewski and R. A. Tremmel.

8. "Verbesserung des Korrosionsschutzes von Zink durch Mitabscheidung von Metallen der 8. Nebengruppe." E. Knaak, H. Koehler, J. S. Hadley. Presented at: Deutsche Gesellschaft fuer Galvanotechnik Dreilaendertagung, September 14, 1984 in Konstanz, West Germany.

9. "Electrolytic Stripping - A New Generation of Metal Stripping Processes", Paper presented at SUR/FIN '83, - L. C. Tomaszewski

10. "Acid Versus Alkaline Etching", W. M. Hastie, Circuits Manufacturing, August 1983, p. 25 - 28.

Research Session F

Diffusion Induced Grain Boundary Motion

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DIFFUSION INDUCED GRAIN BOUNDARY MOTION

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This study is part of and related to a broader study of low temperature interdiffusion of electrodeposits with their substrates. It is well established that at low temperatures, i.e. near ambient temperatures and below, grain boundaries play a major role in overall diffusion kinetics. Because grain boundaries make up such a small fraction of the total volume of a polycrystalline sample, the fractional amount of a diffusing species carried by the grain boundaries is small at elevated temperatures where lattice diffusion is relatively rapid. At low temperatures, however, the lattice diffusion becomes so slow that the contribution to the total diffusion by the grain boundaries becomes dominant. This happens because although small in volume fraction the grain boundaries permit atom motion at a significant rate at low temperatures where as lattice diffusion has almost ceased. The practical implication is that if one wishes to minimize low temperature interdiffusion, the number of grain boundaries per unit volume should be minimized, that is, the coarser the grain structure the better it is if one is solely concerned with minimizing low temperature interdiffusion. For example, nickel, which is often used as a diffusion barrier in electronic applications, would lose its effectiveness if it were too fine grained. Though not practical in general, the ultimate diffusion barrier would be a single crystal with a low lattice diffusivity. This might be achieved in special cases with an epitaxial deposit on a single crystal substrate.

Further complicating the situation is the more recently recognized phenomena of diffusion induced grain boundary motion, DIGM. In the last several years a large number of observations have been reported in which, for a system with an otherwise stable grain structure, the grain boundaries are caused to move by the diffusion of a second component into the grain boundaries of the original system. This is of direct relevance to low temperature interdiffusion. If a grain boundary moves during an interdiffusion anneal, the volume swept out by the grain boundary is the effective grain boundary volume rather than that of the static grain boundary. Thus a system with moving grain boundaries is equivalent in its ability to transport atoms by diffusion to a much finer grained static system. To repeat, if DIGM occurs, the fact that the system is coarse grained is not sufficient to assure a small contribution to interdiffusion by the grain boundaries at low temperatures.

Because DIGM is a relatively newly recognized phenomena and a complex one at that, it is not fully understood. There is at present no generally accepted theory of DIGM. To further our understanding of DIGM, this study was instituted to see if there was any relationship between the degree of solubility of two components in each other and their ability to cause DIGM in each other. A number of systems were studied for DIGM with varying mutual solubility. In the following list of systems studied the first named element is the substrate or solvent metal and the second named element is the solute material which was deposited on the substrate and whose diffusion into the substrate will be studied to determine its ability to cause DIGM. The systems

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investigated were: Cu-Zn, Pd-Cu, Cu-Au, Ni-Cu, Ni-Au, Co-Cu and Ag-Cu.

Some typical examples of the observations made in this study are reported below.

Ni-Au Marz grade nickel foil was electroplated with copper from an acid copper sulfate both and diffusion annealed. Metallographic examination of the diffusion annealed samples showed that the nickel grain boundaries were in fact caused to move by the diffusion of copper into the nickel.

A sample annealed at 600°C for twenty hours was analyzed using an electron microprobe to study the local variations in copper concentration in and near regions where the grain boundary had moved. Note that in the same sample a scan of the microprobe beam across a grain boundary in the nickel which had not moved, that is at a location where no motion had occurred, showed no copper. This is what one should expect and is why a microprobe can't detect grain boundary segregation. The amount of solute in and near the static grain boundary is so small relative to the volume that the microprobe is sampling that it won't detect the copper even if it were present as a 100% copper atomic layer. On the other hand, see figure 1, a typical plot of the characteristic X-ray intensity profile when crossing a region of grain boundary that has moved shows unambiguously significant copper concentration in the swept out region. The intensity was not corrected for absorption etc by, for example, a MAGIC program because for such a narrow thickness a quantitative analysis would require that the intensity profile be deconvoluted. That is the fact that a finite volume of the sample is activated by the microprobe beam instead of a point would need to be taken into account. This was not done so the 'raw' intensity profile is reported.

Cu-Au Gold was electrodeposited from an Ehrhardt bath on MARZ grade copper strip and diffusion annealed at 200,300 and 400°C for 24 hours. Samples were polished and etched to show the grain boundaries of copper. Figures 2 and 3 are typical micrographs showing the migrated boundaries of copper due to the diffusion of gold through them.

A sample annealed at 400°C for 24 hours was analyzed using an electron microprobe to study the local variations in the concentration of gold across the migrated regions of the grain boundaries. It was found that the concentration of gold was higher in the boundary swept regions than in the unswept regions of the grains. Figure 4 shows a typical characteristic x-ray intensity profile of gold (proportional to the concentration of gold) across a boundary swept region.

Ni-Au Gold was electrodeposited from an Ehrhardt bath on MARZ grade nickel foil and diffusion annealed at 600, 500, 400°C for 20, 50 and 120 hours respectively. After the diffusion anneals, samples were polished and etched to show the grain boundaries of the nickel. Figures 5 and 6 are typical micrographs showing the migrated grain boundaries of nickel due to the diffusion of gold through them.

In all the systems studied, the general observation was that the higher the degree of mutual solubility the greater the magnitude of DIGM. Or, conversely, in systems with minimal solubility DIGM was not observed. This further suggests that an ideal barrier to interdiffusion would be a material in which neither the substrate nor the deposit it is separating have any significant solubility.

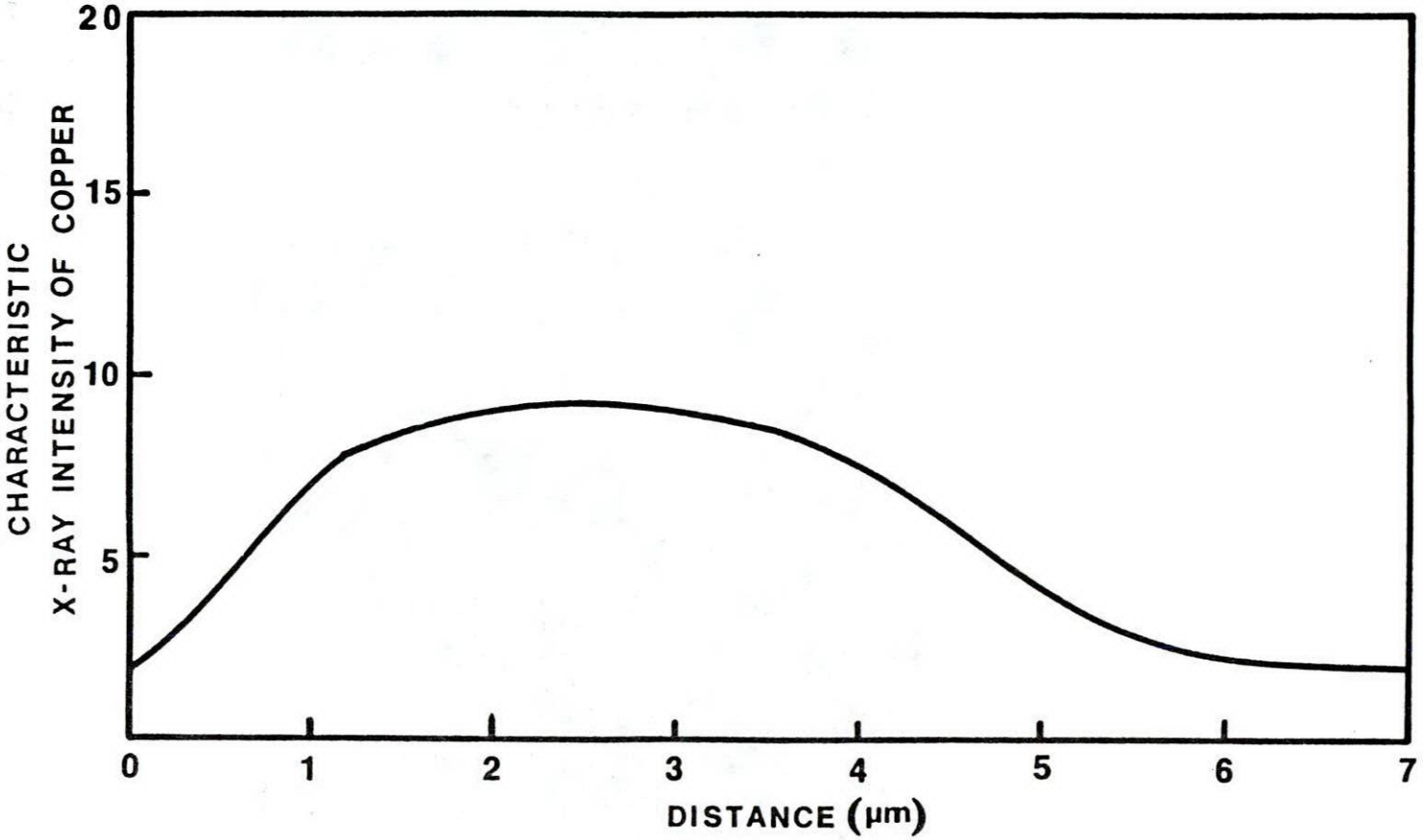

Figure 1. Nickel-Copper System. Characteristic x-ray intensity of copper with distance across a boundary swept region.

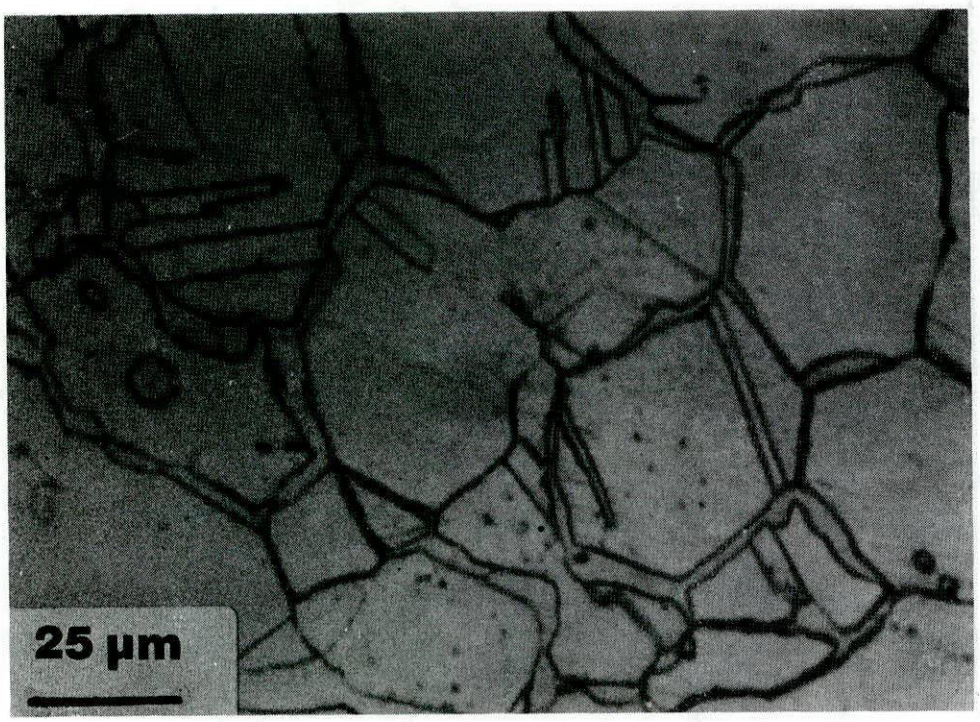

Figure 2. Optical micrograph of copper showing migrated boundaries due to the diffusion of gold through them. Annealed at 400°C for 24 hours.

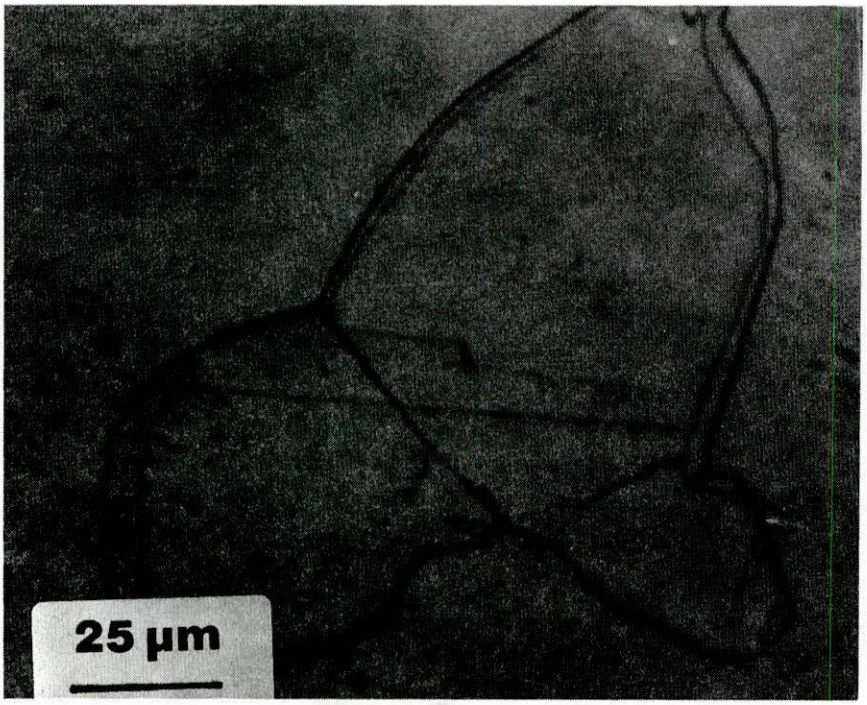

Figure 3. Optical micrograph of copper showing migrated boundaries due to the diffusion of gold through them. Annealed at 300°C for 24 hours.

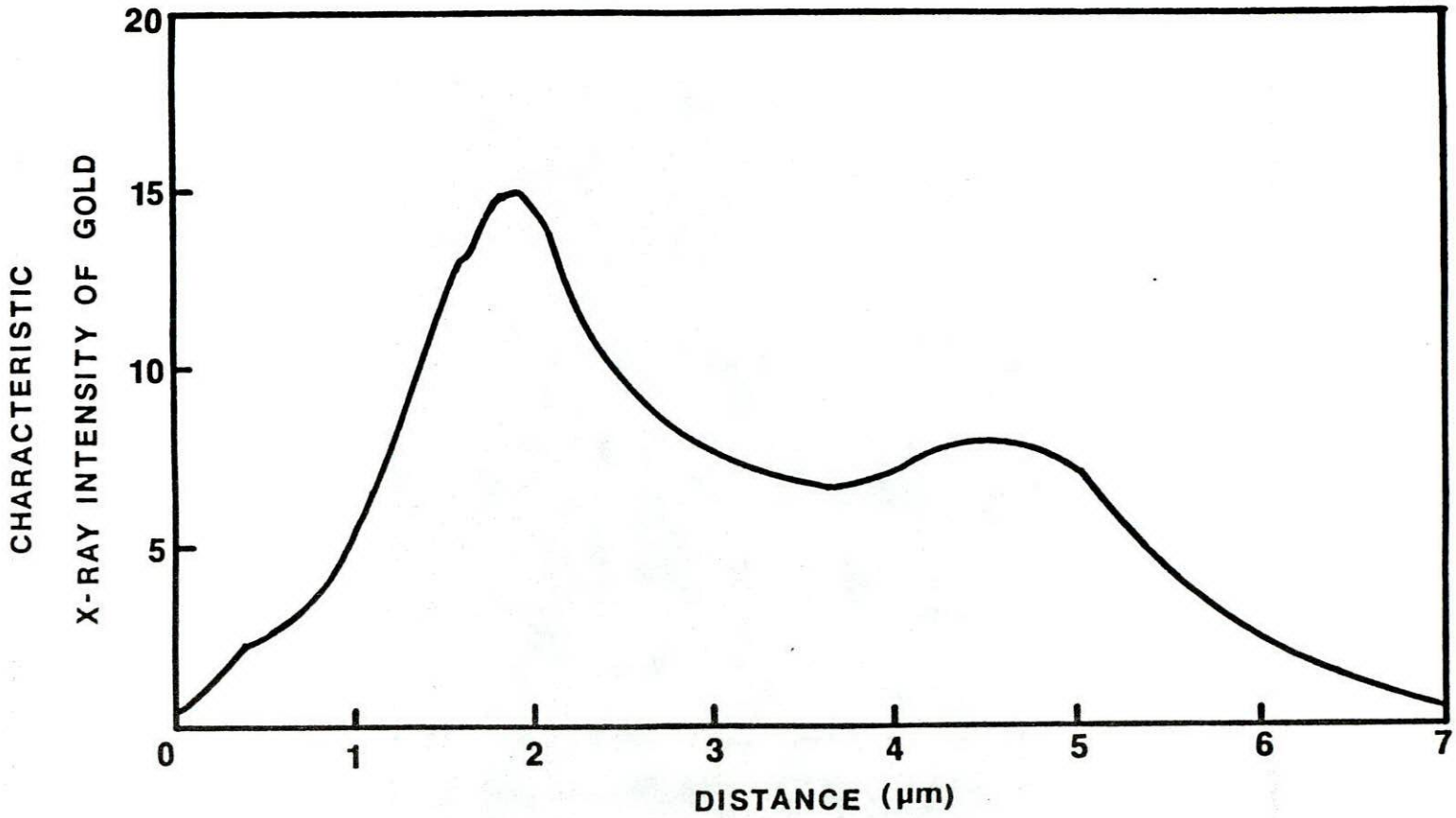

Figure 4. Copper-Gold Sysem. Variation of characteristic x-ray intensity of gold with distance across a boundary swept region.

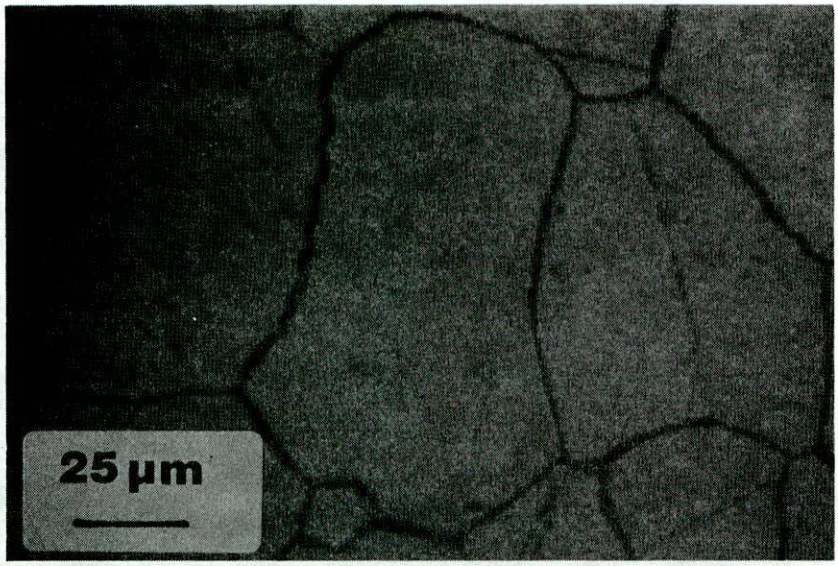

Figure 5. Optical micrograph of nickel showing migrated boundaries due to the diffusion of gold through them. Annealed at 600°C for 20 hours.

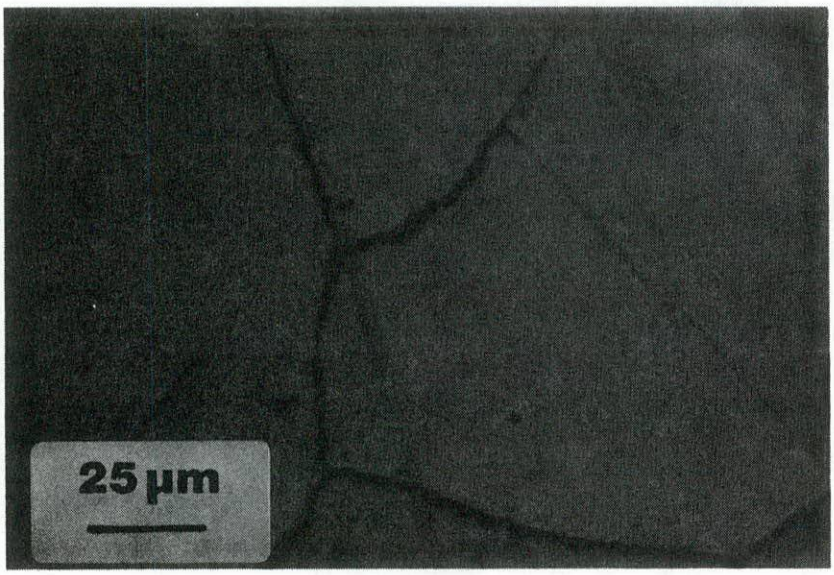

Figure 6. Optical micrograph of nickel showing migrated boundaries due to the diffusion of gold through them. Annealed at 500°C for 50 hours.

F-2

Research Session F

Destruction of VOC's by a Catalytic Paint Drying Device—AES Project 64

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DESTRUCTION OF VOC'S BY A CATALYTIC PAINT DRYING DEVICE

by --AES PROJECT 64

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ABSTRACT

Volatile Organic Compounds (VOC's) are emitted from a number of different types of sources, one of which is paint drying and curing ovens. A device that catalytically oxidizes fuel to generate infrared (IR) radiation recently has been introduced by SUNKISS Thermoreactors, Inc., as a new technology for paint drying and curing. During its operation, the device also oxidizes some of the paint solvents that are evaporated in the oven, thus reducing overall emissions of VOC's into the atmosphere.

A system was constructed at the University of Central Florida (UCF) to experimentally test the SUNKISS device, in order to quantify its VOC destruction capabilities. The system consisted of flow control and measuring devices, analytical equipment and a one cubic meter chamber in which the SUNKISS device was mounted. Three paint solvents-hexane, methyl-ethyl-ketone (MEK), and toluene - were dispersed in air streams that flowed through the chamber at various rates. The solvent destruction efficiency of the device was shown to be a strong function of the air residence time in the chamber, but was independent of VOC concentration. Hexane and MEK behaved similarly while toluene was more reactive. Observed VOC destruction efficiencies ranged from less than 20% to over 50%. Some slight degree of fuel non-combustion was observed as was a very small amount of CO generation.

DISCLAIMER

Although the research described in this article has been funded in part by the U. S. Environmental Protection Agency under assistance agreement number CR 810768-01-1 to the American Electroplaters' Society, it has not been subjected to the Agency's required peer and administrative review and, therefore, does not necessarily reflect the views of the Agency and no official endorsement should be inferred. Nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

INTRODUCTION

Volatile Organic Compounds (VOC) are emitted from a number of different types of sources, one of which is paint drying and curing ovens. In conventional ovens, items are dried by hot air or by electric infrared lamps. The solvents that evaporate are discharged to the atmosphere with the dryer effluent air unless that air is routed through a final control device (FCD) such as an incinerator. Solvent concentrations in the oven exhaust air are typically in the range of 100-1000 ppm.

The amounts and types of VOC emitted from the process depend greatly on the type of paint, the type of process, and the configuration and rate of air flow through the paint booth, flash dryer and oven. Many VOC are photochemically reactive and can contribute to high oxidant levels in the ambient air. Some VOC are carcinogenic or present other direct hazard to human health. As a result, many large paint drying and curing operations have been required to institute control measures to reduce the final emissions of VOC to the atmosphere.

Recently, a novel type of paint drying device was introduced commercially. It works by oxidizing fuel gas on a catalyst and emitting infrared radiation in wavelengths adsorbed by paint pigments. A number of such devices are placed in the oven and oriented towards the painted parts to achieve paint drying and curing. According to tests by the manufacturer, the SUNKISS units achieve significant energy savings compared to conventional hot air or infrared (electric) lamp ovens. Recent installations of the SUNKISS system include several automotive, bus and truck painting facilities in the U.S. and Canada. A schematic diagram of the device is presented in Figure 1.

Another benefit of the device is that some of the solvent vapors in the oven are oxidized on the catalytic surface during the drying process. Because of this concurrent VOC destruction, total mass emissions rates of VOC from the oven can be reduced, perhaps substantially enough to eliminate the need for an FCD. The degree of VOC destruction was of interest to the U.S. Environmental Protection Agency and the American Electroplaters' Society because of the potential benefits of the device to the environment and to industry.

The main objective of the study conducted at UCF was to quantify the VOC destruction efficiency of the SUNKISS device under controlled laboratory conditions. Secondary objectives were (1) to demonstrate the absorption of IR by a painted surface, (2) to test the effect on the VOC destruction efficiency of a painted object emplaced in the oven, and (3) to test the effectiveness of recent engineering modifications (namely, a higher pressure fuel jet and thicker catalyst pad) on the VOC destruction efficiency.

EXPERIMENTAL EQUIPMENT AND PROCEDURES

System Description

The experimental apparatus constructed specially for this project is shown schematically in Figure 2. Basically, the equipment consisted of air flow measurement and control devices, a solvent saturator system, a reaction chamber, and sampling and analytical apparatus. House air, filtered through glass wool, silica gel, and activated carbon, flowed through at least two rotameters in parallel. A measured rate of air was bubbled through liquid solvent in a double saturator system and produced a saturated stream of solvent vapor in air at 0°C. That stream was diluted by another measured flow of pure air to create a stream of air at a desired concentration and desired total flow rate that then was fed into the reaction chamber.

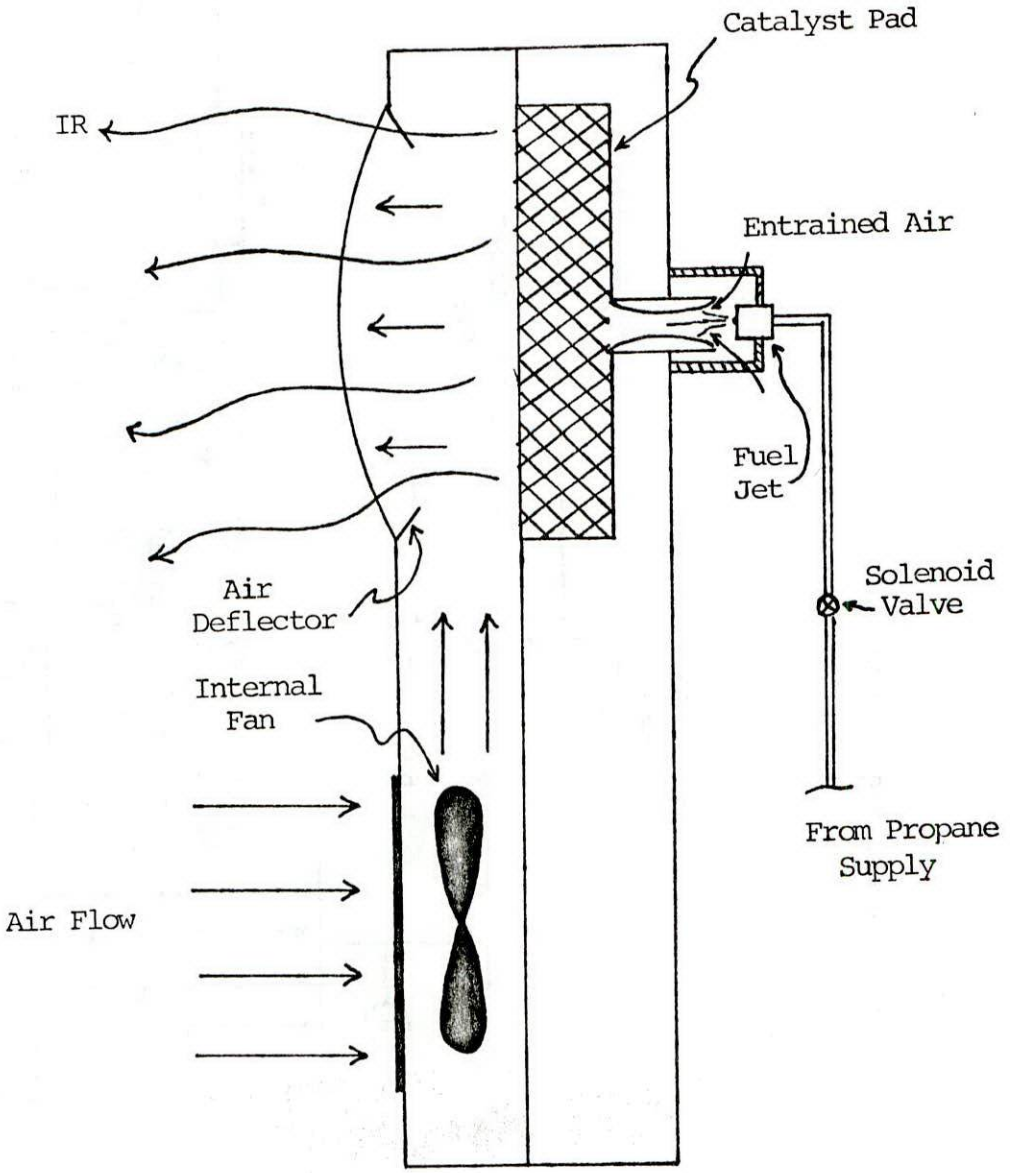

Figure 1. Schematic Diagram of SUNKISS Device

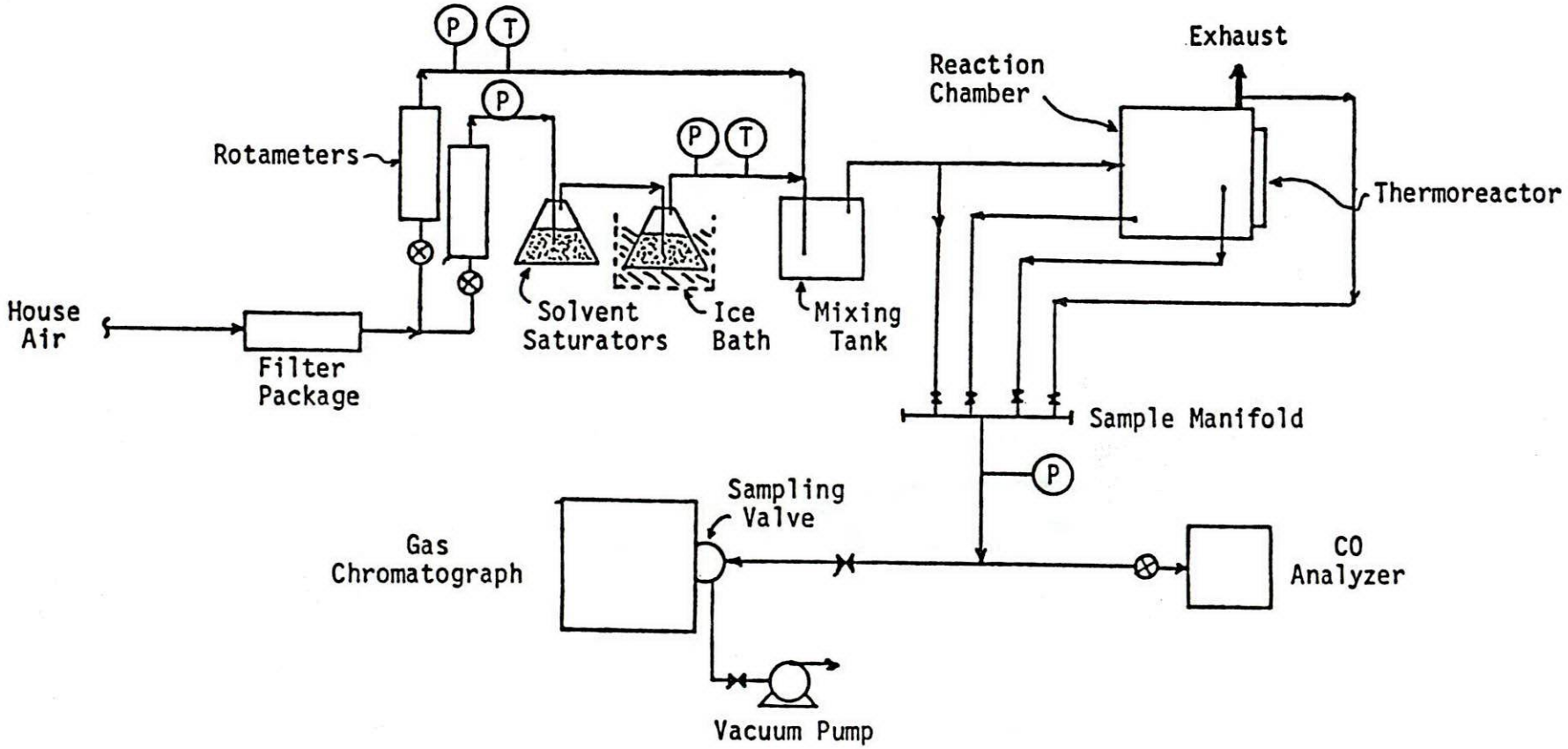

Figure 2. Schematic Flow Diagram of System

The reaction chamber was a welded steel box enclosing approximately one cubic meter of space. The SUNKISS device was mounted on the side opposite the air inlet and an exhaust stack was mounted on the top on the inlet end of the chamber. The SUNKISS Unit has an internal 60 cfm fan that provided some mixing of the air in the chamber, and was augmented by a 200 cfm fan mounted co-axially with the air flow inlet. The SUNKISS fan blew chamber air across the front face of the catalyst pad; some of the VOC was absorbed and oxidized on the surface of the catalyst.

Several sample lines and thermocouples were placed at strategic locations in the chamber. Samples were withdrawn by a vacuum pump through a gas sampling valve mounted on an ANTEK 2400 chromatograph equipped with a flame ionization detector. Samples were also routed to a Thermoelectron Model 48 CO analyzer.

Flow Measurement and Control

Air flow measurement and control was accomplished with manually controlled rotameters, each of which was calibrated carefully with either an accurate wet test meter or an accurate dry gas meter. UCF house air first was passed through a filter package consisting of a layer of glass wool, followed by granular activated carbon, followed by silica gel, and then by a final layer of glass wool. The air was then split into four possible streams, the flow rate of each of which could be individually measured and adjusted. The piping was arranged so that the main air flow rate bypassed the solvent saturator system, while one, two, or three of the other streams could be routed through the saturator. Thus, almost any combination of total air flow rate (from 2 cfm to 8 cfm) and solvent-in-air concentration from 200 to 2000 ppm could be created and maintained during the operation.

Prior to the start of experimental runs, a careful calibration program was undertaken to calibrate all flow meters and all instrumentation to achieve a satisfactory degree of accuracy and precision. The results were gratifying in that there was a high degree of repeatability from run to run. A typical rotameter calibration curve is presented in Figure 3.

Solvent Saturator System

The purpose of the solvent saturator system was to produce a reproducible and reasonably accurately known concentration of VOC in air. A wide range of concentrations could be produced by blending a stream of solvent-free air with an independently controlled stream of completely saturated air.

Primary air was passed through a dual saturator system consisting of two 1000 ml Erlenmeyer flasks, teflon tube bubblers, and a copper cooling coil. Saturation of 40-50% was obtained in the first stage which operated at 25°C. The air then was passed through copper coils submerged in a 10°C water bath and then into a second saturator. The second saturator was surrounded by a 0°C water-ice bath. In the second stage, 100% saturation was achieved due to additional vapor-liquid contact, and probable condensation of VOC picked up in the first saturator. Dilution air was metered through a second calibrated rotameter by-passing the saturator system and was blended with the saturated

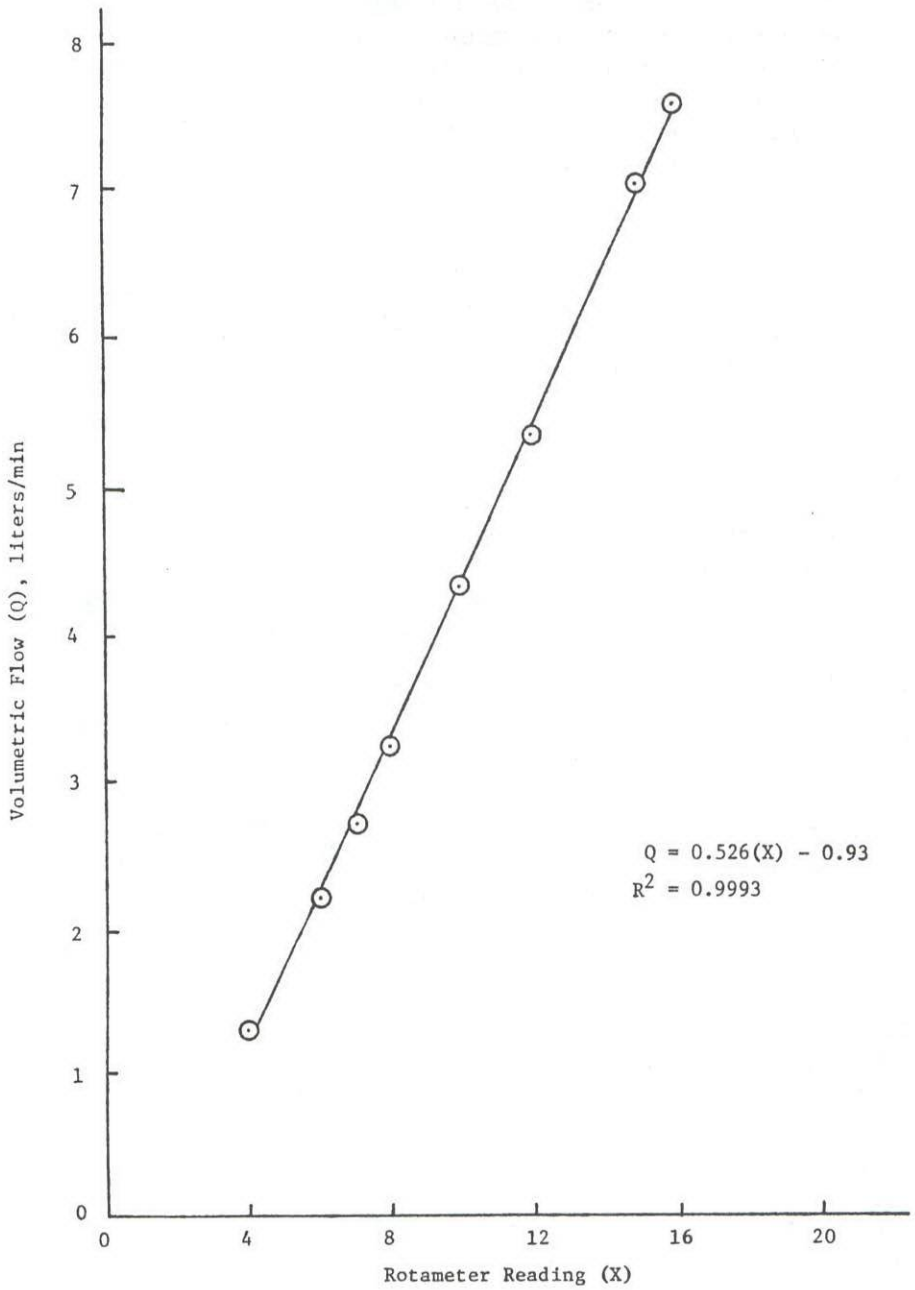

Figure 3. Calibration Curve for Solvent - Carrier Air Rotameter (Tube No. FP-1/4-16-G-5/84; for Air at 22°C, P = 1.00 atm)

stream to achieve desired concentrations. A mixing tank insured complete mixing prior to the combined stream being passed to the reaction chamber.

Reaction Chamber

The chamber was designed to enclose approximately one (1.0) cubic meter of space. The chamber was built from 11-gauge steel welded at all seams. Thus, it was structurally sound, leak-proof, able to withstand all possible operating temperatures, and did not have any potential for self-emission of fumes (as plywood or composites might). The SUNKISS unit was mounted at one end of the chamber (opposite from the air entrance).

The inlet gas (the pre-mixed stream of air with a low concentration of VOC) entered through a diffuser-type entrance near the bottom of the chamber and directly across from the SUNKISS unit. Both the total inlet gas flow rate (from about 2 to 8 cfm) and the inlet VOC concentration (from about 200 to 2000 ppm) could be independently controlled. Inlet and outlet gases were monitored for concentration and temperature, plus sample ports were built into the chamber to enable samples to be taken from within the chamber itself.

Test Procedure

The events involved in a typical experimental run are described below. All instruments (i.e., gas chromatograph, CO analyzer, chart recorder) were allowed sufficient time for warmup and stabilization as per manufacturers' instructions. The appropriate solvent was poured into the saturators and all fittings were checked for leaks. The GC column temperature was adjusted (based on experience in this study) to provide the most consistent and accurate results for each solvent used.

The individual stream flow rates to achieve desired solvent concentrations and total inlet air flow rates were adjusted via inline rotameters. To assure representative results, steady state conditions had to be obtained in the test chamber. The chamber average residence time, t_R (t_R = chamber volume/air flow rate) varied for the different flow rates. Hence, at each different flow-rate we waited a period of 4 x t_R before beginning the sample testing.

Each time a sample was analyzed for VOC, 3 or 4 samples at 1 minute intervals were analyzed and the average of the peak heights on the chart recorder was allowed to represent the true VOC concentration. Chamber inlet samples were taken as well as chamber outlets. The mean of the outlet solvent peaks was compared to the mean of the inlet tank peaks and both were recorded. CO was also measured. Propane peaks were observed and recorded as well. VOC destruction efficiencies were calculated based on inlet air molar flow rate x VOC inlet concentration vs. estimated outlet gas molar flow rate (including propane combustion products plus and entrained air) x outlet VOC concentration.

The above procedure was repeated at least three times for each specific test (each air flow rate and concentration), and a final destruction efficiency was calculated as the average of all the replications.

RESULTS AND DISCUSSION

Initial Operating Tests

Initial tests of the SUNKISS unit were performed with the SUNKISS unit on with only fresh air (no VOC) entering the chamber. A VOC response was observed on the GC, which implied that some uncombusted propane fuel might be escaping into the chamber. Introduction of some hexane into the inlet air and observation of two separate peaks on the GC confirmed that propane gas was indeed entering the chamber. Disappearance of one peak when the propane fuel valve was closed further proved that one peak was propane. Recognition of the problem of propane non-combustion led to more detailed testing during the solvent destruction efficiency tests. In later tests, we calculated the percent propane combustion to be in the 98% to 99.8% depending on total air flow rate. Also, modifications of the SUNKISS device during the latter part of this research partially alleviated this problem of propane non-combustion. Quantitative propane results will be presented later in this paper.

Effect of Solvent Concentration

Several tests were conducted at 170 l/min (6 cfm) air flow but at different inlet concentrations of hexane in air. Basically, chamber inlet and outlet (and some interior points) concentrations were measured to determine the percentage destruction efficiency for the SUNKISS unit.

Because the total molar flow rate out of the chamber was not equal to the inflow rate of solvent laden air (the fuel gas plus entrained ambient air also entered the chamber), the VOC destruction efficiency was calculated as follows

$$E = \frac{n_o C_o - n_e C_e}{n_o C_o} = 1 - \frac{n_e C_e}{n_o C_o} \qquad (1)$$

where: n_o = inlet molar flow rate of stream of air with VOC

n_e = total molar flow rate of exhaust gases

Equation (1) properly accounts for the dilution effect - that is, the fact the VOC concentrations in the outlet stream will be somewhat lower than in the inlet due solely to dilution by the addition of other gases.

It was determined from data supplied by the manufacturer that the propane injection rate was approximately 0.087 gmole/min. Furthermore, based on data from the manufacturer, we calculated that the ambient air entrained by the inlet jet of the fuel (the primary air) was approximately 0.133 gmole/min. Complete propane combustion produces 7 moles of gases for 6 consumed. Thus,

the total molar flow of gases exiting the chamber was equal to the sum of the moles of solvent laden air flowing in plus 7/6 times the propane flow plus the entrained ambient air flow. In other words, the molar flow rate out was equal to moles of solvent laden air in plus 0.23 gmoles/min. Molar expansion due to oxidation of the VOC was ignored.

Quite a few individual solvent destruction tests were accomplished using hexane in air. All replications of individual tests were quite reproducible. Certain concentrations of hexane-in-air and certain air flow rates into the chamber were replicated as many as five or six times. The destruction efficiency for each test never varied more than two percentage points from the mean. The results are shown in Figure 4.

Effect of Chamber Residence Time

After it was shown that destruction efficiency was essentially independent of inlet hexane concentration, the effect of inlet air flow rate was investigated. For a fixed volume chamber, the volumetric air flow rate into the chamber is related to the inverse of the average residence time. The average residence time in a CSTR is actually best calculated by the volume of the chamber divided by the exhaust gas rate. In our experiments, the exhaust gas volumetric flow rate was higher than the measured air inflow rate due to the fuel and primary air inflow, and due to the volume expansion of the gas in the chamber due to increased temperature. The ideal gas law was used to calculate the outlet exhaust volumetric flow.

Effect of Solvent Type

In addition to hexane, two other common paint solvents were tested: methyl-ethyl-ketone (MEK) and toluene. In essence, the MEK destruction efficiencies nearly duplicated those observed with hexane. The MEK data trended a slight bit lower than hexane and showed a slight bit more scatter, but the same essential behavior was evidenced. The results for toluene showed significantly more solvent destruction than with either hexane or MEK. All the destruction efficiencies are plotted vs. residence time in Figure 5.

Painted Object Tests

As part of a planned attempt to more closely simulate conditions in a real oven, a painted (black) metal plate was placed inside the test chamber during the toluene tests. The plate measured approximately 40 cm by 65 cm, and was placed normal to the IR from the catalyst pad about 40 cm from the device. The purpose of the plate was to simulate a painted part being cured. Destruction efficiencies were increased only about 2 percentage points over what had previously been observed for any given solvent at any given air flow rate.

Two identical steel plates (except that one was painted and the other was not) were placed in the oven. To each plate, a thermocouple was attached to measure surface temperature. At the start of the test, a steady stream of air was flowing through the oven and the SUNKISS unit was turned on. The temperature of the painted plate's surface increased quickly to a significantly

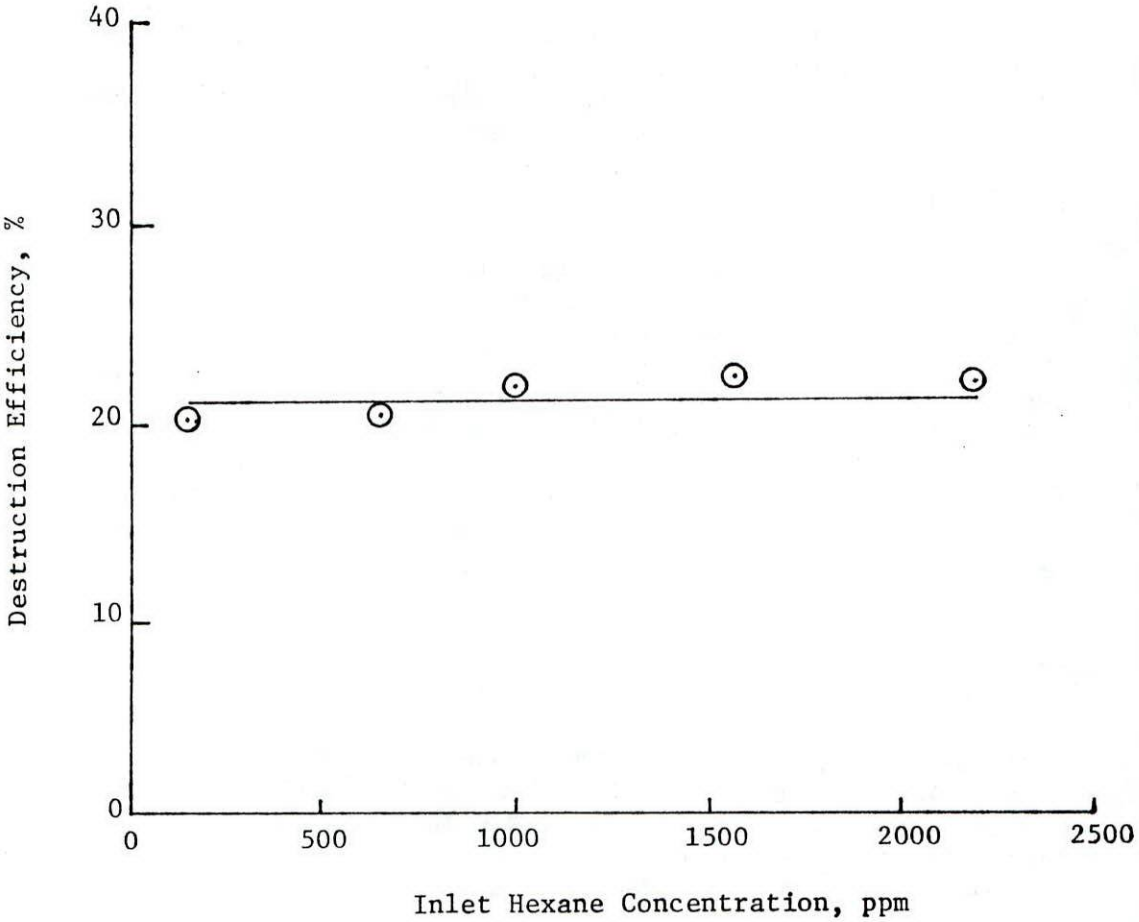

Figure 4. Hexane Destruction Efficiency vs. Inlet Hexane Concentration

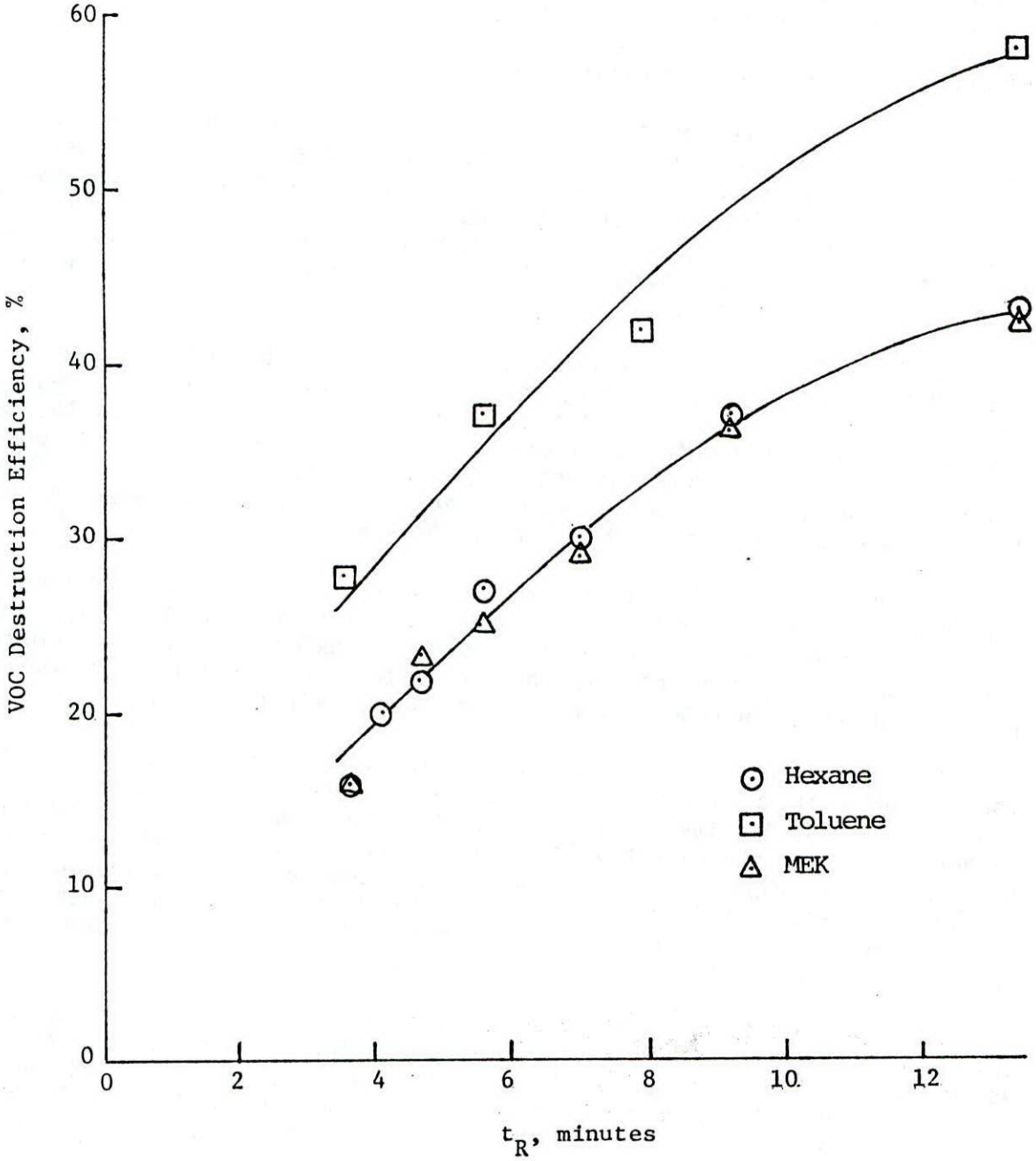

Figure 5. VOC Destruction Efficiency vs. Gas Residence Time

higher temperature than the unpainted plate. At steady state, the painted plate was about 40°C hotter than the unpainted plate which essentially achieved the inside chamber air temperature.

Effect of SUNKISS Device Modifications

During the course of this research project, the manufacturer introduced modifications to the basic device that were intended to increase solvent destruction efficiency and to decrease residual (unburned) propane concentrations. The modifications were basically (1) smaller fuel jets with an increased fuel supply pressure, and (2) a thicker catalyst pad with more catalyst surface area. Each of these modifications was tested in the UCF experimental test system.

To install the new system, we merely replaced the old catalyst pad and the old fuel injection orifice by the new ones. The propane fuel pressure was increased from 11 inches of water to 2 psig. Hexane was used as the solvent and several air flow rates were tested (all at an inlet hexane concentration of 1000 ppm). Three replications were made at each of six flow rates and hexane destruction efficiencies were determined. Also, propane and CO concentrations were measured at each inlet air flow rate.

The results of the above tests showed a slight (but non-negligible) improvement in VOC destruction. In addition, propane non-combustion with the new system (new pad-new jets) was reduced considerably at all flow rates compared with that observed with the old system. CO concentrations were lower at the high air flow rates but higher at the low air flow rates.

In calculating the destruction efficiencies, we had to take into account the increase in dilution effect due to the new jets. The new jets were designed to pass the same molar rate of fuel into the SUNKISS device but at a higher velocity. The higher velocity entrains more ambient air in through the back of the catalyst pad and permits more complete combustion of propane. However, the additional air adds to the total volumetric flow of gases through the chamber thus diluting the concentrations of VOC, propane and CO somewhat compared with the original system.

Estimates of the air entrainment rate of the newly modified system were obtained from the head of technical services for SUNKISS, Inc. It had been estimated previously that with a propane supply pressure of 11 inches of water, and with the old jets, about 0.113 cfm (about 0.13 gmoles/min) of ambient air were drawn into the chamber. With the new jets, at 2 psig, the ambient air entrainment rate was about 0.663 cfm or 0.78 gmoles/min. At the lower air flow rates into the chamber (2, 3 or 4 cfm), there is a significant percentage dilution due to the additional primary air brought in with the new system. It should be noted that the calculations of destruction efficiencies that follow depend on the above estimates of air entrainment rates. The outlet air flow rates from the chamber were not measured in this work.

After accounting for the additional air dilution due to the new jets, the VOC destruction efficiencies were calculated for the new jets - new pad system. Also, because chamber residence times at each inlet air flow rate

were decreased due to the additional primary air flow, the residence times were re-calculated also. The fairest comparison is to plot the efficiencies against gas residence time as shown in Figure 6. From this plot, it can be seen that VOC destruction efficiencies did improve with the new system.

In order to fairly compare propane combustion under the new system vs. the old system, the molar flow rates of propane out of the chamber were calculated under each system. The rate of propane into the SUNKISS device was assumed constant at 0.10 gmole/min. The percent of propane combusted was calculated for each system and compared for each inlet air flow rate.

In order to fairly compare CO production under each system, the CO generated was expressed as a percentage of all the carbon atoms combusted. That is, first the molar rate of hexane that was destroyed in the chamber was calculated. Then, that rate was multiplied by the number of carbon atoms per molecule of hexane (6). Next, the molar propane combustion rate was multiplied by the number of carbons in propane (3). The two numbers were summed to give a total carbon atom combustion rate. The molar flow rate of CO exiting the chamber was calculated and divided by the total carbon atom combustion rate to give the CO generation percentage. The propane and CO results are presented in Table 1, and the calculation equation for CO is presented below:

$$CO_{gen} = \frac{C_{CO}\, n_e}{6 \times E_{Hex} C_{Hex_o}\, n_o + 3 \times E_{Prop}\, n_{Prop}} \times 100 \qquad (2)$$

where: CO_{gen} = CO generation percentage

C_{CO} = CO concentration in exit gases, mole fraction

n_e = flow rate of exiting gases, gmole/min

E_{Hex} = hexane destruction efficiency

C_{Hex} = inlet hexane concentration

n_o = inlet air flow rate, gmole/min

E_{Prop} = propane combustion efficiency

n_{Prop} = propane inlet flow rate, gmole/min

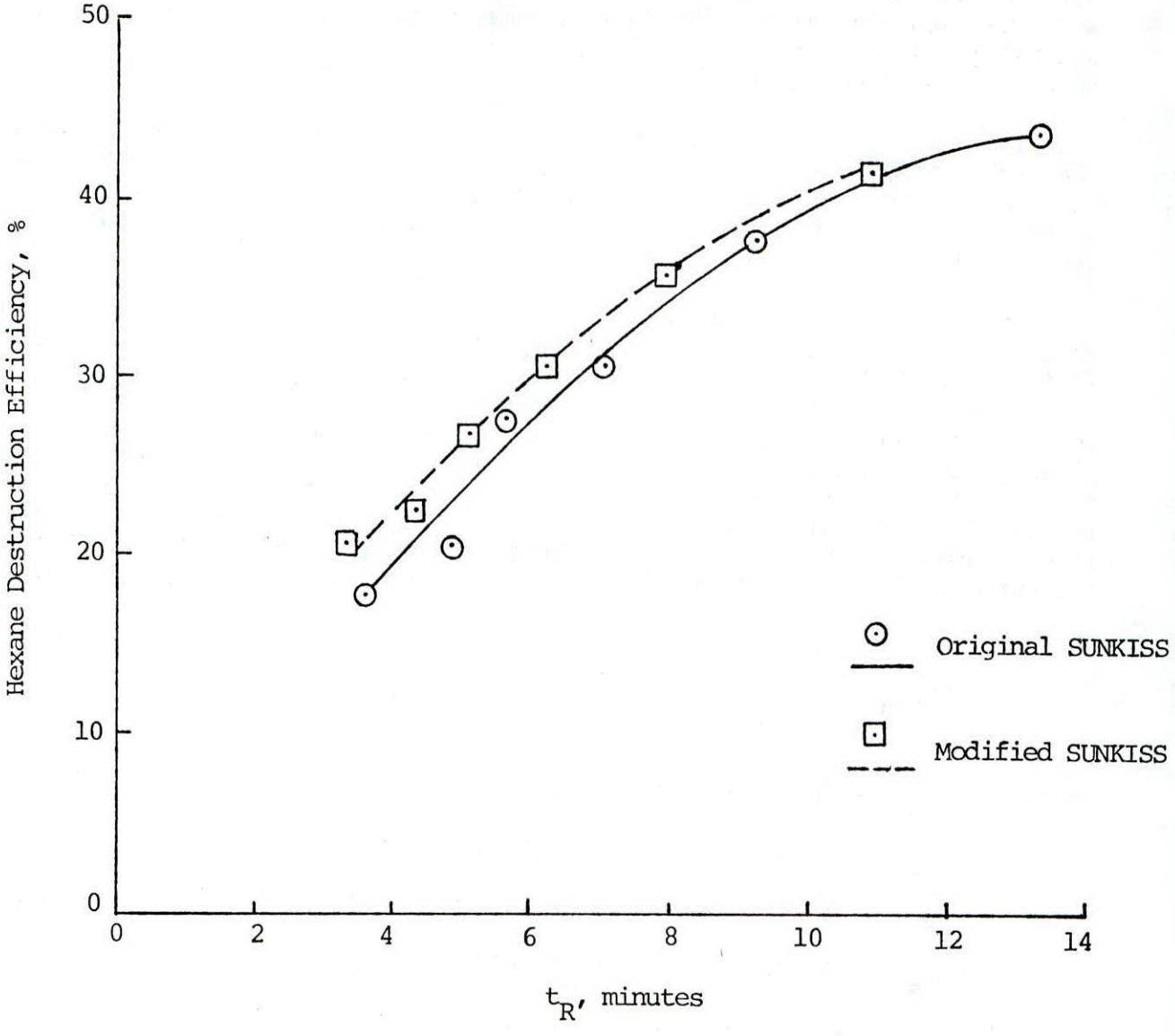

Figure 6. Hexane Destruction Efficiency vs. Gas Residence Time, Original and Modified SUNKISS System.

TABLE 1

PROPANE COMBUSTION AND CO GENERATION: MODIFIED SUNKISS VS. ORIGINAL SUNKISS

	ORIGINAL SUNKISS		MODIFIED SUNKISS	
Inlet Air Flow Rate cfm	Propane Combustion[a] %	CO Generation[b] %	Propane Combustion %	CO Generation %
2	97.8	0.03	99.4	0.07
3	98.4	0.06	99.6	0.05
4	98.8	0.08	99.7	0.06
5	99.2	0.07	99.7	0.06
6	99.4	0.07	99.8	0.05
8	99.6	0.07	99.8	0.05

(a) Based on molar flow rates of propane into and out of the chamber

(b) Based on total moles of carbon atoms combusted

CONCLUSIONS AND RECOMMENDATIONS

The solvent destruction capability of the SUNKISS thermoreactor has been tested under laboratory conditions. This catalytic device has been shown to be effective in oxidizing VOC in air in a completely mixed chamber with destruction efficiencies primarily dependent upon air flow rates (residence times) in the chamber. Observed destruction efficiencies ranged from less than 20% to above 50%. The destruction efficiencies were essentially independent of VOC concentration, but were higher for toluene than for either hexane or MEK. These destruction efficiencies were significantly lower than those typical of a final control device (such as a vapor incinerator) but may be high enough to contribute significantly to an overall VOC control program.

Some slight degrees of fuel non-combustion and a very small amount of CO generation were observed, particularly at the lower total air flow rates. The IR generated by the device is absorbed by a painted surface resulting in higher surface temperatures than for unpainted steel, thus enhancing the drying and curing process. The newer SUNKISS system (thicker pad, smaller fuel jets, and higher fuel pressure) resulted in better VOC destruction efficiencies and in more complete propane combustion and is recommended over the older system. The SUNKISS system can dry and cure painted objects and help reduce VOC emissions to the atmosphere. It is worthy of consideration as part of any proposed operation that involves solvent evaporation inside enclosures.

ACKNOWLEDGMENTS

The author wishes to acknowledge the financial support of the U. S. EPA and the American Electroplaters Society, the technical assistance of SUNKISS Thermoreactors, Inc., and the very able experimental work of UCF graduate students Jeff Nangle, Igor Runge, and Steve Ramsey.

F-3

Research Session F

The Effect of an Addition Agent on the Structure and Electrochemical Properties of Acid-Copper Electrodeposits — AES Project 62

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The Effect of an Addition Agent on the Structure and Electrochemical Properties of Acid-Copper Electrodeposits

--AES Project 62

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Introduction

Some results of an investigation carried out under AES Research Project 62 dealing with the relationship between the microstructure of copper electrodeposits and such electrochemical parameters as the overpotential and the double-layer capacitance were reported(1) last year at the Annual Technical Conference of this Society. The written communication dealt with single-crystal copper deposits plated in an additive-free, highly purified acid-sulfate solution on {100} substrate surfaces of the same metal. In the oral presentation the results of deposition on copper single-crystal substrates having a {111} parallel to their surfaces were also reported. A paper is currently being prepared for submission to Plating and Surface Finishing which will include all results of copper deposition in the additive-free plating solution.

This communication deals with the effects of the addition of o-phenanthroline to the acid-copper plating solution. The other plating condition and the investigated properties were the same as when deposition took place in the additive-free solution.

Experimental Procedure

The experimental procedure was described in the previous paper(1) and is therefore only briefly recapitulated here. The substrate were disk-shaped copper single crystals 12.5 mm in diameter and about 2 mm thick. The electropolished surfaces were essentially parallel to either a {100} or a {111} crystal plane. The plating solution contained 0.5M copper sulfate, 0.1M sulfuric acid and 10^{-5}M o-phenanthroline. The current density was 2 mA/cm^2. The plating times varied from 10 to 500 seconds so that charge densities of 20 to 1000 mC (millicoulombs)/cm^2 were passed. The double-layer capacitance was determined from the change of overpotential at the start of deposition. A value of the double-layer capacitance was also obtained at the end of deposition from the overpotential change resulting from the imposition of a current pulse. During deposition the cathode potential was monitored. The structures of the deposits were observed by transmission electron microscopy by the use of Pt-Pd shadowed carbon replicas. Small latex spheres were again placed on the replicas before shadowing in order to determine the height of the various structural features.

Results and Discussion

The addition of o-phenanthroline to the plating solution had a considerable effect on the structure. When the substrate surfaces had a {100} crystallogrpahic plane parallel to it, no resolvable structure developed in deposit thicknesses up to about 0.05 μm. The double-layer capacitance which is indicative of changes in the actual surface area being plated is depicted

in Figure 1. The abscissa in Figure 1 is the charge density which is propor-

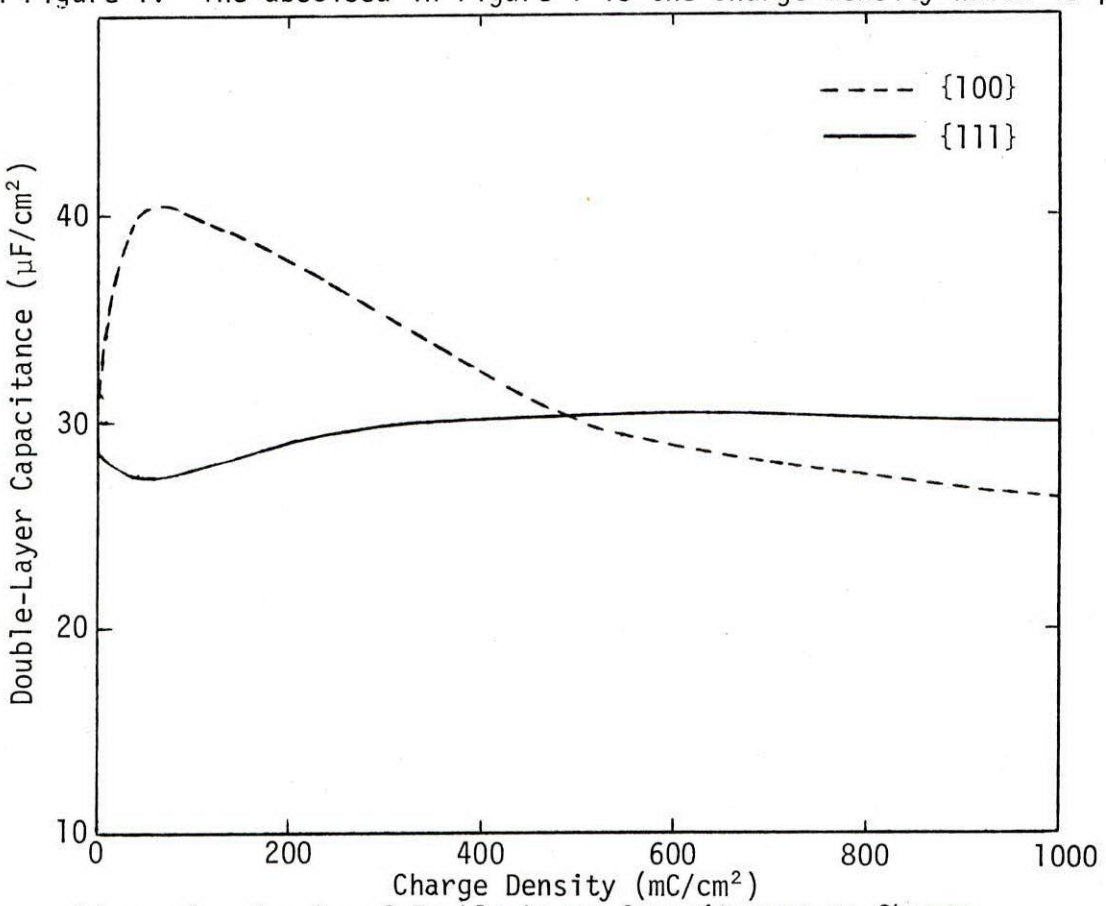

Figure 1. Graphs of Double-Layer Capacitances vs Charge Density for Deposition on {111} and {100} Substrate-Surface Planes.

tional to the deposit thickness when the efficiency is 100% as is the case in acid-copper solutions. It is seen in Figure 1 that except for a small decrease near the start, there is no significant change in the double-layer capacitance with thickness. This electrochemical property therefore corroborates the structural information that the surface remained smooth. The deposit apparently grew by the lateral spreading of layers the heights of which were too small to be resolved by electron microscopy. The initial decrease in the double-layer capacitance was probably due to adsorption which will be discussed later.

When a {100} plane was parallel to the substrate surface, crevices developed at a deposit thickness of about 50 nm. These crevices were quite small but grew deeper and longer with increasing thickness. Crevices in a 0.1 μm thick deposit are shown in Figure 2. The crevices are seen to lie in two directions which are perpendicular to each other. It is believed that the crevices were caused by preferential adsorption of the addition-agent molecules. Nakahara(2) found that o-phenanthroline molecules tend to align themselves along <100> directions of which there are two perpendicular ones in a {100} plane. The molecules probably blocked deposition thereby creating the crevices. Weil and Jacobus(3) observed a similar phenomenon in nickel

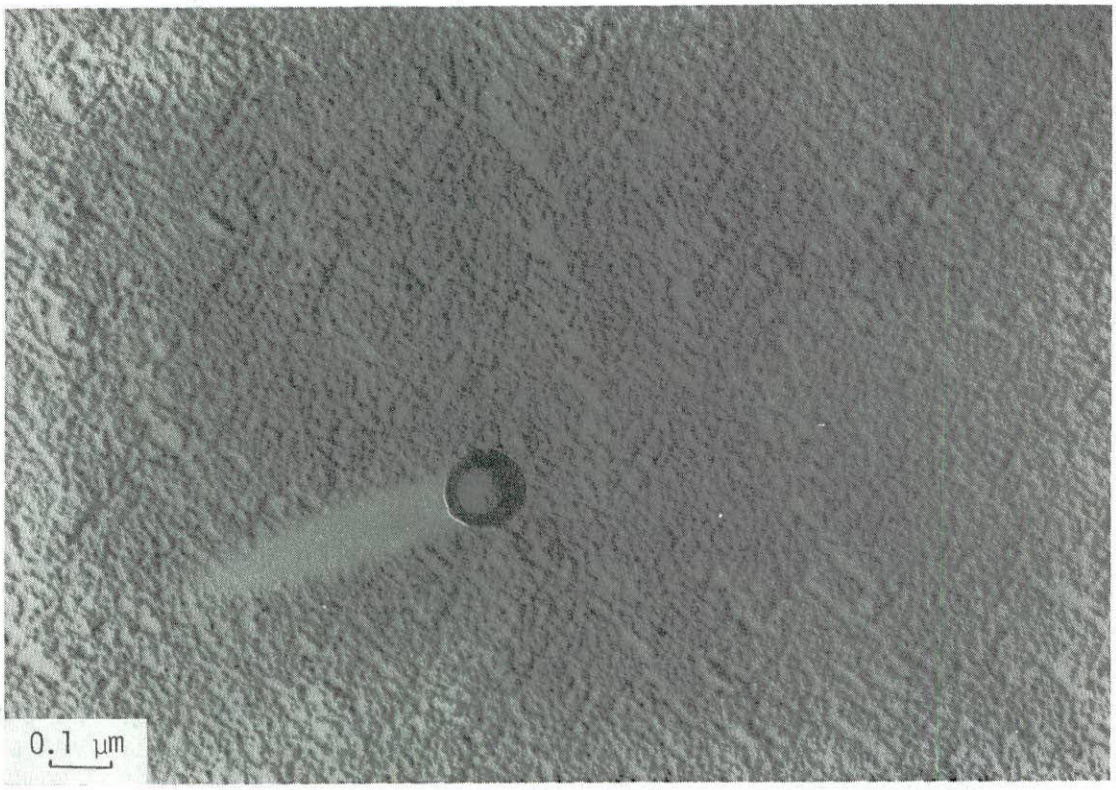

Figure 2. Electron Micrograph of Replica of Copper Deposit Plated on {100} With Charge Density of 200 mC/cm^2.

electrodeposits in that molecules of a brightener were preferentially co-deposited creating crevices which caused a hazy appearance. The probable reason no crevices formed when the substrate surface was parallel to {111} is that this plane contains no <100> directions on which preferential molecule alignment would occur. Furthermore, as the {111} plane is the most densily packed one, molecules can move more easily over such a surface favoring a more uniform distribution.

The double-layer capacitance vs charge density for deposition on substrate surfaces parallel to {100} planes is also depicted in Figure 1. The maximum at about 100 mC/cm^2 is undoubtedly associated with an increase in the effective surface area being plated resulting from the development of crevices. A decrease in the double-layer capacitance can result from adsorption of foreign substances in this case the o-phenanthroline. The adsorption then decreases the effective area being plated. It seems likely that the decrease in the double-layer capacitance was at least partially caused by the adsorption of the addition agent. As already mentioned, addition-agent adsorption was also the likely cause of the decrease in the double-layer capacitance during the initial stages of deposition on {111} planes.

The relationships between the overpotential and the structure are fairly complicated. Different crystallographic planes have different overpotentials.

Thus when new planes develop such as on the sides of crevices or the pyramids which were observed in deposits from additive-free solutions, the overpotential changes. Even the edges of very thin layers can constitute a different plane. If there are many such layers, their edges even if they are only a few interatomic distances high, can constitute a significant portion of the surface area and results in overpotential changes. If the surface becomes rougher, the effective area being plated increases. The true current density then decreases as does the overpotential. The adsorption of foreign substances can also increase the overpotential. As already pointed out, there can be a decrease in the actual area being plated resulting in a higher current density and a greater overpotential. The blockage of growth sites by addition-agent molecules can result in the requirement for nuclei formation which requires a higher energy, i.e., a larger overpotential.

The variation of the overpotential with deposit thickness on {111} and {100} substrate surfaces was such that it could be interpreted in terms of the above discussed phenomena. There was evidence for the increased area due to the crevice formation. When the substrate surface was parallel to {111}, the overpotential indicated that there was very little development of other crystal planes which again corroborated the structural observations. Greater adsorption on {100} planes was expected because it is favored by the more open atom structure of this plane. The experimental results indicated it to be so.

It can be concluded that the correlation of the structure and the electrochemical properties is not a direct one when there are additives present in the plating solution. The structure is easier to interpret. However, as the electrochemical measurements are made during deposition, they provide information not obtainable from structural data. Studies of the structure and the electrochemical procedure are needed if the plating processes are to be understood.

References

1. M. Mirzamaani and R. Weil, Proc., 71st Ann. Technical Conference, AES, (1984) Session E.
2. S. Nakahara, J. Electrochem. Soc., 131, 2246 (1984).
3. R. Weil and W. N. Jacobus, Jr., Plating, 53, 102 (1966).

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F-4

Research Session F

On the Morphology of Pits in Electroplate — AES Project 66

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ON THE MORPHOLOGY OF PITS IN ELECTROPLATE --AES PROJECT 66

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Introduction

When non-conducting motes, such as gas bubbles, solid particles, or grease drops adhere to the cathode during electroplating, the metal deposits around the mote and not under it because the electrode surface is masked from current. The resulting hole in the deposit is circular for small motes and can be teardrop-shaped for large ones (1). The pits occur mainly on downward-facing surfaces but may occur on vertical and upward-facing surfaces as well. Pits in electrodeposited metal are serious defects in the quality of electroplate. A deep pit which penetrates to the substrate metal can be an avenue of corrosion because the relatively noble electroplate acts as an enormous cathode for later pit corrosion of the base lower metal. Thus one must not merely reduce pitting, but must eliminate it to ensure the complete protection of the substrate.

Non-conducting motes appear in plating operations for a variety of reasons. The polarization required to plate nickel also produces a small amount of hydrogen gas which appears as small slowly growing bubbles on the plated surface (2). Air from a leaky pump or carbon dioxide resulting from use of nickel carbonate, which becomes less soluble as the bath temperature rises, may appear on electrode surfaces as baths are heated. Solid particles can enter a bath from faulty anode bags, from corrosion of overhead machinery, from activated carbon oil removers, or from filter aids themselves. Greases and oils, often used in the manufacture of the plated object or as lubricants in the plating shop superstructure itself can also be the source of pitting problems.

The morphology of the pits must be governed by the distribution of current around the mote, but quantitative treatments of the current distribution around dielectric objects on electrodes are few because solving Laplace's equation in the complicated asymmetric environment is difficult; nevertheless, solution of the problem for a spherical mote tangent to an infinite planar electrode is possible (3). A schematic of such a mote appears in Figure 1. Laplace's equation with homogeneous boundary conditions such as zero potential at the electrode surface, zero flux at the bubble surface, and a disturbance vanishing at infinity due to the bubble governs the primary current distribution on the plane. Solution of the problem yields the current distribution around the sphere which appears in Figure 2. The abscissa is normalized distance from the contact point while the ordinate is normalized current density. Zero at the point of tangency, the current

rises to 80% of its undisturbed value at the outermost circle on the plane shadowed by the bubble and reaches a maximum 2% greater than the undisturbed value at a distance of one diameter from the contact point. At a distance of three diameters, the current density is not substantially different from the undisturbed value. As a result of this distribution of current, the sphere should rest in a basin of electroplate as shown in Figure 3.

When the electrode reaction requires surface overpotential to drive it at the specified rate, the current distribution may be more uniform than the primary distribution. Calculating the resulting secondary current distribution around motes on an electrode, however, requires a numerical solution; nevertheless dimensional analysis of the problem yields some conclusions. Two parameters characterize nonuniform current distributions in the case where kinetics of the reaction are finite (4).

$$J = (\alpha_a + \alpha_c)\, i_o a F / \kappa RT$$

$$\delta = J(i_{avg}/i_o)$$

α : kinetic transfer coefficients

i_o : exchange current density

a : radius of sphere

F : Faraday's constant

κ : conductivity

R : Gas Law constant

T : absolute temperature

The first is a ratio between the exchange current density and ohmic parameters such as length and conductivity. The second parameter is a dimensionless current level. Values of either parameter much greater than unity indicate that ohmic effects dominate and the current distribution resembles the primary case no matter what the value of the other parameter. Low values of both parameters indicate that kinetics limit the process and make the current distribution uniform. Although derived for the rotating disk, these quantities can readily be applied to a sphere on an electrode if the radius of the bubbles is used as the length parameter. Figure 4 shows values of J and δ as a function of bubble size for physical parameters appropriate for aqueous electrolytes, in particular for copper plating. The values of the two parameters tend to be less than unity for motes less than one millimeter in characteristic dimension, an indication that the actual microscopic current distribution is more uniform than the primary current distribution.

In this work the effect and usefulness of these two parameters are demonstrated experimentally in plating of copper around spheres of various sizes that rest on the electrode. The distribution of the electroplate around the spheres is analyzed photographically and compared with the result of the primary distribution calculated from theory.

Experiments

The apparatus appearing in Figure 5 was constructed entirely of glass for the purposes of this experiment. The cylindrical central tube is the cathode chamber and a smaller tube, separated from the central tube by a porous disk, is the anode chamber. The third tube is the reference electrode compartment. Sample copper cathodes were attached to the teflon support at the bottom that was then inserted into the cell bottom during operation. The cell features a water jacket for temperature control and support at the top for a magnetic stirring bar to provide mixing.

Operation of the cell consisted of placing a sample particle on the cathode plug, inserting this into the center tube, draining deoxygenated copper sulfate/sulfuric acid electrolyte from the reservoir into the three cell compartments and commencing electroplating. A constant current/voltage power supply provided charge to the experiment. After plating for a period of time, the electrolyte was drained from the cell and the cathode plug removed for analysis.

The 2.54 cm. diam. plugs plated with copper were overcoated with nickel from a Watts nickel bath, which preserved the details of the electroplate during sectioning of the sample with a 1/32 inch micro-sectioning blade made by Buehler Limited. The sectioned sample disk was then hot-mounted, polished, and etched with a 1:1 mxiture of acetic and nitric acid that differentiated between the crystal structure of the plate and the substrate metal. Photographs were taken with the aid of a metallographic microscope which magnified by a factor of 40. One mil of electroplate appeared as one millimeter in the final photographs.

Results and Discussion

The results of three experiments, having experimental parameters and variables appearing in Table 1, are presented for discussion.

Table 1

Parameter	Case 1	Case 2	Case 3
Molarity copper sulfate	.5	.5	.5
Molarity sulfuric acid	1.0	1.0	0.
Sphere radius, cm	.159	.635	.635
Conductivity	.345	.038	.345
Exchange c.d., a/sq cm	.002	.002	.002
Current density, a/sq cm	.040	.040	.040
Sum of transfer coeeffs.	2.0	2.0	2.0
J	.072	.29	5.8
δ	1.4	5.8	30
Time of plating, min	240	240	240

The exchange current densities were calculated from formulas given by Newman (4) that were based on data of Mattsson and Bockris (5). The aim was to obtain a range of values for the polorization parameters J and δ to demonstrate their relevance to pit morphology. The large sphere and low conductivity solution yielded the largest values of the parameters, while the small sphere and the highest conductivity yielded the lowest values. Crossections for each of the three runs are shown in Figure 6 along with the values of J and δ. The dotted lines in the photographs mark the size of the sphere. Approximately five mils of electroplate were plated in each case, but the plate was distributed in various manners among the three runs. In Case 1, the current is nearly uniform everywhere except directly underneath the bubble and the deposit is compact. In Case 2, the deposit is insignificant under the bubble near the point of tangency and begins some distance from it. The deposit is rough on the outer portions of the disk where the current density was the highest but it is compact underneath the sphere where the current densities were the lowest. The transition from a compact to rough deposit is evident. In Case 3 the transition from a more uniform to a nonuniform distribution is complete.

The highest values of the polarization parameters are associated with the largest sphere and the least conductive solution while the lowest values of the parameters are for the case of the smallest sphere. Correspondingly the current distribution is the least uniform in the former case and most uniform in the latter case. For the high values of J and δ the sphere rests in a basin of electroplate because the current follows the shortest path to the electrode, the ohmic portion of the voltage dominates. For the low values of the parameters, surface overpotential is the more significant voltage component so the current spreads underneath the sphere in order to minimize the local current density everywhere.

The results are shown graphically in Figure 7, in the same manner as Figure 2. The local current density in each case was obtained by measuring the thickness of the plate at various radial distances from the center and inserting it into the following equation:

$$i = \rho \, hnF/Mt$$

g(r): density of copper
h: thickness of plate at point r
n: 2, for copper
F: Faraday's constant
M: molecular weight of copper
t: time of plating

which follows from Faraday's law. The superficial current density was used to normalize the local current densities in Figure 7. Where the polarization parameters are the highest, Case 3, the data follow the curve well until roughness of the deposit make analysis difficult. Where both parameters are less than unity, Case 1, the deposit is more uniform.

In Figure 6, the morphology of the electroplate in Case 1 is like a cup that formed around the underside of the sphere. Though one might initially think that the current distribution in this case was not perfectly uniform because a pit formed, this is not so. The current distribution initially was practically uniform, metal was plated everywhere until it approached the underside of the sphere. When the plated surface reached the underside of the sphere, current could no longer enter the space between the sphere surface and the plate. By this mechanism the plated metal grew up around the sphere and formed the cup that appears in Figure 6.

Conclusion

The morphology of pits in electroplate depend, in the absence of additives which have specific action, on the electrical competition between the ohmic and surface overpotential components of the electrode potential. Where the ratio of either kinetic parameters or current level to ohmic resistance is high, the current distribution around a mote on the surface resembles the primary distribution. Where both the kinetics and current level are low with respect to ohmic parameters, the current distribution in most cases must resemble the one represented by Case 1 for motes less than a millimeter in diameter and superficial current densities on the order of 100 ma/cm^2 or less, thus for the small gas bubbles which can stick to nickel during electroplating builds to the underneath side of the mote and seals further current from the area.

Acknowledgement

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References

1. L. Gianelos, "Troubleshooting of Nickel Plating Solutions," Plating and Surface Finishing 64 #9, 32 (1977).

2. K, Graham, Electroplating Engineering, Third Ed. Van Nostrand Reinhold Company, New York (1971).

3. P. Sides and C. W. Tobias, Journal of the Electrochemical Society 127, 288 (1980).

4. J. Newman, Electrochemical Systems, Prentice Hall, Inc., Englewood Cliffs, NJ (1973).

5. E. Mattsson and J. O'M. Bockris, Trans. Faraday Soc. 55, 1586 (1959).

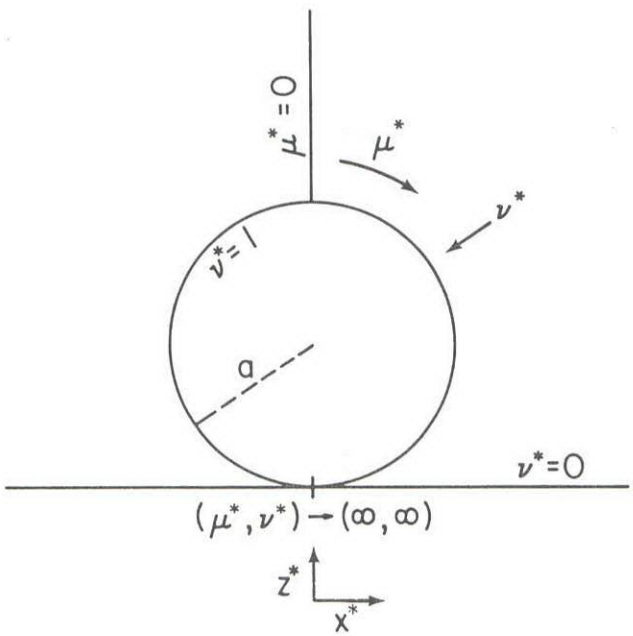

Figure 1. A schematic of a single spherical mote resting on a plane.

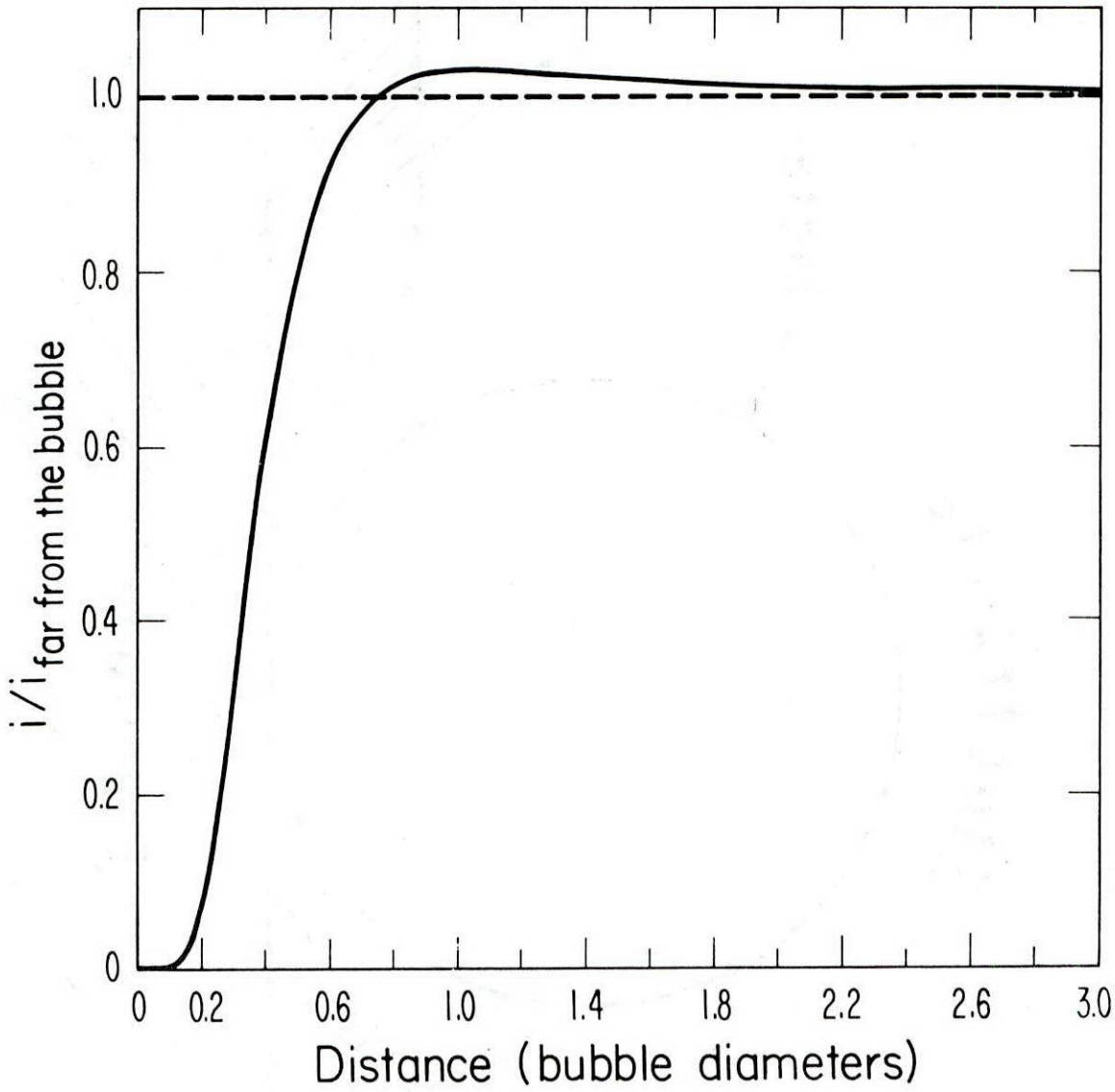

Figure 2. Primary current distribution around a dielectric sphere resting on a plane.

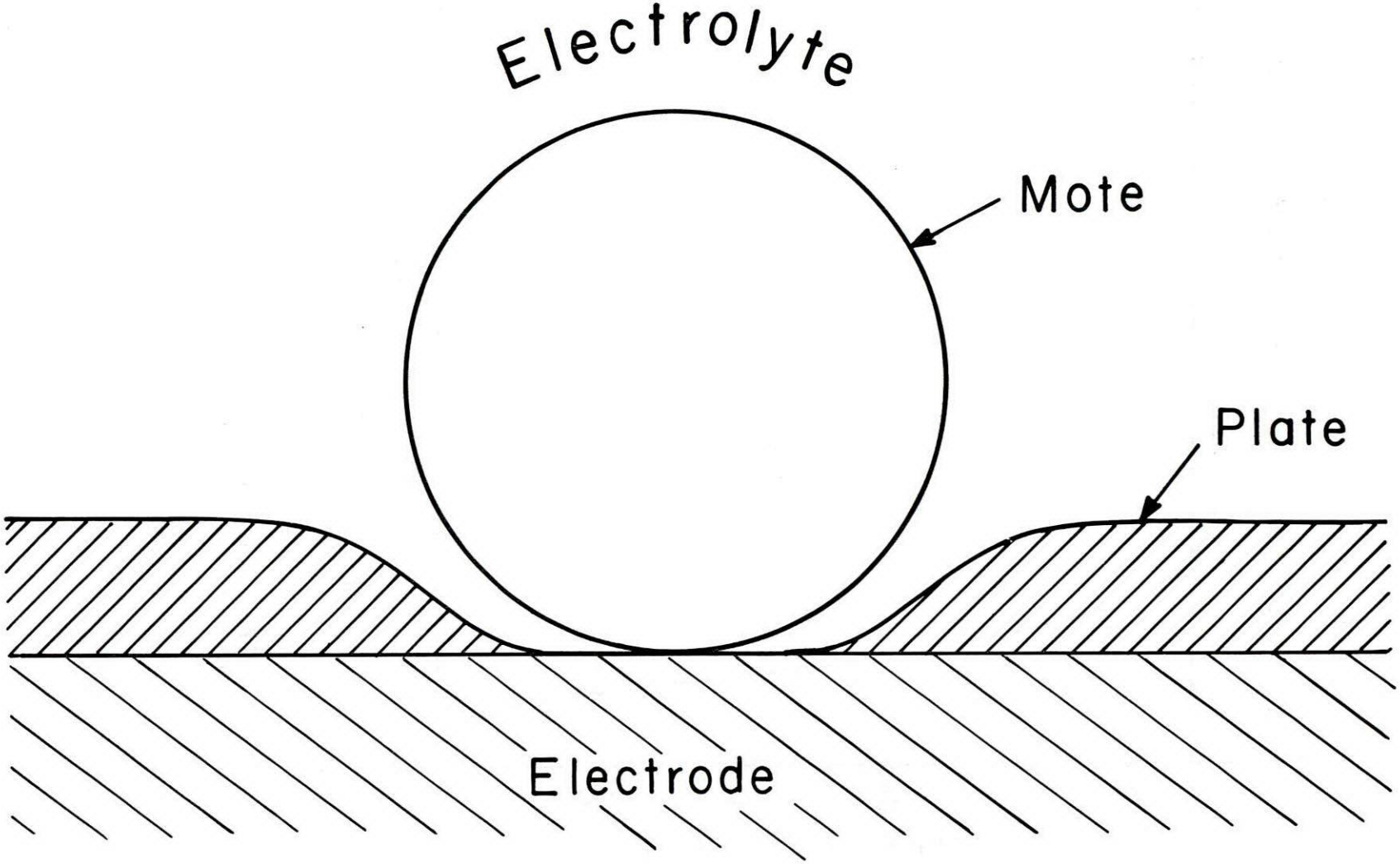

Figure 3. Schematic of the morphology of a pit which would form if the primary current

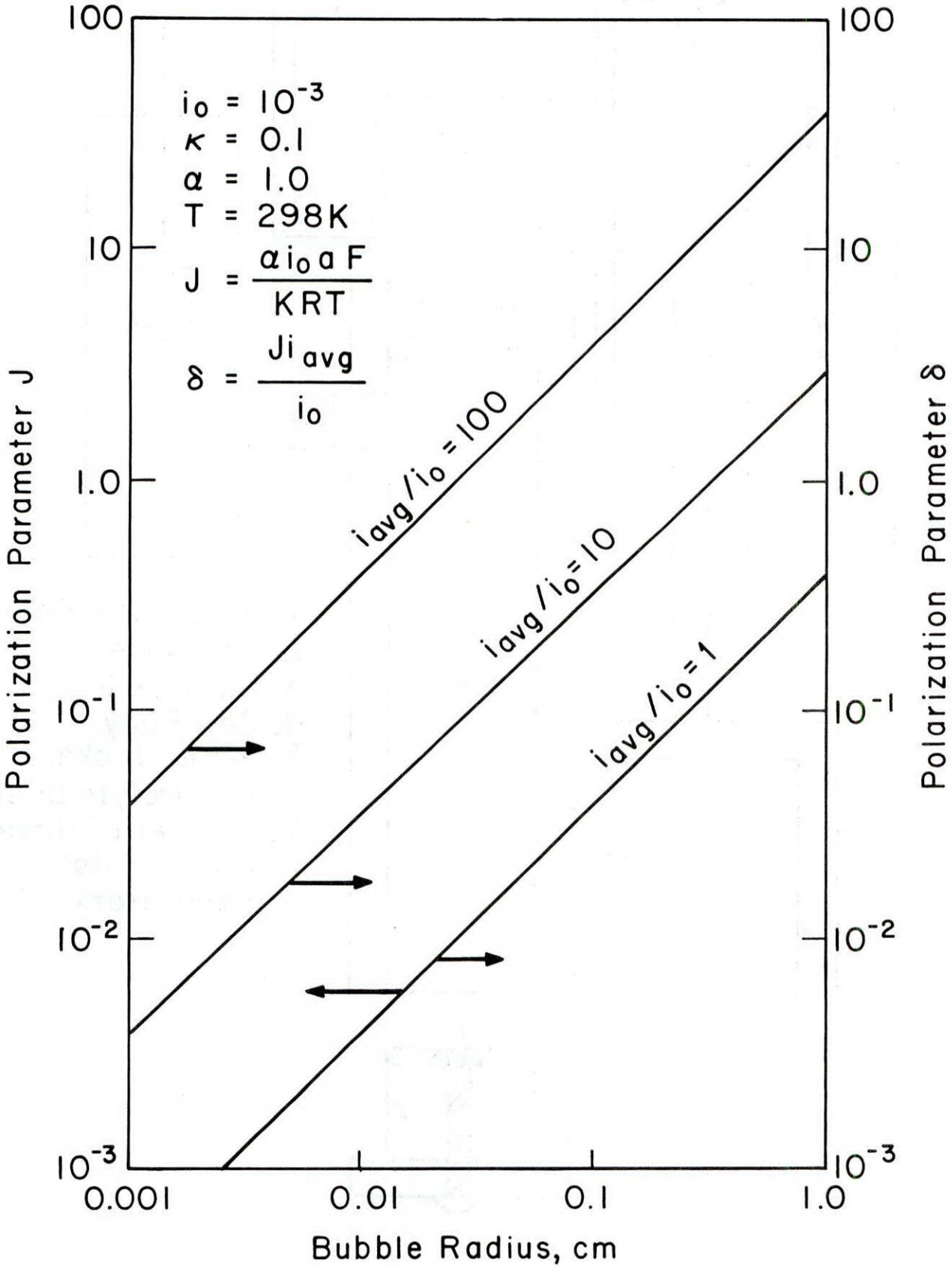

Figure 4. Polarization parameters J and δ for aqueous plating conditions.

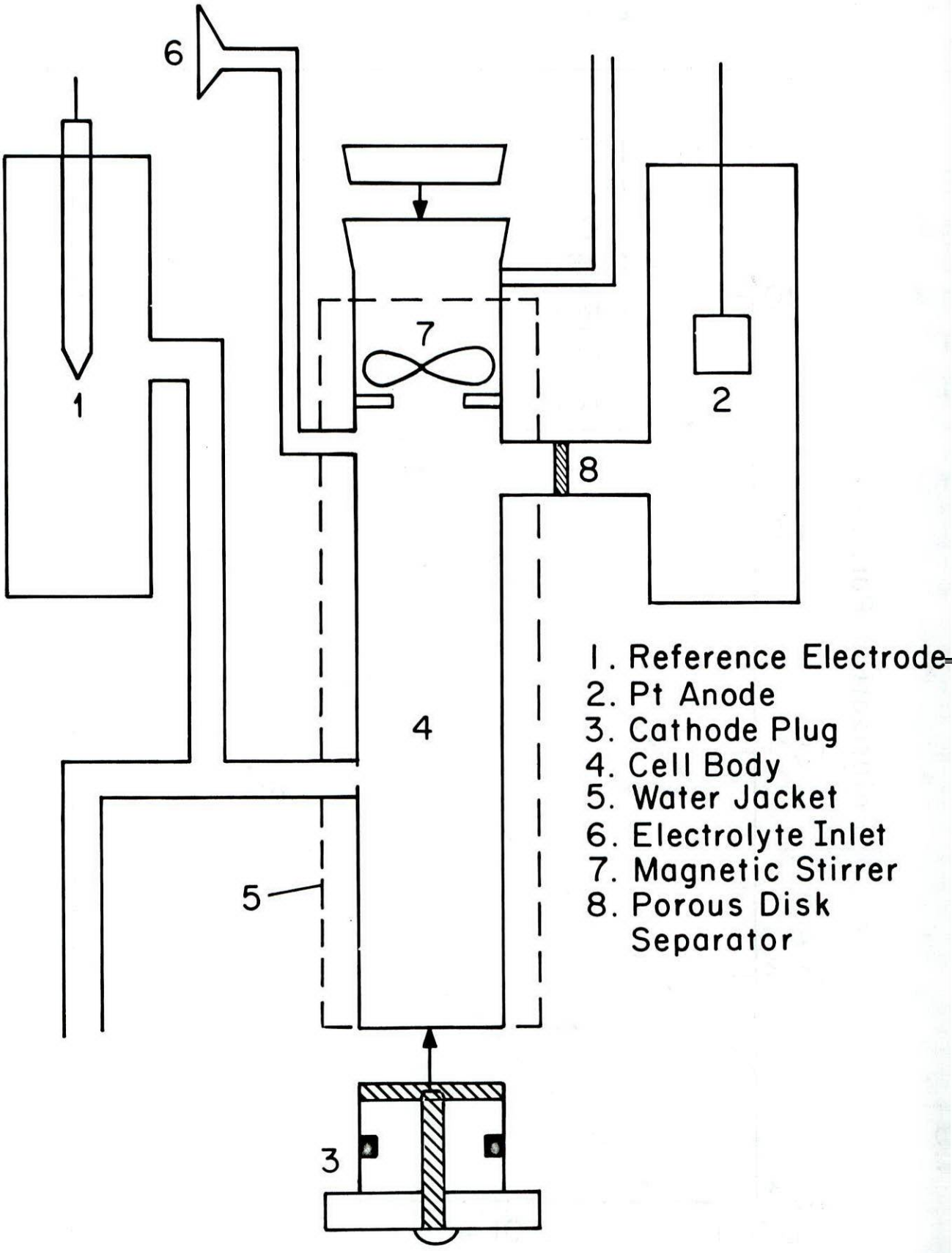

Figure 5. Schematic of the apparatus for the electroplating experiments.

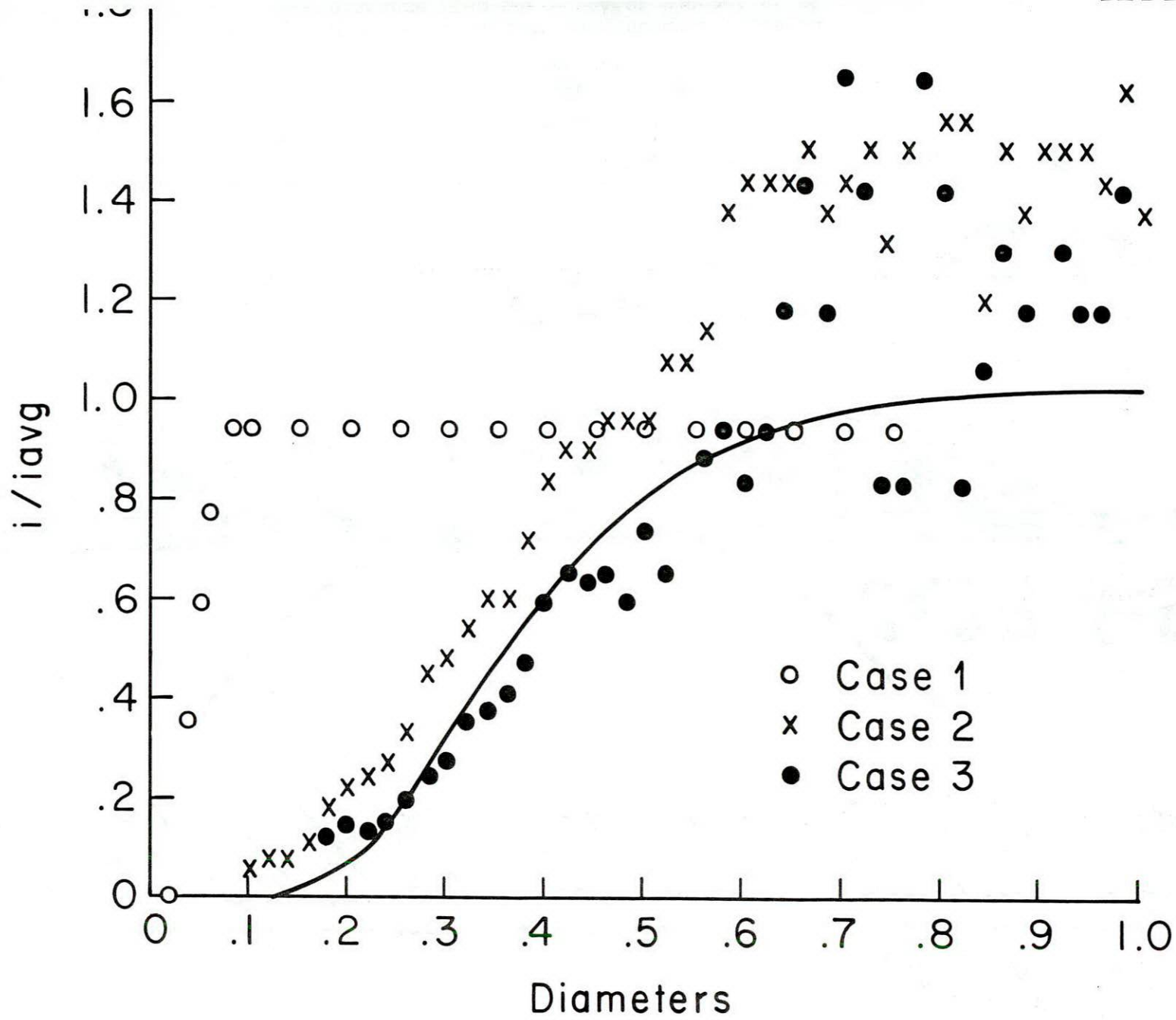

Figure 6. Crossection of three copper disks plated with approx. .005 in. of copper around dielectric spheres resting on the surface.

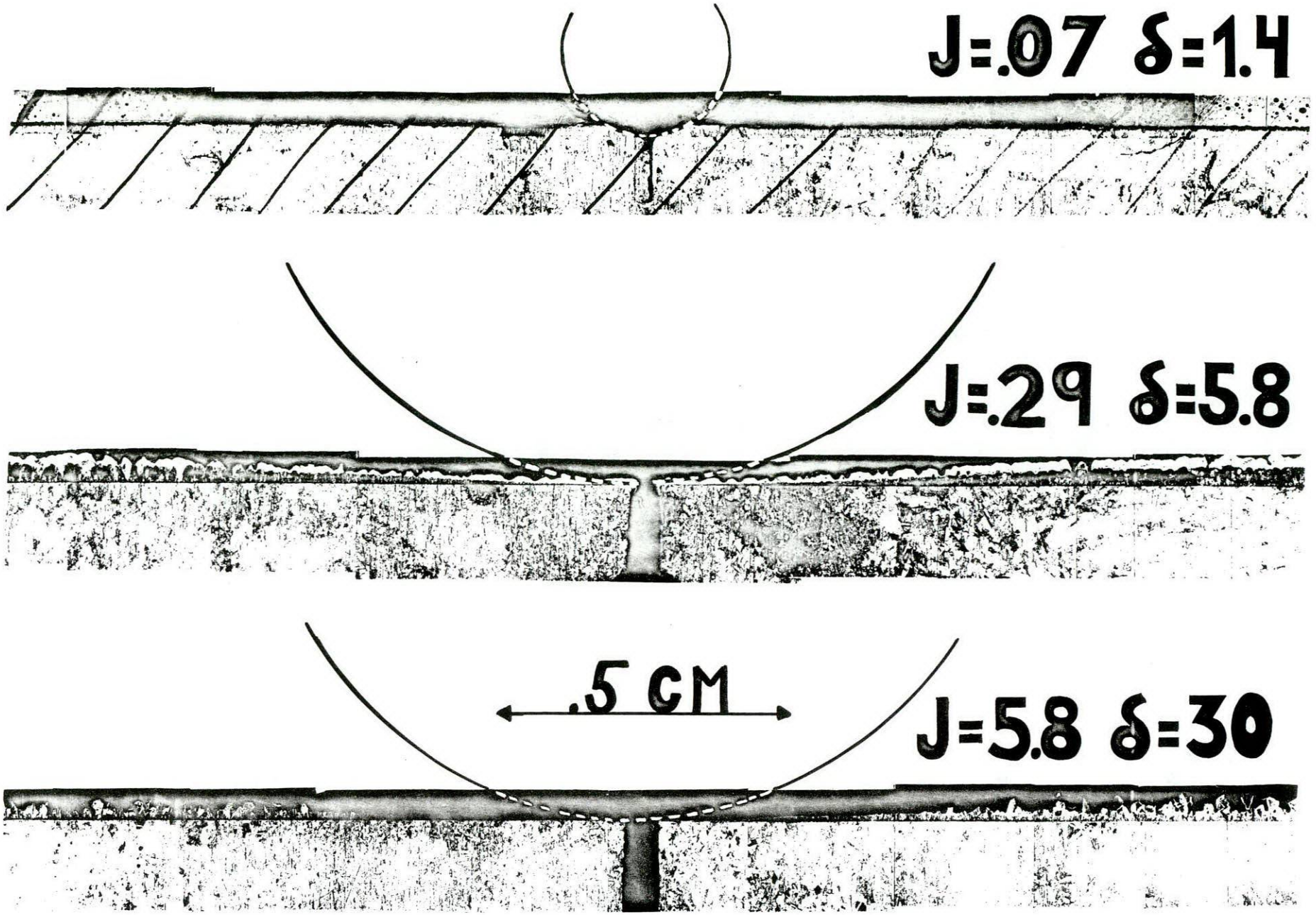

Figure 7. Plot of normalized current density versus distance from the point of contact of the

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Research Session F

Application of Small Perturbation Electrochemical Techniques for Predicting the Corrosion Resistance of Chromated Galvanized Steel — AES Project 65

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APPLICATION OF SMALL PERTURBATION ELECTROCHEMICAL TECHNIQUES FOR PREDICTING THE CORROSION RESISTANCE OF CHROMATED GALVANIZED STEEL

--AES PROJECT 65

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Introduction

Electrodeposited zinc coatings are applied in order to protect steel against corrosion. These zinc coatings can be made more corrosion resistant by treating them in a chromic acid solution, where a chromate conversion coating is formed on the zinc surface [1].

Adequate control of coating bath parameters is essential in maintaining the corrosion protection properties of the chromate conversion coating. Therefore, the corrosion resistance of the coating must be rapidly and reliably tested. However, this cannot be accomplished by the usual testing methods. The present standard testing procedure is ASTM B 117-73, in which the sample is salt sprayed and the time to white rust is measured. The reliability of this accelerated corrosion test in predicting the behavior of test pieces under real conditions remains controversial [2]. The time length involved in this test is sometimes several days, far too long for adequate and systematic control of the conversion coating bath parameters.

The purpose of this paper is to describe a method, based upon impedance measurements, for evaluating the corrosion resistant properties of the coating. It has been shown by Lengyel, et al. [3], that ac impedance measurements are sensitive to chromate conversion coating type and quality, although they made no quantitative conclusions. Jardy, et al. [4] have described a method, based upon impedance measurements, for evaluating phosphate conversion coatings on electrodeposited zinc. Also, it has been shown by Epelboin, et al. [5], Macdonald, et al. [6], and others [7-9] that ac impedance measurements can be used for accurate and reliable determination of corrosion rates. In this paper, the experimental results obtained to date at The University of Akron are presented. The results indicate that the charge-transfer resistance, determined from an ac impedance analysis, can be used as an indicator of the corrosion resistance of the chromate conversion coating. The charge-transfer resistance is shown to be dependent upon the quality of the chromate conversion coating and its thickness. Also, the results indicate that surface morphology plays an important role in the frequency response of the chromated galvanized steel.

Brief Review of AC Impedance Theory

In recent years, the use of the complex plane for analysis of electrochemical reactions has been widespread and has found considerable application. Small perturbations of potential, about the open circuit potential, only slightly alter the reactions occurring at the interface between the surface and the electrolyte. If the amplitude of the perturbation is less than 5 mV, the Butler-Volmer equations, describing simple charge transfer kinetics, are linearized and the impedance can be described as a linear combination of resistances, capacitances, and inductances. The advantage of ac impedance techniques over traditional dc polarization techniques is that the surface layer is not polarized and physically or chemically altered by the applied potential. By studying the impedance diagram, characteristic properties of the surface layer are obtained.

The electrochemical cell can be represented by a network of resistances and capacitances, the so-called equivalent circuit [8,9]. Determination of the components of the equivalent circuit will provide a characteristic measure of the corrosion resistance, which will vary between coating type and in coating thickness.

The values of the equivalent circuit that corresponds to the coating are R_1 and C_1 in Figure 1. These values provide information on the compactness and corrosion resistance of the coating. In theory, the values of the resistances and capacitances determined are frequency independent, but in reality, they are sometimes a function of frequency. This dependency is shown by a depressed semicircle on the complex impedance diagram, as shown in Figure 2. The frequency dependence of the resistance and capacitance has been attributed to the roughness of the electrode surface [10,11]. From Scanning Electron Microscope (SEM) photographs, the surface of the electrodeposited zinc was observed to be rough.

A computer algroithm, CIRFIT, developed by Kendig, et al. [12], is used to analyze this depressed semicircle behavior according to the following model

$$Z = R_{el} + \frac{R_{ct}}{1 + (j\omega\tau)^{\beta}}$$

where R_{el} = electrolyte resistance
R_{ct} = resistance to charge transfer
C_{dl} = double layer capacitance
j = $\sqrt{-1}$
ω = frequency in radians per sec
τ = time constant, product of R_{ct} and C_{dl}.
β = beta, the non-linear factor.

Experimental Method

The electrochemical cell design is based upon the design reported by Cahan, et al. [13]. It provides a uniform current distribution on the working electrode. The placement of the reference electrode in this design minimizes solution ohmic losses in the measurement and eliminates any masking effects due to the presence of a capillary probe. A sparging tube and gas trap arrangement allows for a controlled atmosphere during the test. Special attention was given to the seal between the cell and working electrode and to the electrical contact in order to minimize any system contribution to the measured impedance and to improve the cells high frequency characteristics. The sample area exposed to the electrolyte was 0.97 cm^2.

Steel panels (2.67" x 3.95") with a zinc coating are obtained from McGean-Rohco, Inc. The panels are stripped of the zinc coating by immersion in a 50% (vol) HCl bath. The panels are wiped with a damp cloth to remove residue left from the stripping and they are then ready to plate. This procedure eliminates the introduction of any proprietary additives or electrocleaners into the plating scheme. The panels were zinc plated in the center of the bath with two anodes placed on each side of the panel. By plating in-house, greater experimental reproducibility is achieved. Plating was done out of a sulfate bath with a composition suggested by Creutz [14].

The composition of the chromate conversion coating bath was based upon the composition reported by Bishop, et al. [15]. The Cr^{6+} concentration was scaled down from the original formulation to 1 g/l. The pH was maintained at 1.84 by the addition of sulfuric acid. The application of the coating was done reproducibly by using an apparatus, which resembled an impinging jet. After the sample was dipped for a predetermined time, it was rinsed twice in deionized-distilled water at 24°C and dried in a stream of air at 24°C. The samples were then left for 24 hours to allow the coating to harden.

The electrolyte chosen was a buffered borate solution, such as used by Cahan, et al. [16-19] for passivation studies of iron. The borate buffer was deoxygenated for 1 hour with nitrogen prior to the experiment and nitrogen was passed over the electrolyte during the experiment. The tests were conducted at 24°C. The electrode potential was referred to a homemade $Hg/Hg_2SO_4/1.0M\ H_2SO_4$ reference electrode (E_{ref} = 0.426V vs. SCE) via a capillary designed into the cell structure itself. The counter eletrode was a ruthenized titanium mesh. All measurements were conducted at the open-circuit (I=0) potential.

The ac impedance was measured using the EG&G Princeton Applied Research Model 368-2 AC Impedance Measurement System. The system includes the PAR Model 273 Potentiostat/Galvanostat, which is reported to be capable of response up to 100 kHz. The frequency range analyzed was 10 mHz to 100 kHz.

After the impedance measurements, some of the samples were analyzed using a Scanning Electron Microscope (SEM) and photographs were taken.

Results and Discussion

The ac impedance response was measured on zinc plated steel with and without a chromate conversion coating. Different dip times were studied in order to determine if ac impedance measurements are sensitive to chromate coating thickness. Intuitively, a longer dip time corresponds to a thicker coating. The dip times studied were 0, 15, 30, 45, 60, and 90 seconds. In order to determine reproducibility, eight tests were performed on electrodeposited zinc with no conversion coating and seven with a 15 second dip. The ac impedance response in both cases were found to be reproducible. Therefore, subsequent testing of longer dip times were made using two samples each. The results from the longer dip times also indicated reproducibility was obtained. The quality of the chromate conversion coating for the dip times of 60 and 90 seconds was poor. The coating was fragile and sensitive to abrasion. This poorly adhering coating would probably provide poor corrosion resistance in actual service conditions.

Figure 3 illustrates a typical ac impedance response plotted on a complex impedance diagram. The data demonstrates that at least two relaxations are observed in the electrical properties of the interface. At frequencies below 1 Hz, diffusional limitations in the ac impedance response were encountered. This is described as Warburg impedance. The solution resistance was determined to be 70 $\pm$ 10 ohms.

The high frequency semicircle was found to be invariant with coating thickness (different dip times) and whether or not a chromate conversion coating was present on the electrodeposited zinc surface. A value for the resistance and capacitance for the high frequency semicircle was determined for each test and the average is presented below:

$$R_{nf} = 167 \pm 18 \text{ ohms}$$

$$C_{nf} = 0.0360 \pm 0.004 \ \mu F$$

A carefully selected set of experiments were conducted to determine the physical significance of the high frequency response. The experiments indicate that the cell design is responsible for this response, but further experiments are presently being conducted to verify this conclusion.

Figure 4 is a complex impedance diagram illustrating that ac impedance measurements are sensitive to the chromate conversion coating. As shown, the ac impedance response of a chromate coated sample is significantly different from an uncoated sample.

The low frequency semicircle, illustrated in Figures 3 and 4, correspond to the polarization resistance and the double layer capacitance, in parallel. Since the frequency range of this semicircle is between 10 Hz and 5000 Hz, we can assume that the polarization resistance is equal to the charge transfer resistance [5]. The experimental data were treated using CIRFIT [12], which is an analysis of equation (1). The parameters determined from this analysis algorithm are the charge transfer resistance, R_{ct} and beta, the non-linear factor. For an ideal ac impedance response, which is a semicircle on the complex impedance diagram with its center on the real axis, beta is equal to 1. When the ac impedance is less than ideal, beta is less than 1. This corresponds to a depressed semicircle on a complex impedance diagram with its center below the real axis.

Figure 5 is a plot of the magnitude of the charge transfer resistance, R_{ct}, versus dip time and beta versus dip time. As illustrated, the charge transfer resistance for a 15 second dip is 20 times that of the charge transfer resistance of an uncoated electrodeposited zinc sample. As the dip time increases, the value of the charge transfer resistance decreases. As the dip time approaches 60 to 90 seconds, the charge transfer resistance is essentially the same as that for an uncoated sample. One hypothesis for explaining this phenomena is that the reactions occurring at the interface change as the coating thickness increases.

In this hypothesis, we assume that the anodic reaction occurring at the interface of an uncoated electrodeposited zinc surface is a simple zinc dissolution reaction. When the coating is applied, at a 15 second dip time, the zinc reacts with the coating solution to form zinc-chromium oxides and hydroxides. Therefore, the zinc dissolution reaction is inhibited and the charge transfer resistance is increased. At longer dip times, the surface contains chromium oxides and hydroxides with the zinc well below this surface. Thus, the charge transfer resistance measured for a thick chromate conversion coating could correspond to a different anodic reaction than that of

zinc dissolution. Also, as the dip time increased from 60 to 90 seconds, the charge transfer resistance remained constant, indicating that the reactions occurring at the interface were the same under both of these conditions. This would happen if the zinc was totally isolated from the electrolyte and the coating composition remained constant, with only the thickness increasing. An increase in conversion coating thickness would not have an observable effect on the ac impedance response because the coating is very conductive [1]. A significant amount of additional measurements would have to be conducted to evaluate this hypothesis.

In Figure 5, beta is plotted against dip time. Beta, the non-linear factor, corresponds to the roughness of the electrode surface. For uncoated electrodeposited zinc, beta was determined to be approximately 0.8. This value is very close to 0.79, which approximates that for a first order branch RC network that would theoretically describe the ac impedance response of an occluded surface [11]. For a 15 second dip coating, beta increases, corresponding to a smoothing of the surface. As shown in the SEM photograph in Figure 6, this is indeed the case. As the dip time is increased, beta again approached 0.8. This corresponds to the surface having fractures and cracks, resulting in a rougher surface.

Therefore, it appears as though beta could be used as a quality control measure of coatings. A large value of beta, as compared to a beta determined from an uncoated zinc sample, would indicate a high quality coating with adequate adherance to the zinc surface. A beta equal to the beta of an uncoated zinc sample would indicate a poorly adhering coating, probably providing poor corrosion protection. Thus, the determination of beta from an ac impedance response of a coating may provide an indication of the coatings corrosion resistance and the coatings adhesion to the zinc surface.

Presently, the dip time is being correlated with chromium weight per unit area. This should provide a more meaningful interpretation of the charge transfer resistance and beta factor.

Conclusions

AC impedance electrochemical techniques are being investigated as a means of predicting the corrosion resistance of chromated electrogalvanized steel. Measurements indicate that the low frequency response is related to the electrical properties of the coatings. The high frequency response appears to be an artifact of the cell design, but additional measurements are needed to verify this conclusion. The lower frequency response is a function of coating thickness and

quality. These responses were interpreted in terms of a non-linear model. The estimate of the parameters, the charge transfer resistance and beta, appear to be consistent with physical observations. These parameters may prove to be useful for predicting the corrosion resistant properties of the chromate coatings.

Acknowledgement

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REFERENCES

1. Biestek, T. and J. Weber, Electrolytic and Chemical Conversion Coatings, (Portcullis Press Ltd, 1976).

2. Williams, L. F. G., Surface Technology, 5, 183-94 (1982).

3. Lengyel, B., Zs. Baroti - Labar, R. Kahan, Materials Chemistry, 7, 183-94 (1982).

4. Jardy, A., R. Rosset, and R. Wiart, J. Appl. Electrochem., 14, 535-45 (1984).

5. Epelboin, I., Gabriellei, C., Keddam, M., and H. Takenouti, "Alternating Current Impedance Measurements Applied to Corrosion Studies and Corrosion Rate Determination," Electrochemical Corrosion Testing, ASTM STP 727, 150-66 (1981).

6. Macdonald, D. D. and McKubre, M. C. H., "Electrochemical Impedance Techniques in Corrosion Science", Electrochemical Corrosion Testing, ASTM STP 727, 110-49 (1981).

7. Haruyama, S. and T. Tsuru, "A Corrosion Monitor Based on Impedance Method," Electrochemical Corrosion Testing, ASTM STP 727, 167-86 (1981).

8. Mansfield, F., M. W. Kendig and S. Tsai, Corrosion, 36, 5, 301-7 (1981).

9. Mansfield, F., M. W. Kendig and S. Tsai, Corrosion, 38, 11, 570-80 (1982).

10. DeLevie, R., Advances in Electrochemistry and Electrochemical Engineering, Vol. 6, (Interscience-Wiley, 329-97, 1969).

11. Scheider, W., J. Phys. Chem. 79, 2, 127-36 (1975).

12. Kendig, M. W., E. M. Meyer, G. Lindberg and F. Mansfeld, Corrosion Science, 23, 9, 1007-1015 (1983).

13. Cahan, B. D., Z. Nagy, and M. A Genshaw, J. Electrochem. Soc., 119, 164-9 (1972).

14. Creutz, H. G. and S. Martin, Plating and Surface Finishing, July, 681-6 (1975).

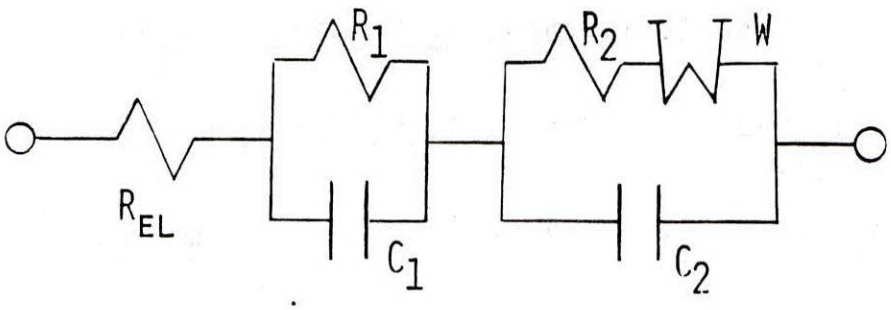
15. Bishop, C. V., D. M. Burdt, and K. R. Romer, GALVANOTECHNIK 71, 11, 1199-1206 (1980).

16. Cahan, B. D. and C. T. Chen, J. Electrochem. Soc., 129, 4, 700-5 (1982).

17. Chen, C. T. and B. D. Cahan, J. Electrochem. Soc., 129, 1, 17-26 (1982).

18. Cahan, B. D. and C. T. Chen, J. Electrochem. Soc., 129, 3, 474-80 (1982).

19. Cahan, B. D. and C. T. Chen, J. Electrochem. Soc., 129, 5, 321-5 (1982).



WHERE: R_{EL} = ELECTROLYTE RESISTANCE,
R_1 = COATING RESISTANCE,
C_1 = COATING CAPACITANCE,
R_2 = CHARGE TRANSFER RESISTANCE,
C_2 = DOUBLE LAYER CAPACITANCE,
W = WARBURG IMPEDANCE.

Figure 1: Equivalent Circuit Model For An Electrochemical System.

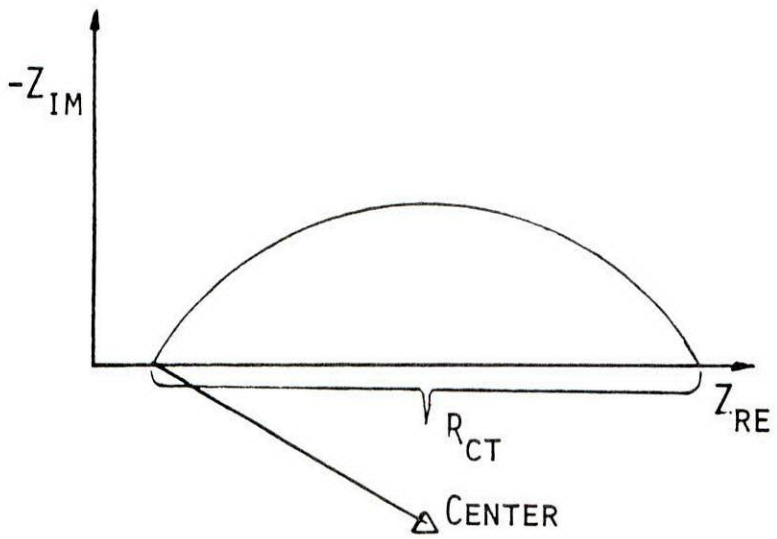


Figure 2: Complex Impedance Diagram Illustrating Depressed Semicircle Behavior.

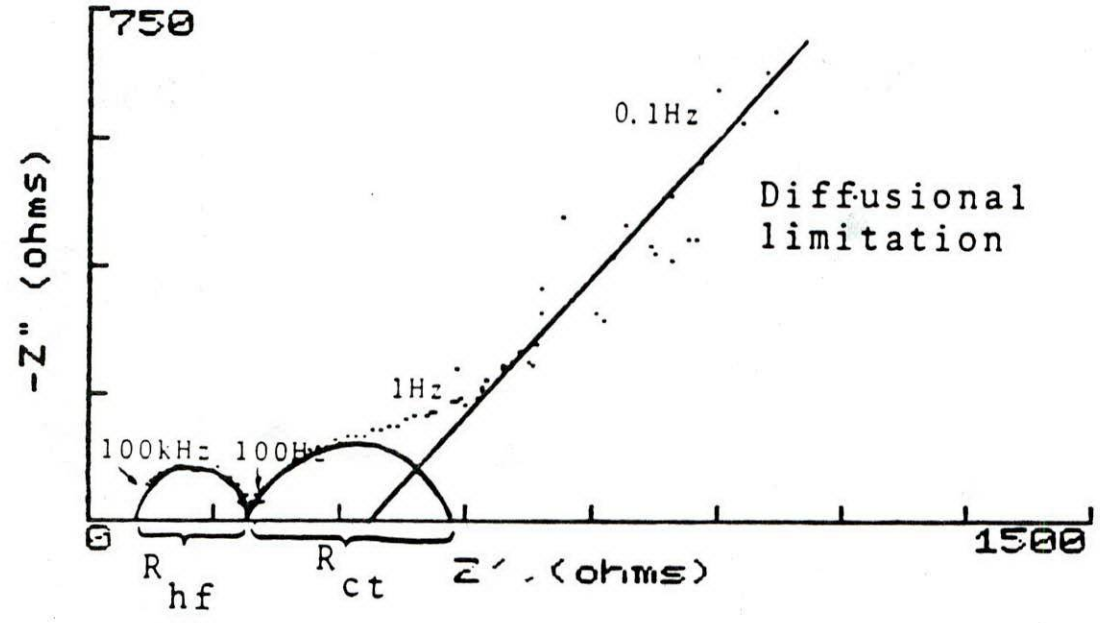


Figure 3: Complex Impedance Diagram. Typical AC Impedance Response. Equivalent Circuit Resistances are Defined. R_{hf} = High Frequency Resistance. R_{ct} = Charge Transfer Resistance.

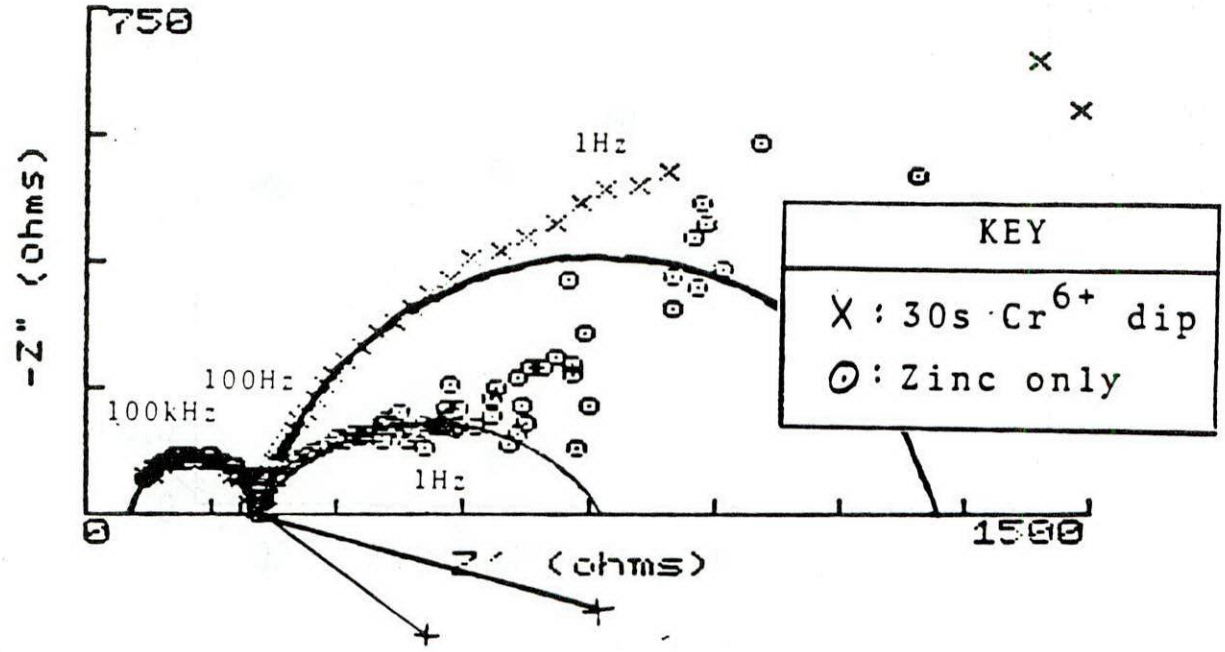


Figure 4: Complex Impedance Diagram. Illustrates Difference In AC Impedance Response Between A Coated Sample And One That Has No Conversion Coating.

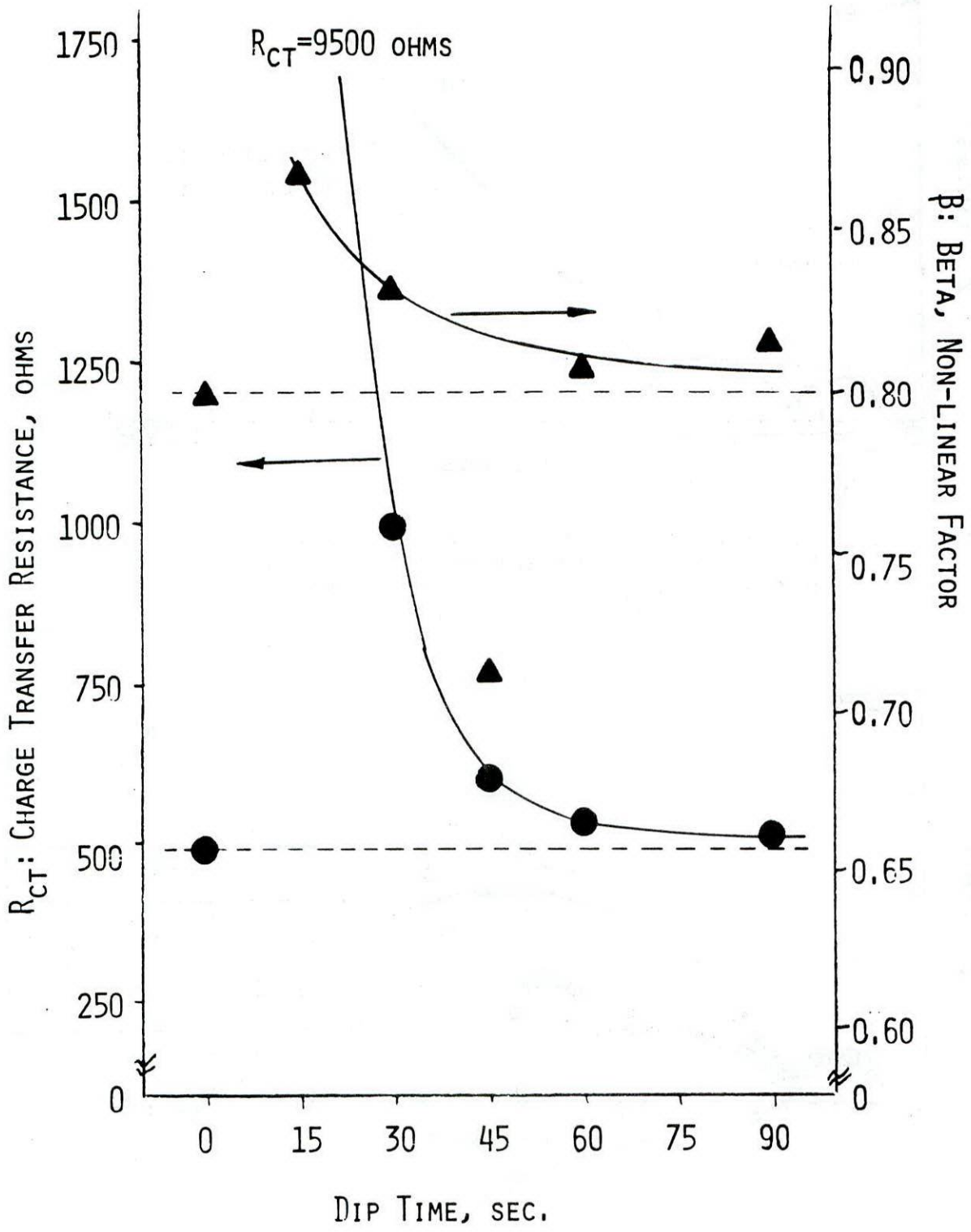
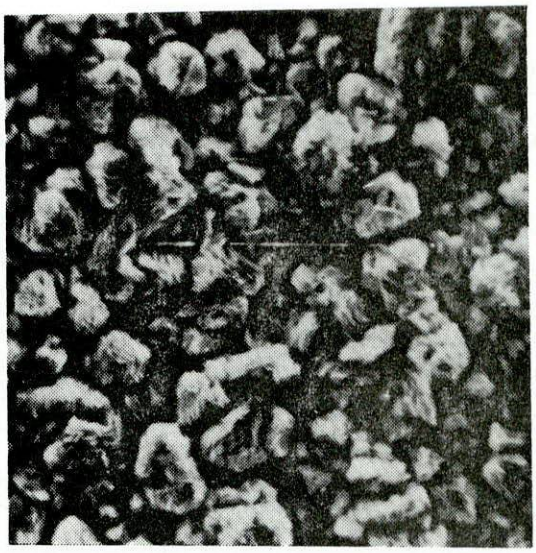


Figure 5: Charge Transfer Resistance and Beta, the Non-Linear Factor Versus the Dip Time of the Coating.



(a)



(b)



(c)

Figure 6: Scanning Electron Microscope Photograph. Magnification = 1000X. (a) Zinc only. (b) 15 sec yellow dip. (c) 60 sec yellow dip.

G-1

Decorative II
Session G

Improved Decorative Plating with Automatic Vibratory Plating

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IMPROVED DECORATIVE PLATING WITH

AUTOMATIC VIBRATORY PLATING

VANGUARD RESEARCH ASSOCIATES, INC.

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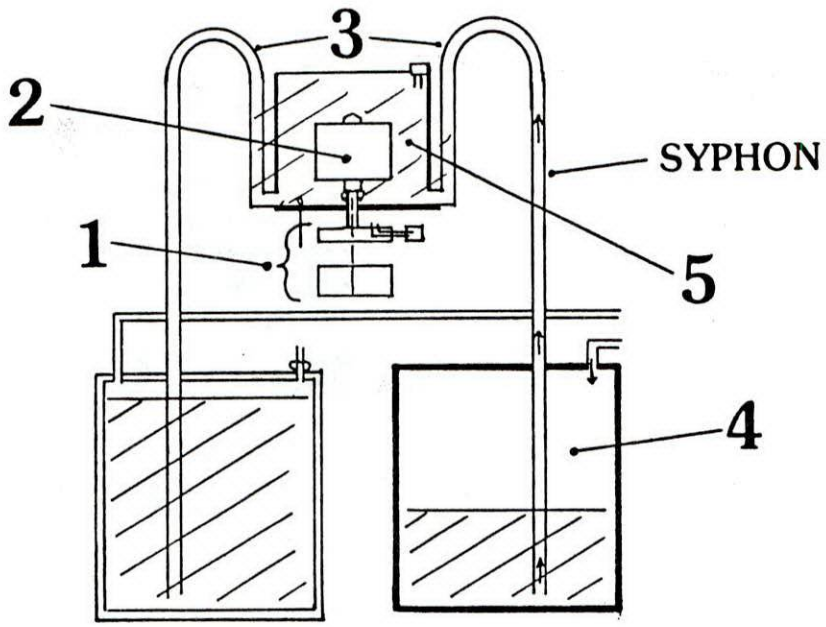
The vibratory plating system (1) used in our evaluation has been already presented to the American Electroplaters Society at The Second AES Symposium On Economic Use And Substitution For Precious Metals In The Electronic Industry, in Danvers, MA, on October 5 - 6, 1982.

It is an automatic plating machine engineered for the treatment of small parts, including all necessary equipment for cleaning, activating, plating and drying. The unit is designed around a vibratory basket or rack, inserted in a plating tank in which the solutions for cleaning, activating and plating are transfered one after another according to a pre-progammed sequence.

The following drawing shows the basic principle of the machine:



1. VIBRATOR with axle
2. Plating basket or rack
3. Siphon
4. Storage tank
5. Operational or plating tank

I. SEQUENCE OF EVENTS:

(1) Parts are loaded on a vibratory plating rack or into a basket shown in (2).

(2) Optimum vibration is set up by adjusting the vibrator (1). Vibrations are transmitted to the plating rack or basket through the axle (6). A leak proof system prevents the solutions from leaking out. The axle is also the electrical contact for the plating rack or basket.

(3) Solutions are introduced - as per a pre-programed sequence - into the plating tank (5) from the storage tank (4) through a siphon system (3) by means of compressed air introduced into the storage tank (4). Each storage tank has its own siphon.

(4) Solutions are siphoned out of the plating tank by simply releasing the air pressure in the storage tank.

(5) The plating tank is equipped with an automatic anode changer commanded by the program. After the plating sequence, the anode is removed and rinsed.

(6) Two kinds of rinses can be selected and sequenced as desired in the programing of the machine. They are: (1) a shower rinse and (2) a full immersion rinse.

(7) Parts can be dried in the vibratory basket or on the rack to avoid distortion or tangling, etc.

(8) The temperature controls, rectifier, programing system (by perforated tape or a micro-processor) are located in a console.

II. VIBRATIONS AND PLATING:

The data presented in our paper at the Second AES Symposium On Economic Use And Substitution for Precious Metals in the Electronic Industry, in Danvers, MA, on October 5 - 6, 1982, shows that - in bulk plating - substantial precious metal savings - in the order of 10% - can be achieved, in the electronic industry, through better distribution within a lot and less thickness variation from lot to lot.

Better distribution - within a lot - is achieved, in bulk plating, by improved tumbling and better solution exchange because of the vibrations generated by the machine.

Lesser thickness variation - from lot to lot - is the consequence of the complete automation of the machine, which completely eliminates operator's errors. Lots are removed from the plating tank at the precise time chosen virtually eliminating overplating, which is of the upmost importance at present gold prices.

Quality is also enhanced by the automation of each plating step including rinsing, etc. Once a plating cycle has been determined and optimized, it is simply reproduced - time after time - from lot to lot - without any errors or changes whatsoever .

It has been our finding that vibrations do much more than improve distribution and have significant and beneficial effects, in bulk plating as well as in rack plating, such as:

(1) Deposits are less porous because of improved solution exchange, better rinsing and quick elimination of hydrogen bubbles during plating.

(2) Improved corrosion resistance because of better throwing power and solution exchange (and better rinsing) in deep recesses or spots reputed impossible to reach, etc.

(3) Less contamination of the all the solutions because of:

    (a) Very low "drag in".

    (b) Very low "drag out".

    (c) Complete absence of airborne contamination (completely sealed tanks).

    (d) Low rate of evaporation - eliminating contamination by water additions.

III. BULK PLATING:

In our modern world COST REDUCTION is the constant challenge being met by every manufacturing operation. Somehow - just to remain competitive - one has to produce a product of better or comparable quality cheaper than that of the competition.

The decorative plating industry is particularly sensitive to high costs since many highly polished parts must be rack plated - Hence are labor intensive. One way to reduce racking cost is to simply eliminate it! Platers know that is simpler to say than to do....and many attempts to barrel plate such parts have, to-date, simply failed to produce good results.

We now enter the area in which vibratory plating can be of help. In the vibratory system described here, the parts are plated in BULK in a basket operating on a principle entirely different than that of a barrel. In a barrel the parts tumble and fall in a relatively uncontrolable fashion, which introduce nicks and scratches on polished parts. A situation simply unacceptable in decorative plating.

As a general rule the heavier the polished parts the more difficult they are to barrel plate.

In vibratory plating the parts are not tumbled by the mechanical rotation of the barrel but by the vibrations generated by the

machine in very much the same fashion parts move in a "Syntron-bowl" or in machines of similar concepts. The vibrations are controled by a command module, adjusted and optimized for every type of parts. As a general rule for highly polished parts, to avoid damages, vibrations are kept as low as possible.

The vibratory baskets are very important and can be designed to optimize the results for specific parts. The configuration and geometry of the part to be plated has to be taken in consideration. The basket usually includes a step and various styles of deflectors to promote movement and mixing of the parts. The step height and style of deflectors changed as necessary or, in some cases, even eliminated.

The same basket can be used to dry the parts in the air dryer which requires little to no vibrations.

We have found that in many cases the following can be achieved:

(1) Constant very good mixing of the parts without mechanical constraint, render possible to plate in bulk some parts reputed impossible to barrel plate.

(2) The very flat parts can be plated without sticking together.

(3) The pin like parts without damaging the tips or the edges or leaving rack marks.

(4) The polished parts without loosing brighteness because of nicks and the like.

IV. PLATING OF CHAINS.

Chains are extremely difficult to plate by conventional means because they have a tendency to bunch up together. The 'bunch up' action combined with the lack of motion simply prevents copper and nickel to be thrown were needed the MOST - that is between the chain links - to protect the base copper from the severe corrosion conditions chains are exposed to.

Technically speaking, chain plating is one of the most interesting vibratory plating application and the results are simply surprising. During cleaning, activation, and plating, apparently, the vibrations break the contact long enough to allow the copper and the nickel to be thrown between the chain links - where it's needed the MOST - without affecting the adhesion.

The results are a high quality chain comparable in corrosion resistance - and look - to the more expensive gold filled chains.

A special rack is used in the operation and the chains are allowed to hang down freely - that is very important - so the vibrations can "move" the chain from its support:

(1) There are no rack marks.

(2) Racking cost is low since the chains are simply placed on one of the several hooks of the rack.

(3) Distribution is excellent since the chains are constantly in motion.

Because of the limited size of our present plating tank (see note 2) the practical economical chain length to be plated is 20 inches. However we have plated 24 inches long chains by drastically reducing the number of parts plated.

The number of chains plated in one cycle is:

24-inch long chains:	80
18-inch long chains:	425
shorter chains :	1000

A typical plating cycle is: (area plated 1360 in² [88 dm²])

(1) Copper : 2 minutes @ 20 ASF (2 amp/dm²) 50 u" (1.25 micron)

(2) Nickel : 14 minutes @ 37 ASF (3.7 a/dm²) 200 u" (5 microns)

(3) Gold : 2 minutes @ 5 ASF (.5 amp/dm²) 10 u" (.25 micron)

The complete plating cycle, including cleaning, activation, all rinses, etc. - but not drying - takes 38 minutes. All rinses include a full immersion rinse followed by a spray rinse.

V. CONCLUSION:

We feel that vibratory plating can provide a very valuable tool as a new approach to decorative plating. Some parts previously rack plated can now be plated in bulk. The quality of some products can be improved by taking full advantage of the vibration generated by the machine and, in many instances, generate a gold saving in the order of 10%.

Many applications other than the examples given above can be found to take full advantage of the vibratory plating system presented in this paper.

NOTE 1: VIBROBOT, Neuchatel, Switzerland, Vanguard Research Associates, 239 St.Nicholas Avenue, South Plainfield, New Jersey, 08080.

NOTE 2: A special machine with a plating especially sized to accommodate longer chain lengths can be designed without any major problem.

G-2

Decorative II
Session G

Revolutionary Automated Plating System For Mass Production Based Upon Vibratory Technology

Pierre Andre' Schopfer
Meco USA Inc.
Glendale Heights, IL

REVOLUTIONARY AUTOMATED PLATING SYSTEM FOR MASS PRODUCTION BASED UPON VIBRATORY TECHNOLOGY

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Meco USA Inc.
Glendale Heights, IL

Within the last ten years there has been a dramatic increase in demand for greater quantity and quality of electronic components in the connector and semiconductor industry. The strong competitive impetus for producing these parts with the highest possible quality and at the same time the lowest cost, has encouraged the development and implementation of unique equipment to accomplish this.

The electroplating field which contributes very importantly to the performance and reliability of these components is no exception to this advance in equipment technology. It is in this spirit that a team of engineers applied the principle of vibratory plating. They developed a machine with an entirely new approach to plate loose piece parts which were historically done by conventioned barrel methods.

The advantages of vibratory plating have been well established:

1. Excellent distribution of the plated deposit over the surface area of the products.

2. Ability to handle delicate and fragile parts without distorting or damaging.

The novel machine (Figure 1 and Figure 2) incorporates these advantages into a technique whereby a basket is fixed to the bottom of an oscillator unit which vibrates in an axial and tangential fashion. Both the frequency and amplitude are adjustable as desired. The complete unit is moved from one tank to another in sequence like a conventional barrel line. In this way the throughput capacity of barrel methods is merged with the advantages of vibratory plating technology.

In Figure 3 the oscillator and attached basket which we will call an "oscillant unit" is pictured. The unit consists of three main elements.

1. The electromagnetic oscillant motor unit.
2. The basket containing the pieces to be processed.
3. The support frame.

Electromagnetic Motor Unit:

The electromagnetic motor unit consists of a horizontal base plate to which elastic supports are fixed on one side. The vibrations produced by the oscillator motor are dampened by the attached elastic supports. The supports are connected on the other side to a support frame which positions the entire oscillant unit onto the contact v-saddles (Figure 4).

The support frame is fitted with hooks by which the transporter arm takes the oscillant unit from one module (station unit) to another. The rear pair of v-saddles are used as the cathodic connection for plating. The front pair of v-saddles are the DC voltage supply connections which produce the vibration frequency in the oscillant unit.

At the left side of the electromagnetic motor a control box for frequency selection is mounted. Two frequencies which can be preset are available for selection. These can be manually or automatically changed over as desired. This feature is desirable because process solutions having different viscosities will vibrate differently with the same control settings. It is easy to operate at optimum agitation conditions in this manner.

Processing Basket:

The basket (Figure 5, 6, 7, and 8) containing the loose piece parts to be processed is of a unique design. It is designed internally with an inclined ramp and various deflectors which ensure thorough mixing of the pieces in a gentle manner. At the bottom of the basket interchangeable perforated capsules are placed. These allow excellent electrolyte exchange during plating and complete solution drainage of the basket after each process step. Also fitted at the bottom are easily interchangeable stainless steel buttons, which ensure an excellent cathodic electrical contact to the pieces.

The basket is available with various dimensions and different accessory equipment options. For instance, the quantity and dimensions of the capsule holes, the number of cathodic contact buttons, the ramp incline angle, as well as the shape of the internal deflectors all vary according to the quantity and shape of the pieces to be plated.

Support Frame:

The support frame for the oscillant unit has several important functions. Its most obvious purpose is to position the basket properly in the various treatment tanks. Through appendages on the frame the electric DC current necessary for plating and motor frequency vibration are transmitted. In addition the transporter hoist moves the unit as desired with the aid of hooks attached to other appendages on the frame.

The machine is a modular design of which each module (Figure 9) can perform more than one process treatment. The compactness, versatility and ability to perform more than one function in sequence of each standard module allows a great reduction in floor space when compared to a typical barrel line utilizing the same process cycle. Additional modules may be added should production requirements demand more capacity and/or capability.

A standard module is a stainless steel frame which includes the following:

1. Polypropylene treatment tank mounted at the upper part of the frame.

2. One or two polypropylene storage tanks located at the lower part of the frame.

3. A mobile flexible pipe connecting the treatment tank to the storage tanks or to the drain.

4. Rinsing systems of two different types - total immersion and spray rinse.

The storage tanks are connected to the treatment tank by one or two immersion pumps with hose assemblies as required and are also fitted with heaters, thermostats, level sensors and other standard auxiliaries.

During the active phase, the microprocessor control system activates a piston-lever assembly closing the drain. This in its simplest form may best be described as an open end "stand pipe" capable of being lifted or lowered as required. A mobile pipe and drain assembly is positioned at the proper storage tank location (one of 4 positions) by an electrical control circuit to a linear drive motor. The bath is transferred from one of the storage tanks to the treatment tank by one of the immersion pumps. The solution continuously circulates between the storage and treatment tank via overflow of the closed drain pipe and mobile pipe assembly.

After the treatment is completed the drain is opened by lifting and the solution returned to the storage tank by gravity.

Each standard module is capable of two types of rinsing: total immersion and/or spray.

- The total immersion rinse feature performs in the same fashion as described above with the treatment procedure. The mobile pipe is moved to the second position which leads to the drain. The stand pipe assembly is lowered, thus filling the treatment tank and the rinse water overflows back to the drain.

- The second rinse feature utilizes two parallel banks of spray heads mounted at the upper part of the treatment tank. In this instance the drain pipe is in the open lifted position. Rinsing in this manner is very efficient and allows a reduction in water consumption of approximately 70% when compared to the first method.

We can use either rinse method singly, in combination, and as many times as is practical for production.

It is highly recommended that each module be dedicated to groups of compatible treatments in order to prevent cross-contamination of solutions or problems with anodes which must be dedicated to individual processes. Typical examples of compatible treatments are: Nickel plating - drag out - rinsing, Tin plating - drag out - rinsing, Gold plating - drag out - rinsing, etc. Some incompatible treatment in a single module examples also should be listed: Degreasing - rinsing - activation - rinsing, Nickel plating - rinsing - Gold plating - rinsing.

The electronic circuitry is built into a cabinet (Figure 10) for easy centralized control. It contains the microprocessor and other elements such as thermostats, remote controls for rectifiers, ampere - hour - meters, etc.

A hot air dryer can be installed in the line for proper drying of the finished parts. It is placed between the first module and the loading/unloading station. After a deionized water rinse at the last treatment module the oscillant unit is placed in the dryer in a similar manner as a standard module. Drying is carried out smoothly by a special adjustment of the oscillator containing the basket and at a relatively low temperature (approximately 60°C) so the pieces are not damaged by scratching or heat.

The loading/unloading station consists of a stainless steel frame having the same dimensions as the standard modules. The upper part is fitted with a module frame to which the v-saddles used for supporting the oscillant unit (oscillator and basket combination) are fixed. In addition the module frame is connected to a pneumatic piston which moves up and down as required.

In the active phase the transport arm places the oscillant unit on the v-saddles of the mobile frame. The weight of the unit closes a switch which causes the pneumatic piston to tip the oscillator and attached basket 90° to a horizontal position (Figure 11). This allows easy emptying of processed parts after hot air drying into a funnel type bin for collection. If no dryer is installed in the machine the parts are spray rinsed with deionized water to empty the basket easier. They then would be collected and dried "off line" as desired, in a centrifuge dryer for example.

When the basket is empty the oscillant unit is returned to the vertical position again. The basket is loaded manually (Figure 12) with other parts to be processed. As soon as the module with the first treatment in the process sequence is free the transporter arm transfers the oscillant unit to that location.

As an option the loading/unloading station may be automated by the addition of a vibrator belt feeder and weighing system. In the case of very high production, this station can simply be duplicated to satisfy the requirements.

The machine is very versatile in the range of product types and quantities that can be processed. Good mixing of the parts is directly related to good plating quality. As an adjunct to this the following dimensions should not be exceeded:

- Volume/piece = approximately 4 to 5 cm^3 (0.24 to 0.31 cu.in.).
- Length/piece = approximately 8 cm (3.150 in.).

Movement of the pieces by oscillation is particularly advantageous for the following:

1. Flat or delicate pieces.
2. Pieces having blind holes.
3. Conventional pieces needing good plating quality and uniform coating thickness distribution.

There are a number of standard size baskets available. The outer diameter of these baskets ranges in size from 160mm (6.30 inches) to 450mm (17.70 inches).
The maximum load which can be contained in a basket is variable. The largest basket size presently available is limited by two values:

1.The maximum load volume is 8 liters.
2.The maximum load is 15 kilograms.

These values would influence the number and type of modules composing the machine. In some cases it is desirable to have more than one module dedicated to the slower process steps (for example: Nickel) in order to achieve the required production.

Production experience has shown the machine to be well adapted for a wide variety of plating processes - both precious and non-precious metal plating. The usual precious metal processes - Gold, Silver, Palladium and Rhodium have all been successfully plated. Non-precious metal processes typically plated in a barrel line such as Copper, Nickel, Tin, etc., can also be used in this machine and in all cases with the previously described advantages.

Conclusion:

In conclusion I would like to summarize the more salient features of the Osciline:

- Products which are loose individual pieces are efficiently agitated by means of an electromechanical oscillator to promote excellent plating distribution and therefore less precious metal usage.

- Barrels have been replaced by bell-shaped containers powered to give axial and tangential oscillations of which both frequency and amplitude are adjustable. This oscillant movement is not damaging to the pieces.

- The bell-shaped containers are of an open type construction which ensures adequate solution turnover. Because of this feature the voltage required for plating is much less than for barrels.

- Lines are composed of standard modules which allow for easy future modification such as adding more units and increasing production.

- Each container is fixed under an oscillator. This system, called an Oscillant unit, is moved from one tank to another by a microprocessor

- programmed and controlled transporter.

- Should space be a consideration it is possible in each module to have several different storage tanks placed under one treatment tank. Solutions are then transferred in turn (by pump) to the treatment tank as required by the process sequence. In addition, each module can also be used for drag out, and/or rinsing. The rinsing, either spray and/or flood type, can be performed in any sequence and as often as desired.

- The loading and unloading station is placed at the beginning of the line. The Oscillant units are placed on a holding fixture and can be tipped to facilitate unloading. This station may also be automated by the addition of a vibrator belt feeder and weighing system to load the bell-shaped containers.

- Because of the closed construction of the storage tanks where the solutions are contained when not actively processing parts there is little solution evaporation which results in energy conservation.

- The machine can contain a hot air drying module in the automatic process sequence which would eliminate the need for this usual extra manual step when compared to typical barrel methods.

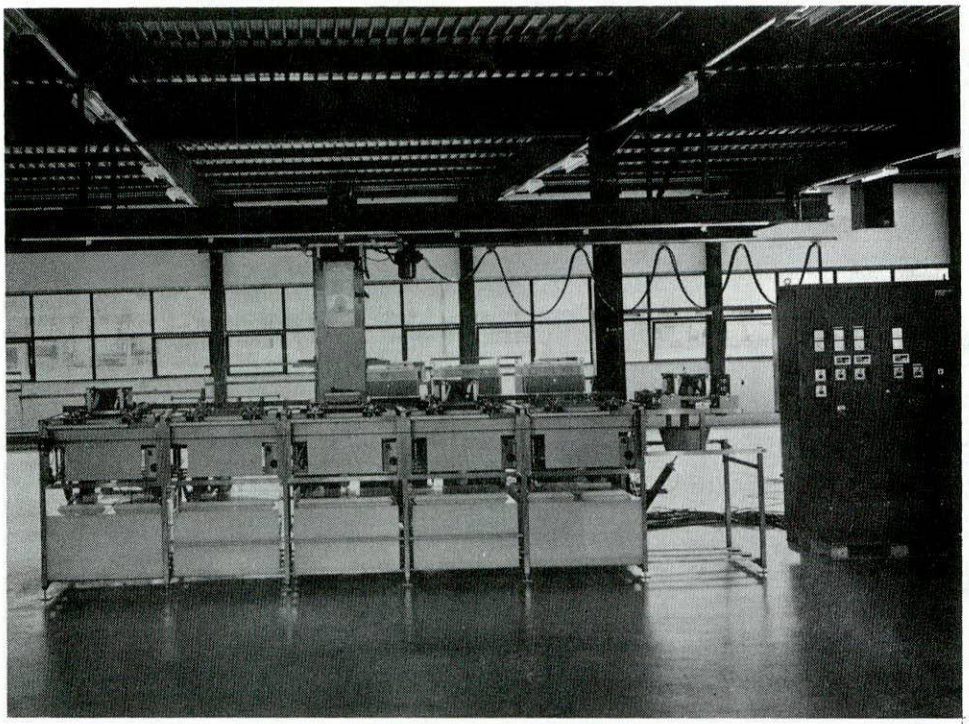

Fig. 1. Complete Osciline Machine with five Modules

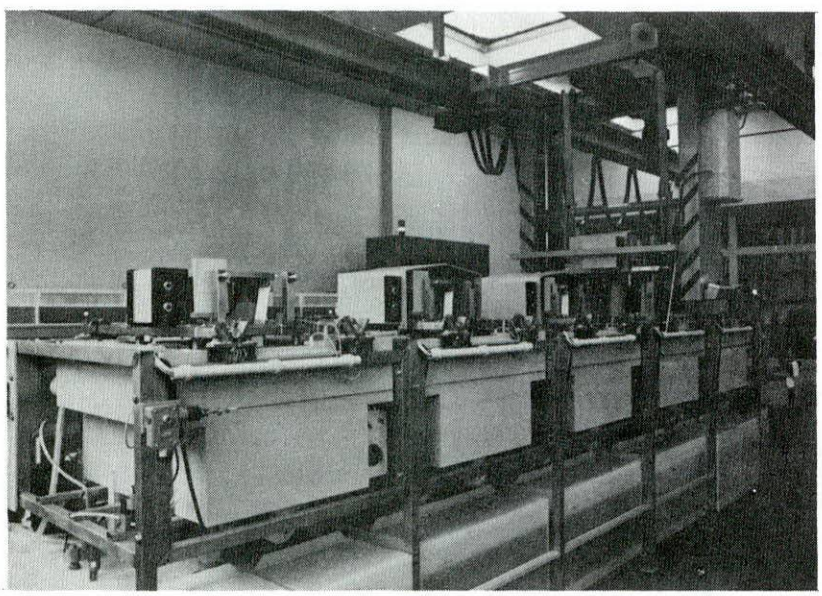

Fig. 2. View Showing Line During Operation

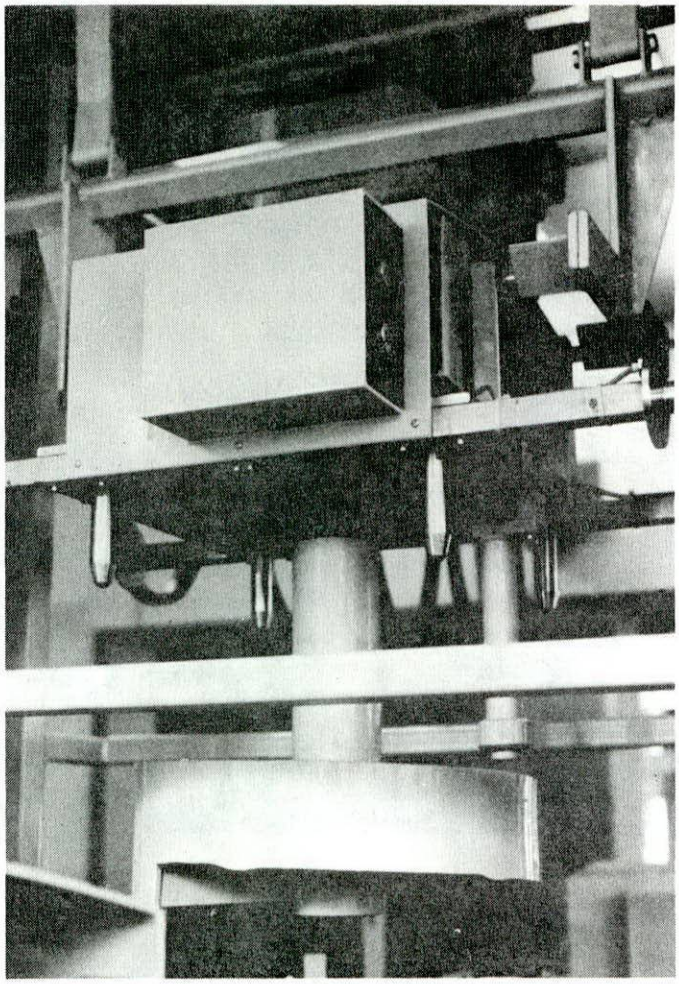

Fig. 3. Oscillant Unit which consists of the Oscillator and Attached Basket

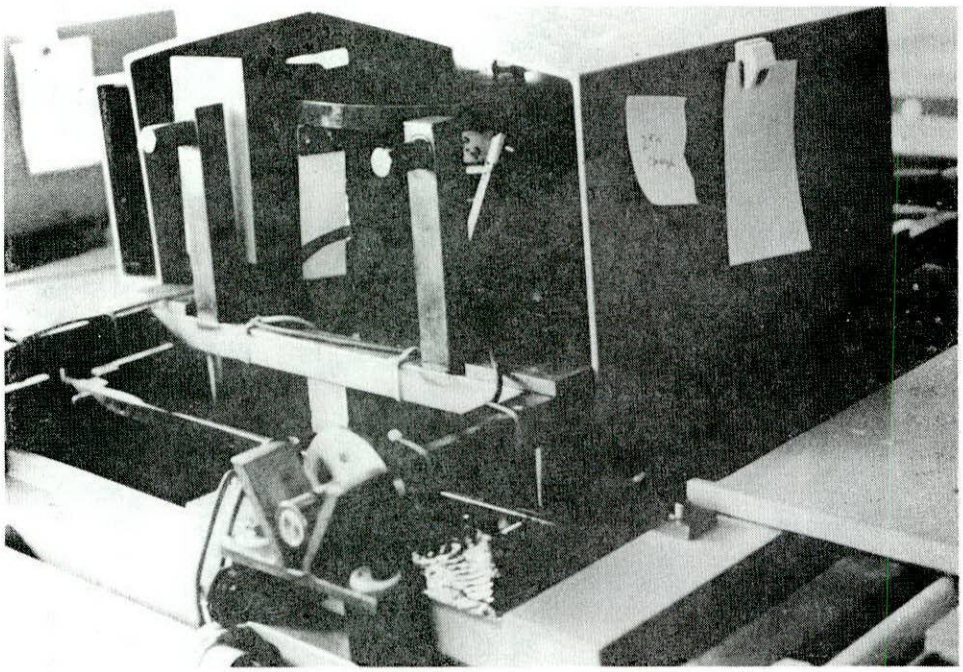

Fig. 4. Oscillant Unit Positioned onto Contact V-Saddles of Module

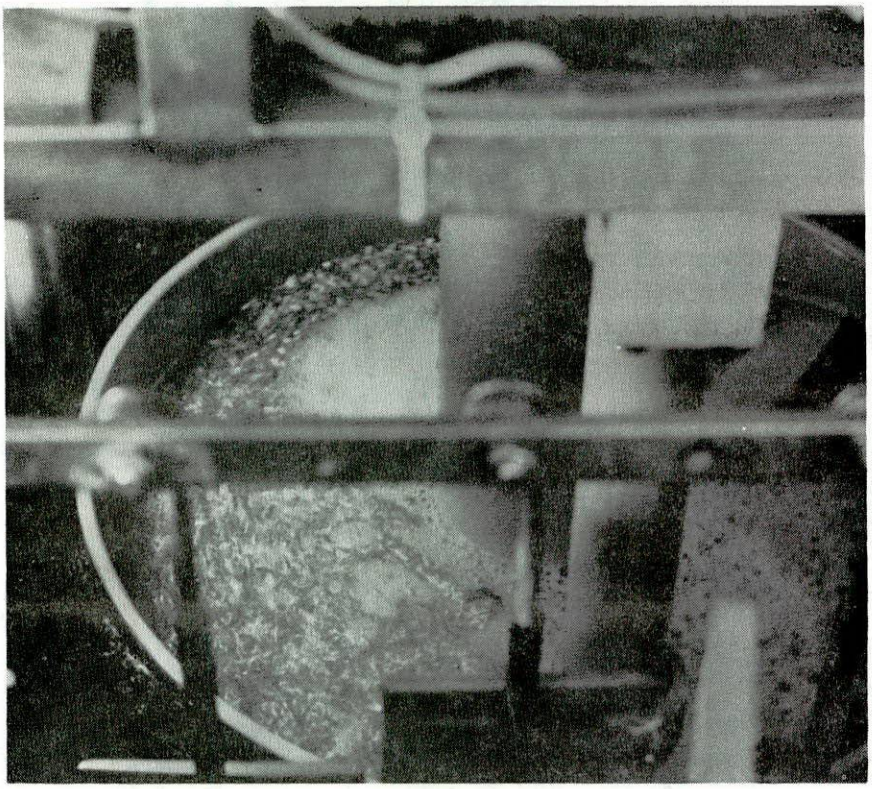

Fig. 5. Top View Showing Parts in Basket During Nickel Plating



Fig. 6. Top View Showing Parts in Basket During Rinsing

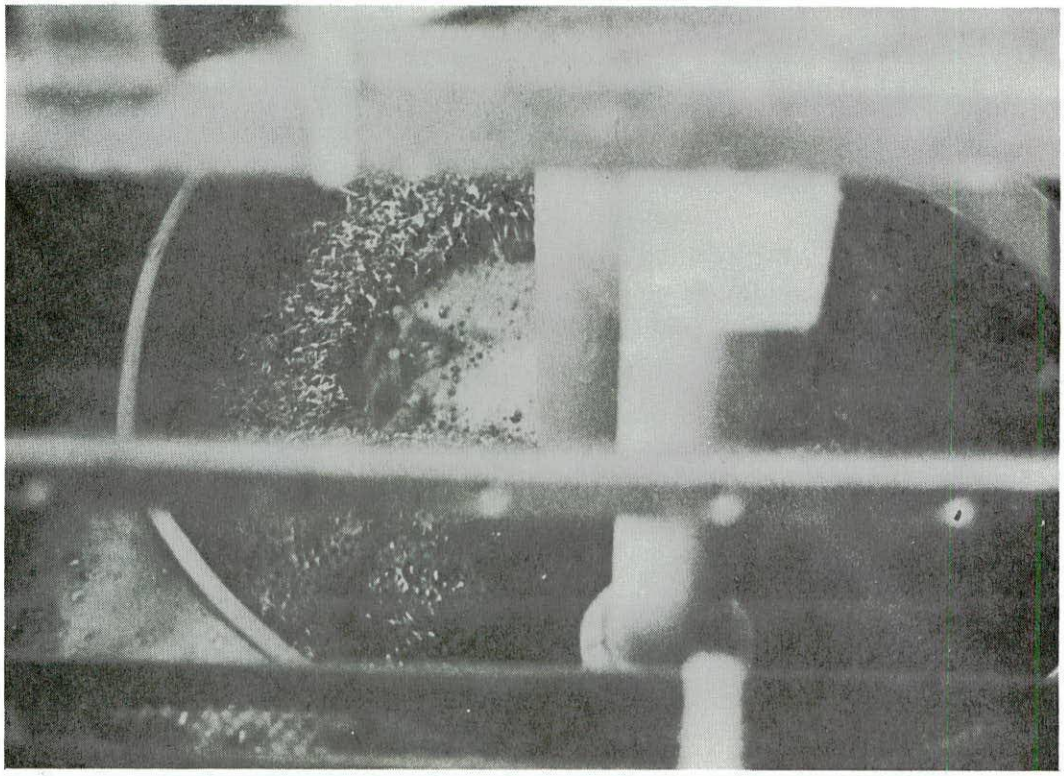

Fig. 7. Top View Showing Parts in Basket Being withdrawn from Gold Plating Solution

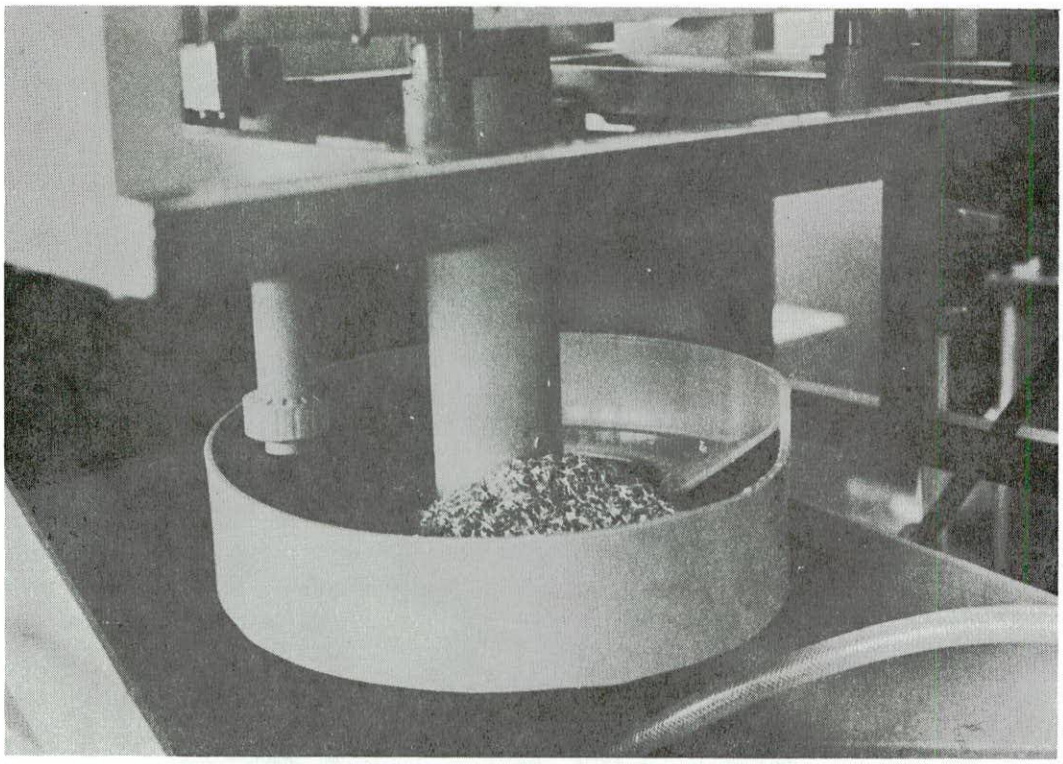

Fig. 8. Top View of Parts Sitting in Load/Unload Station Ready to be Unloaded and Dried Off Line

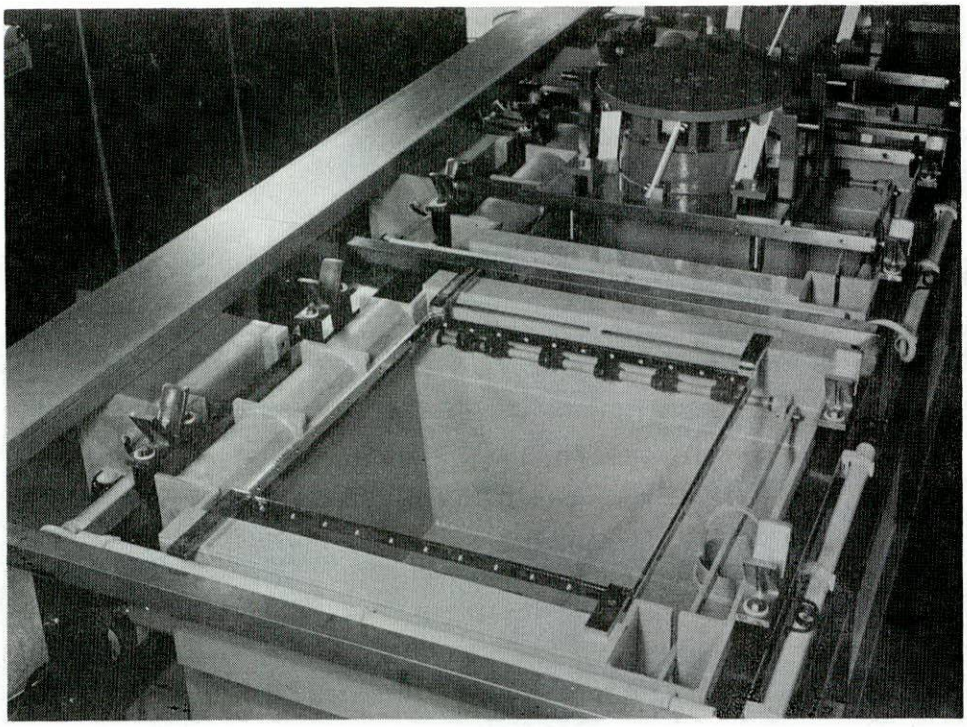

Fig. 9. Top View of Module Showing Spray Rinse Nozzles and Stand Pipe Assembly

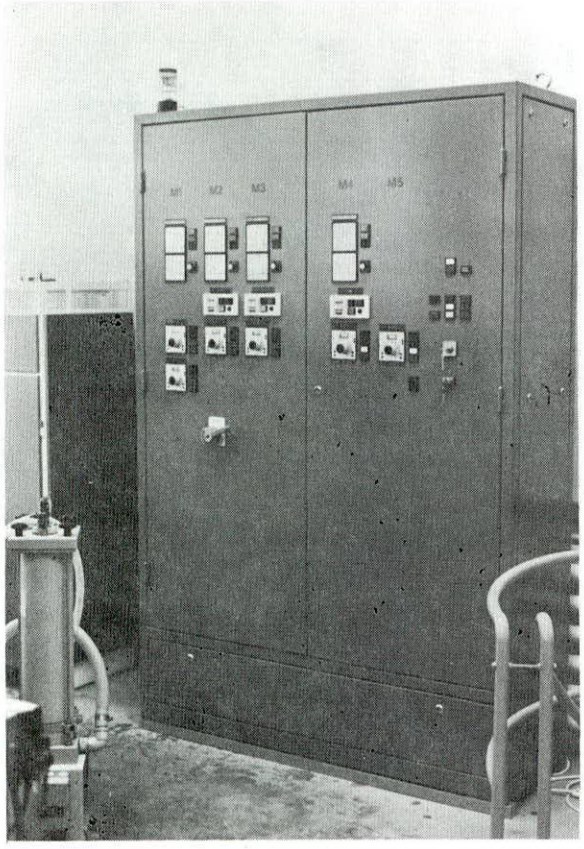

Fig. 10. Control Cabinet Housing Microprocessor and Electronic Circuitry

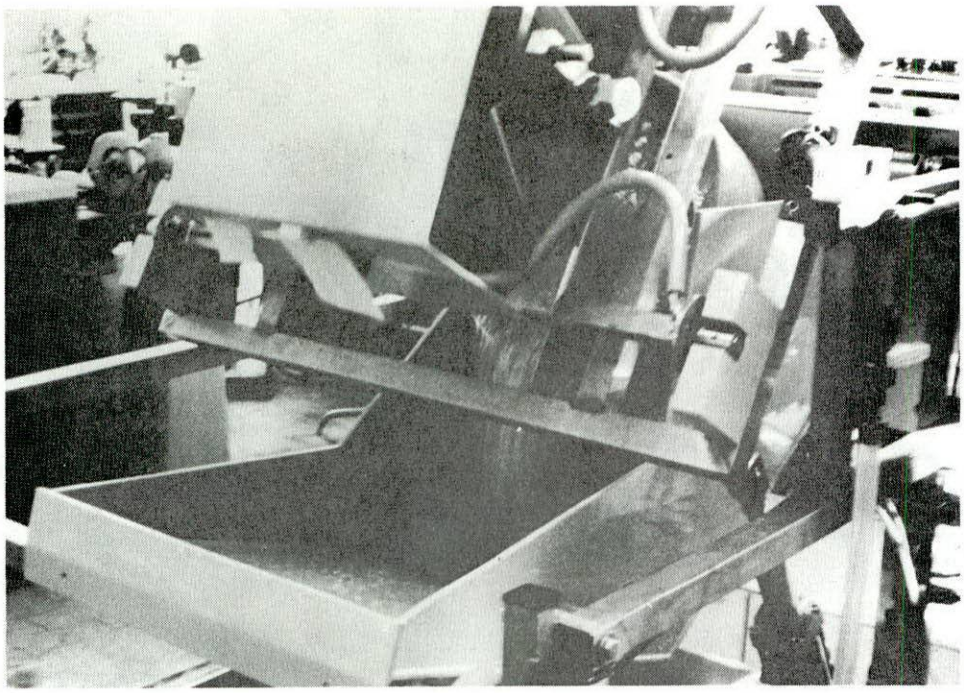

Fig. 11. Oscillant Unit being Tipped 90° to horizontal position for unloading of parts

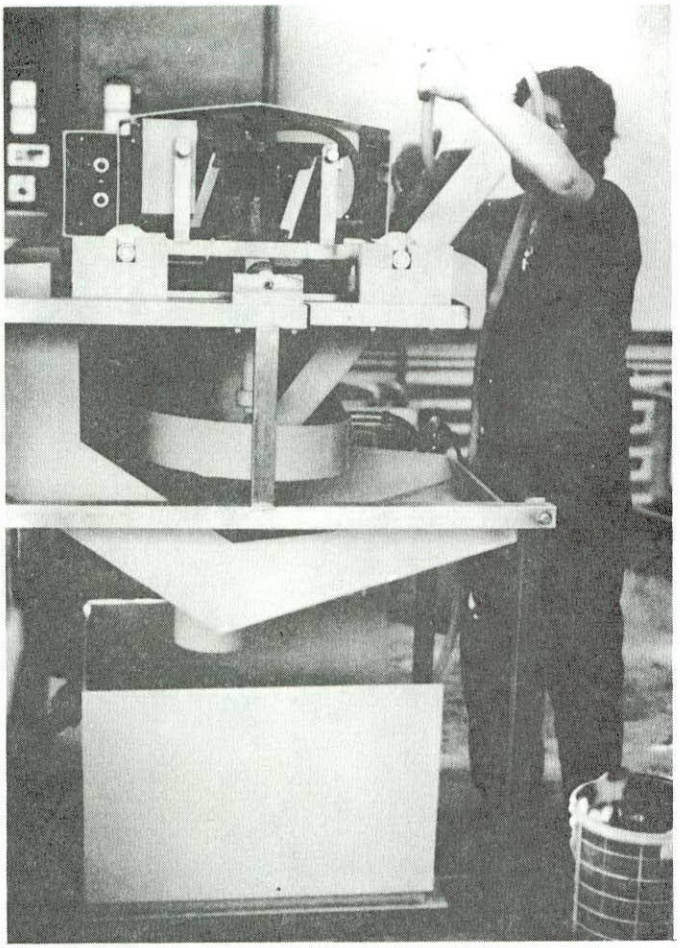

Fig. 12. Operator Loading Basket with Parts for Plating

G-3

Decorative II
Session G

Chloride Free Electrolyte for the Direct Gold Plating of Stainless Steel

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Dr. H.J. Luebke
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CHLORIDE FREE ELECTROLYTE FOR THE DIRECT GOLD PLATING OF STAINLESS STEEL

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ABSTRACT

Even though the literature reports a gold bath for the direct gilding of stainless steel in the late 1930's, most stainless steel is gold plated through the utilization of a Wood's nickel strike. The use of the Wood's nickel strike, due to the high chloride concentration of the system and the galvanic couple between gold and nickel, can cause subsequent corrosion of the gold plated stainless especially when the gold deposits are very thin. This paper describes a novel electrolyte for the direct gold gilding of stainless steel. This system, which is chloride free, is capable of yielding deposits with a superior adhesion and low porosity. This paper will discuss the actual system as well as the deposit characteristics.

INTRODUCTION

In the late 1930's a method of directly plating stainless steel with gold was described by Lukens.[1] Essentially, the electrolyte consisted of sodium gold cyanide dissolved in a solution of sodium cyanide in hydrochloric acid. This electrolyte was used for the preplating of stainless steel pen nibs. However, due to the extremely hazardous nature of the electrolyte which required heavy ventilation because hydrocyanic acid was evolved, only limited use was made of this gold preplate system. Instead, most gold plating of stainless steel was accomplished by the use of a nickel strike to improve adhesion. The nickel strike, as described by Don Wood,[2] is essentially a solution of 2 normal

nickel in 1.5 normal hydrochloric acid. This method of utilizing a nickel strike provided an active surface for the subsequent plating of many other metals such as gold and silver. However, this method has major drawbacks. The high hydrochloric acid content of the nickel electrolyte causes pitting corrosion of the substrate which enhances porosity in the subsequent gold coating. The porosity in the gold coating over nickel will set up a galvanic couple which causes corrosion pits wherever the gold layer is discontinuous. This corrosion problem became more apparent when gold thicknesses were drastically reduced to close to that of a flash layer or just sufficiently thick to provide the yellow color. This reduction of thickness was caused by the increase of gold price.

The gold electroplating of stainless steel is accomplished mainly for decorative applications. Typical item that would be plated are watchcases, watchbands, flatware, and hollow ware. Some of these items, particularly in the watchband area, require that the piece be masked and only certain areas plated with gold so as to not only achieve a two color effect, but also to keep the gold plated stainless areas away from the skin due to the corrosive effect of perspiration. Industrial applications would be the gold plating of stainless steel components utilized in the construction of chemical and medical apparatus as well as stainless steel components in chemical plants. However, as indicated previously, achieving adhesion through use of the Wood's nickel bath causes pitting corrosion and the defects that are formed through this can increase the porosity in the gold topcoat. Also, as mentioned previously, the problems of corrosion set up by the galvanic couple of gold over base metal become even greater with the reduced gold thicknesses utilized today in the decorative industry. It must also be noted that the nickel layer itself can cause problems especially in the watchband industry due to the allergic reaction that nickel causes on skin. Therefore, the objective of this paper is to describe a process for the direct gold plating of stainless without an intermediate layer of nickel and which also should yield a deposit with good adhesion and low porosity. Acids such as hydrochloric are to be avoided to prevent the attack on the stainless substrate. The rest of this paper will describe such an electrolyte as well as the characteristics of the deposits.

ELECTROLYTE FOR DIRECT GILDING OF STAINLESS STEEL

Solutions for the direct plating of stainless steel were developed for two applications. The first describes an electrolyte which is to be utilized primarily as a gold preplate while the second formulation describes an electrolyte that can be used to

build heavier than flash thicknesses. Both electrolytes operate at pH values of less than 1 and therefore cannot use potassium monovalent gold cyanide due to the instability of the monovalent gold cyanide complex at low pH values. Instead, these electrolytes utilize potassium trivalent gold cyanide which is known to be stable at pH values well below 3.[3] Both electrolytes contain cobalt which is codeposited at the rate of approximately 0.5 weight percent to improve the brightness and increase the hardness of the deposits. The electrolytes have been formulated to assure a constant cobalt content in the deposits over a wide range of current densities. Table I shows the operating conditions and plating rates of the preplate and heavy plate systems.

Table 1

Plating Criteria

	Preplate	Heavy Gold
pH	0.6	0.6
Gold Content (g/L)	2	4
Temperature (°C)	Ambient	35°-40°C
Current Density (A/dm^2)	2-6	4-8
Plating Speed (microns/min)	0.04-0.06	0.15-0.2
Cathode Efficiency (mg/A min)	2-3	7-9

Due to the extremely low pH value needed for activation of the stainless, the cathodic efficiency is very low and varies between 5% and 20% of the theoretical, depending upon working conditions. This is further compounded by the fact that gold is present in the trivalent state and a plating rate of 1/3 as much as the conventional gold baths which use monovalent gold is to be expected. However, these baths can be operated at high current densities, for example, 2 to 8 amps per square decimeter and this does somewhat overcome the slow plating rate. If higher plating speeds are desired, they can be achieved by increasing the gold content and the temperature at which the electrolyte is operated.

Many times it is practical to use the acid gold electrolyte just as a preplate and then build up the gold thickness with a traditional hard gold bath. Before plating with a conventional gold system, a gold thickness of at least 0.1 to 0.2 microns must be deposited. However, it is also possible, as indicated previously, to build up this thickness with the same electrolyte utilizing the higher gold and higher temperatures to achieve a faster plating rate. Plating efficiencies and deposition speeds for the two and four grams per liter systems respectively, are

shown in Figures 1 and 2. It is interesting to note that when deposition takes place over copper, a different initial plating rate is obtained than if it had taken place over stainless steel. The efficiency and, consequently, the plating speeds are higher when the deposition takes place over copper particularly at the low current density levels. This effect results from the activation phase preceeding the gold deposition directly onto the stainless, whereas gold deposition on the copper substrate starts immediately. After the activation phase has been completed and the stainless steel is fully coated with gold, the influence of the substrate material no longer exists. However, since the activation phase lasts longer at the lower current density levels, this effect is greater in such cases.

Figures 3 and 4 show the relationship between plating speed, temperature and gold content. For the purpose of eliminating the activation effect on stainless, copper was chosen as the substrate material. For the gold preplate bath working at a concentration of 2 grams per liter gold and ambient temperatures, the plating speed is approximately 0.06 microns per minute. For the heavy gold baths operating at a gold concentration of 4 grams per liter and 40°C and working in the current density range of 4 to 10 amps per decimeter, the plating speed approaches 0.2 microns per minute. By raising the gold content, the plating speed can be increased further. Increasing the temperature would, theoretically, permit higher plating rates, but this can also result in bath decomposition.

In order to achieve good adhesion to stainless steel, it is necessary to provide sufficient activation of the base material. In most cases, the normal form of pretreatment accomplishes this. This consists of ultrasonic cleaning to remove stains followed by cathodic cleaning in an alkaline cleaner. The subsequent steps involve immersion in 5% to 10% sulfuric acid and rinsing before and after. In the case of stainless which requires more activation due to passivity of the surface, it has been found that the activation can be enhanced by adding 10 grams per liter of cyanide to the alkaline cleaner. Also, greater activation is achieved if the cathodic cleaning is followed by anodic cleaning in a bath of the same makeup. The anodic cleaning should be undertaken at room temperature and for a period of less than 20 seconds. This method of activation was found necessary, for example, when plating stainless steel flatware which has been exposed to intensive buffing and because of this was coated with a passive layer.

CHEMICAL AND PHYSICAL PROPERTIES OF THE DEPOSIT

The gold content of the deposit was determined on separate foils by assaying the amount of gold gravimetrically. The values found by this technique range from 99.0% to 99.5%. The principal impurity is the codeposited cobalt. The weight percent of cobalt was determined by microprobe and as well by dissolving the gold foils and determining their cobalt content through atomic absorption spectroscopy. The cobalt content proved to be in the region of 0.5%, but it rose somewhat as the current density increased. The influence of temperature within the operating range of the bath was not pronounced, however, a rise in temperature did slightly reduce the amount of codeposited cobalt. Carbon, hydrogen, nitrogen and oxygen content were also determined. Results are shown in Table 2.

Table 2

Impurity Content

Bath Temp (°C)	Current Density (A/dm^2)	Co	C	H	N	O
			(ppm)			
	2	4000	390	310	815	315
20°	4	5000	435	305	985	490
	10	7700	625	395	990	575
	2	3100	130	145	350	200
35°	4	4300	170	190	330	190
	10	6900	185	175	405	340

The contents of these elements are affected by the current density and temperature in the same manner that the cobalt content is effected, but in the case of the non-metallic element, the temperature effect is greater. These elements were determined by a method described by Knoedler.[4] Interesting to note is that the carbon contents were considerably lower than those found when one analyzed a deposit plated in a typical citrate based cobalt gold electrolyte.

As with deposits plated in a citrate based gold cobalt electrolyte, the non-metallic inclusions influence the brightness, hardness, and abrasion resistance of the deposits. Physical properties are shown in Table 3.

Table 3

Properties

Gold Content	99.0%-99.5%
Hardness (Vickers)	165 HV
Cobalt Content	0.5%
Internal Stress	200-350 N/mm^2 (tensile)
Wear Resistance	Good, no cold welding
Ductility	Good, foils can be bent
Porosity	Very slight

The Vicker's hardness value of 165 HV was obtained on a 20 micron thick coating using a Zwick micro-hardness tester at a contact load of 15 grams.

For testing the abrasion resistance, a standard gold, silver, copper (70-24-6) rivet was moved back and forth laterally across the deposit for 5000 times at an amplitude of one centimeter. This method, as described by Deuber and Luebke,[5] utilized a contact weight of 15 grams. Examining the wear track revealed that no cold welding was obtained and the wear track was extremely narrow and flat. This method of testing which has wide spread acceptance in the connector/contact industry in Europe is less suited for assessing the wear resistance in the decorative industry. Therefore, the wear resistance for decorative applications should be made with a test that is appropriate for the particular item.

The internal stress of the deposit was measured utilizing a method described by Stalzer.[6] The measured tensile stress of 200-350 N/mm^2 is considerably higher than that attained from coatings plated in a typical citrate based cobalt gold electrolyte. However, in the case of ductility, the deposit ductility from the very acid electrolyte is superior in that deposits can be stripped from the substrate and bent without cracking. This would be impossible with deposits plated in the typical citrate based cobalt gold electrolytes.

It can be said that the porosity of deposits from this electrolyte is remarkably low. This conclusion is drawn from our investigations of the corrosion resistance of the deposit when plated directly over stainless steel and compared to deposits from a citrate based cobalt gold system plated over a Wood's nickel strike.

CORROSION TESTING

The objective of our corrosion tests was to compare the corrosion resistance of thin gold deposits plated with the new acidic gold electrolyte directly over stainless with deposits of a traditional citrate based gold plated over stainless which had been preplated with the Wood's nickel strike. The experimental conditions were selected so that they would resemble as closely as possible the actual practice. This was done to permit a satisfactory differentiation when assessing the different coating combinations. When testing corrosion porosity, the principal factors are the thickness of the coating, the nature, and the severity of the corrosion test

In regards to the thickness of the coating, the corrosion protection afforded by the gold deposit, naturally increases with an increase in coating thickness. However, the cost of the deposit goes up drastically, and therefore a compromise must be made. The chosen thicknesses of the gold coatings to be tested were 0.2 and 0.5 microns. Although thicker coatings are encountered, in the actual practice it is difficult to assess the corrosion behavior in these cases. As our evaluations were accomplished on flatware, it is found that indeed the decorative gold plating thickness, as supplied by many commercial manufacturers is in this general range or, in some cases, even thinner.

The corrosion test conditions had to be chosen so as to permit adequate differentiations between acceptable and unacceptable results. If test conditions were insufficiently severe, all specimens would exhibit only slight corrosion whereas if the conditions were excessively severe, all of the specimens would exhibit severe corrosion. Suitable tests conditions were arrived at by means of a preliminary test. Two test methods appropriate to the selected coating thicknesses and base material/gold coating combinations were adopted.

A. The specimens were sprayed with distilled water at 55°C for a period of two days.

B. Salt spray testing was conducted according to German Industrial Standard DIN 50021. The specimens were sprayed with 5% sodium chloride solution at a pH of 6.5-7.2 and a temperature of 35°C for 2-3 days.

The tests were performed in a commercial spray chamber with temperature control. The specimens were set up at an angle of 75° so they were not struck directly by the spray jet, but instead were located in a mist of finely atomized droplets. After removal from the test chamber, the specimens were dried in air at

room temperature without rinsing. The tests were carried out on panels and spoons of the following types:

A. The 5 x 5 centimeter panels were made of V2A stainless steel sheet. Composition of V2A stainless is: carbon - less than 0.07%, chromium - 17.0% to 20.0%, nickel - 8.5% to 10.0%.

B. The spoons were made from 18/10 chrome nickel steel. Composition was: carbon - less than 0.07%, chromium - 16.5% to 18.5%, molybdenum - 2.0% to 2.5%, nickel - 10.5% to 13.5%.

The latter material is in common usage in the flatware industry in Europe. These items of flatware were obtained from a commercial manufacturer in a condition suitable for electroplating. The coating combinations that were tested are indicated in Tables 4 and 5.

Table 4

Combinations With 0.2 Microns Gold

No	Preplate	Intermediate	Gold Plate
1	-	-	Acid Gold Strike
2	Wood's Nickel	-	Acid Gold Strike
3	Wood's Nickel	-	Citrate Gold
4	Wood's Nickel	5 microns bright nickel	Acid Gold Strike

Table 5

Combinations With 0.5 Microns of Gold

No	Preplate	Intermediate	Gold Plate
5	-	-	0.2µ Acid Gold Strike +0.3µ Citrate Gold
6	Wood's Nickel	-	Citrate Gold
7	Wood's Nickel	5 microns bright nickel	Acid Gold Strike
8	Wood's Nickel	5 microns bright nickel	Citrate Gold

Table 4 shows the coating combinations utilizing 0.2 microns of gold thickness as the final layer while Table 5 indicates the final gold thickness as 0.5 microns. The Wood's nickel strike

plating was carried out at 4 amps per square decimeter for a time of 4 minutes. On some of the specimens, the 5 micron intermediate layer of bright nickel was deposited to correspond with a method that is frequently utilized by the flatware industry to improve the substrate.

Most of the gold plating was carried out utilizing the acid gold strike. For comparison purposes a citrate based cobalt gold system operating at a pH of 4.2 and a gold concentration of 2 grams per liter was utilized. The acid gold strike was operated at room temperature and 2 amps per square decimeter. The citrate based cobalt gold system was operated at 50°C and 1.5 amps per square decimeter. Pre-treatment of the test specimens was performed according to the following:

1. Ultrasonic cleaning in a standard alkaline cleaner.

2. Cathodic cleaning in an alkaline cleaner containing an additional 10 grams per liter cyanide at room temperature for 1 minute and at 10 amps per square decimeter.

3. Immersion in 5% sulfuric acid.

The test specimens were rinsed briefly in DI water between each of the steps. All of the test specimens exhibited good adhesion and coverage.

DISCUSSION OF CORROSION TEST RESULTS

Results of the corrosion tests are shown in Figures 5 to 8. The figures on the test article referred to the coating combinations that were indicated in Tables 4 and 5. Figure 5A shows the V2A stainless steel test panel with 0.2 micron gold coating after the water spray test. Figure 5B shows the same sheets after the much more severe 3 day salt spray test. Specimen 1 (acid gold strike without Wood's nickel) behaved much more satisfactory than specimens 2 or 3 (with Wood's nickel strike). The water spray test, in particular, clearly indicated much more serious porosity on specimens 2 and 3 as evidenced by the occurrence of a large number of small brown areas of iron corrosion on the surface. Here, as with the salt spray test, the stainless steel was subjected to quite considerable attack evidently caused by the galvanic cell formation of gold over iron. The use of the Wood's nickel strike drastically increased the number of pores, probably as a result of surface defects caused by pitting. Comparison of specimens 2 and 3, both with the Wood's nickel strike, definitely favors the acid gold strike over the citrate cobalt gold. This pattern of results which was repeated in sub-

sequent cases, demonstrates the exceptional low porosity of the new acid gold coatings when compared with those from a citrate based cobalt gold system. The acid gold strike apparently is capable of eliminating some of the sources of porosity caused by the surface defects. Specimen 4 has an intermediate 5 micron thick coating of bright nickel which covers some of the pore centers caused by the hydrochloric acid activation in the Wood's nickel strike. As with the salt spray tests, Figure 5B in particular, the product of corrosion takes on a different color and form when the intermediate bright nickel layer is used. All in all, the corrosion picture is not greatly improved if an intermediate bright nickel layer is utilized. Figure 6A shows the 0.2 micron thick gold plating on flatware manufactured from the 18/10 chrome nickel steel after the water spray test. Figure 6B shows the same items after the salt spray test. The results are in complete agreement with those obtained on the stainless steel panels. The results obtained utilizing 0.5 micron thick gold coatings are shown in Figures 7A and 7B. Figures 8A to 8D are enlargements from 7A. A comparison between specimens 5 and 6 shows most dramatically the benefits of utilizing the acid gold strike. On specimen number 5 the first 0.2 microns of gold were deposited from the acid gold strike. Here again, the Wood's nickel preplate was not utilized. The number and size of the pores are, in this case, considerably reduced. The coating on specimen 5 can be described as almost non-porous. It is of interest to compare specimens 7 and 8 particularly in the magnified form (Figures 8C and 8D). Both of these specimens have a 5 micron thick intermediate layer of bright nickel. Specimen 7, with a 0.5 micron thick coating of the acid gold strike, exhibits superior corrosion resistance to that of specimen 8 which has the 0.5 micron thick citrate based cobalt gold deposit. Although the influence of the stainless steel is largely eliminated by the intermediate bright nickel layer, the coating from the acid gold strike proves to be considerably less porous than the coating from the conventional citrate based cobalt gold system. The comparison of specimens 5 and 7 show that specimen 5 is superior. The relatively large number of pores on specimen 7 shows that the surface defects caused by the hydrochloric activation still manifest themselves in spite of the 5 micron thick intermediate bright nickel coating.

On the basis of the observed results we can confirm the clearly superior results obtained when utilizing the new acid gold strike. This comes from the generally lower porosity of the system and the avoidance of the hydrochloric pretreatment of the substrate which causes corrosion pitting which cannot be eliminated by subsequent plating. Both of these effects in combination afford good corrosion protection even when plating very thin gold layers.

CONCLUSION

A novel acid gold electrolyte has been described for the direct gold plating of stainless steel without the prior deposition of nickel through the Wood's nickel strike. The electrolyte operates at a pH of 0.6 and at room temperature to 40°C. This electrolyte contains gold as potassium trivalent gold cyanide and cobalt as the brightening agent. The new electrolyte can be operated as a strike bath at a concentration of 2 grams per liter or as a heavier gold plating bath with higher gold concentrations. Deposition speed reaches 0.2 microns per minute at a gold concentration of 4 grams per liter. Deposits with good adhesion are obtained in most cases directly over stainless steel after simple cathodic cleaning. However, in more difficult cases, the activation can be improved by anodic cleaning. The properties of the deposits are similiar to those of the citrate based cobalt gold systems, however, the ductility is far greater.

The corrosion protection given by deposits from the new acid gold system is superior to that afforded by the normal citrate based cobalt gold electrolyte utilizing the intermediate Wood's nickel strike. This is due to the absence of attack on the stainless substrate caused by the hydrochloric acid in the nickel strike and the lower porosity of the deposit.

REFERENCES

1. H. S. Lukens, U.S. Patent 2,133,995 (1938)

2. D. Wood, Metal Industry, 36,330,July (1938)

3. F. H. Reid & W. Goldie, Gold Plating Technology, Electrochemical Publications, Ayr, Scotland, 51 (1974)

4. A. Knoedler, Metalloberflache, 18 263 (1964)

5. J. Deuber & H. J. Luebke, Plating and Surface Finishing, 69, 55, September (1982)

6. M. Stalzer, Metalloberflache, 18, 263 (1964)

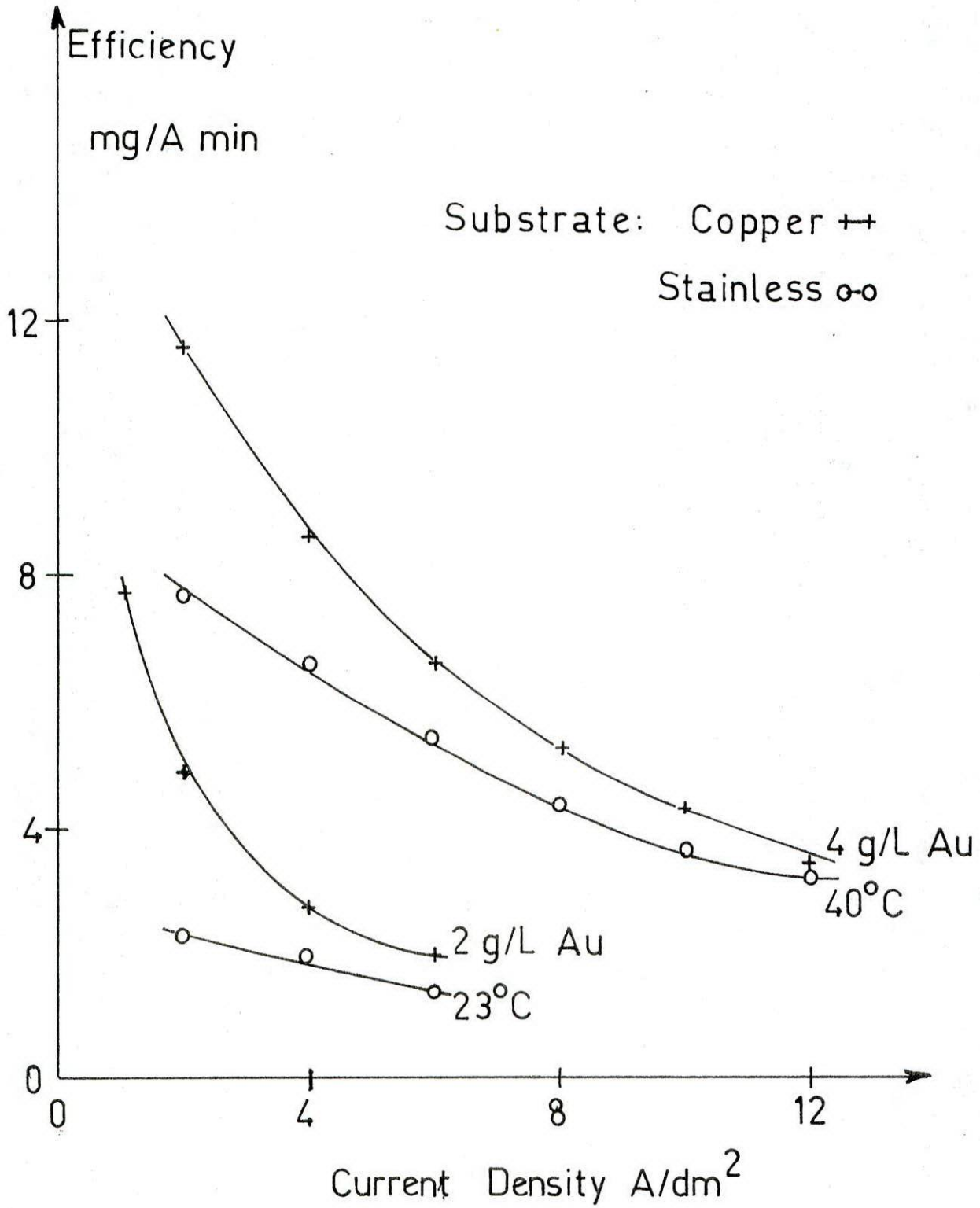
Efficiency
mg/A min
Substrate: Copper +-+
Stainless o-o
12
8
4
0
0
4
8
12
4 g/L Au
40°C
2 g/L Au
23°C
Current Density A/dm²

FIG. 1

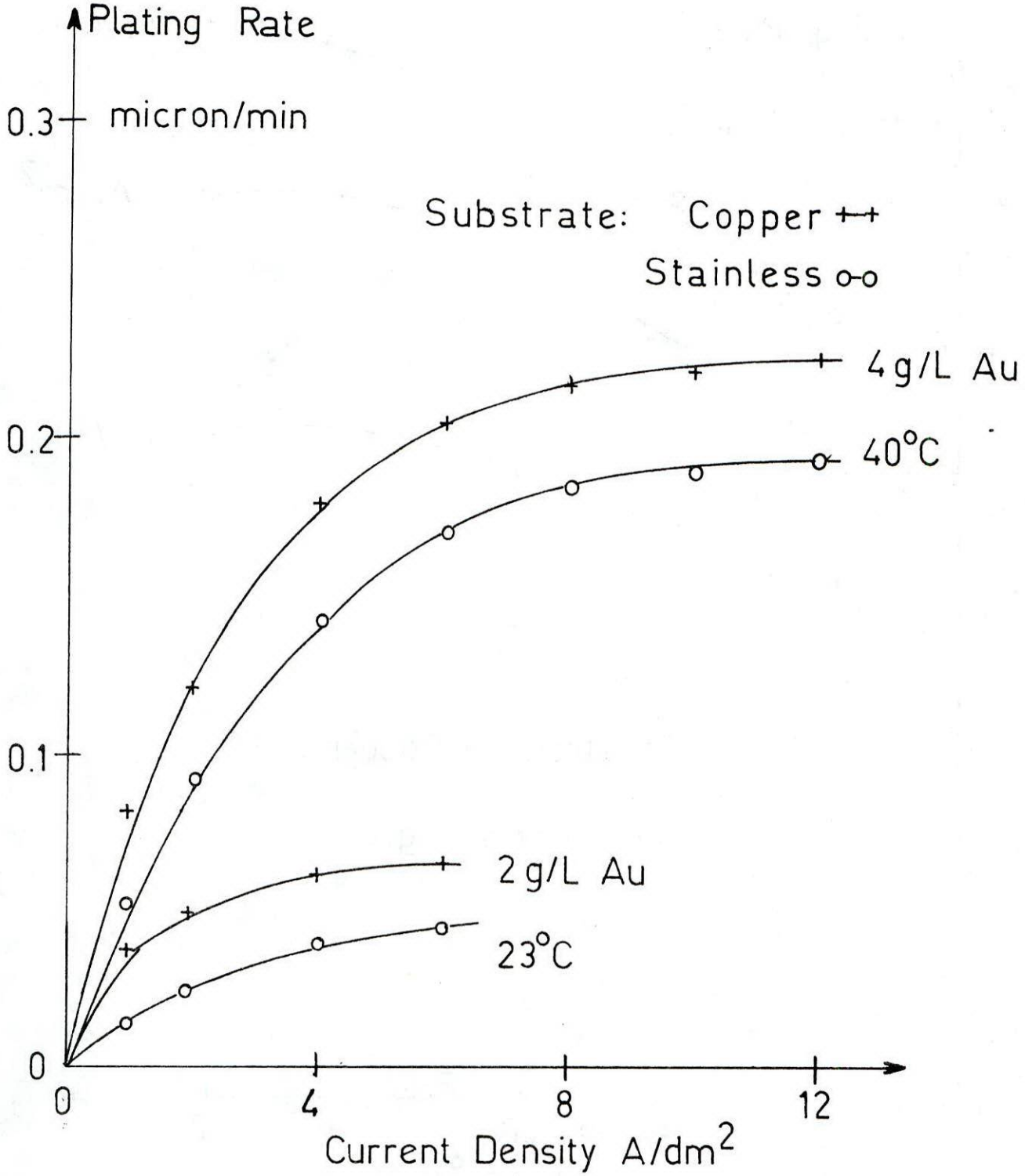
Plating Rate
micron/min
0.3
0.2
0.1
0
Substrate: Copper
Stainless
4 g/L Au
40°C
2 g/L Au
23°C
0
4
8
12
Current Density A/dm²

FIG. 2

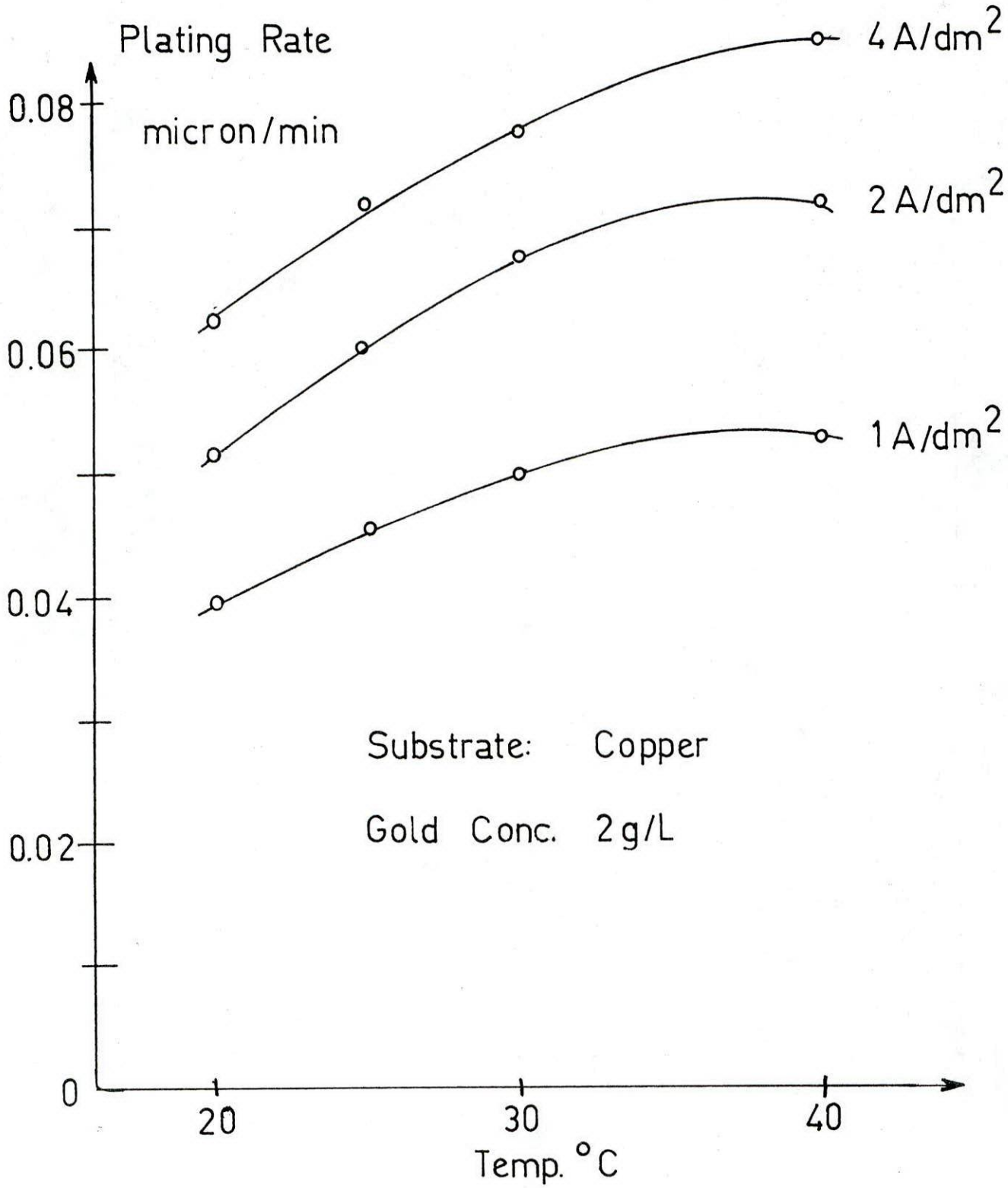
Plating Rate
micron/min
0.08
0.06
0.04
0.02
0
4 A/dm2
2 A/dm2
1 A/dm2
Substrate: Copper
Gold Conc. 2 g/L
20
30
40
Temp. °C

FIG. 3

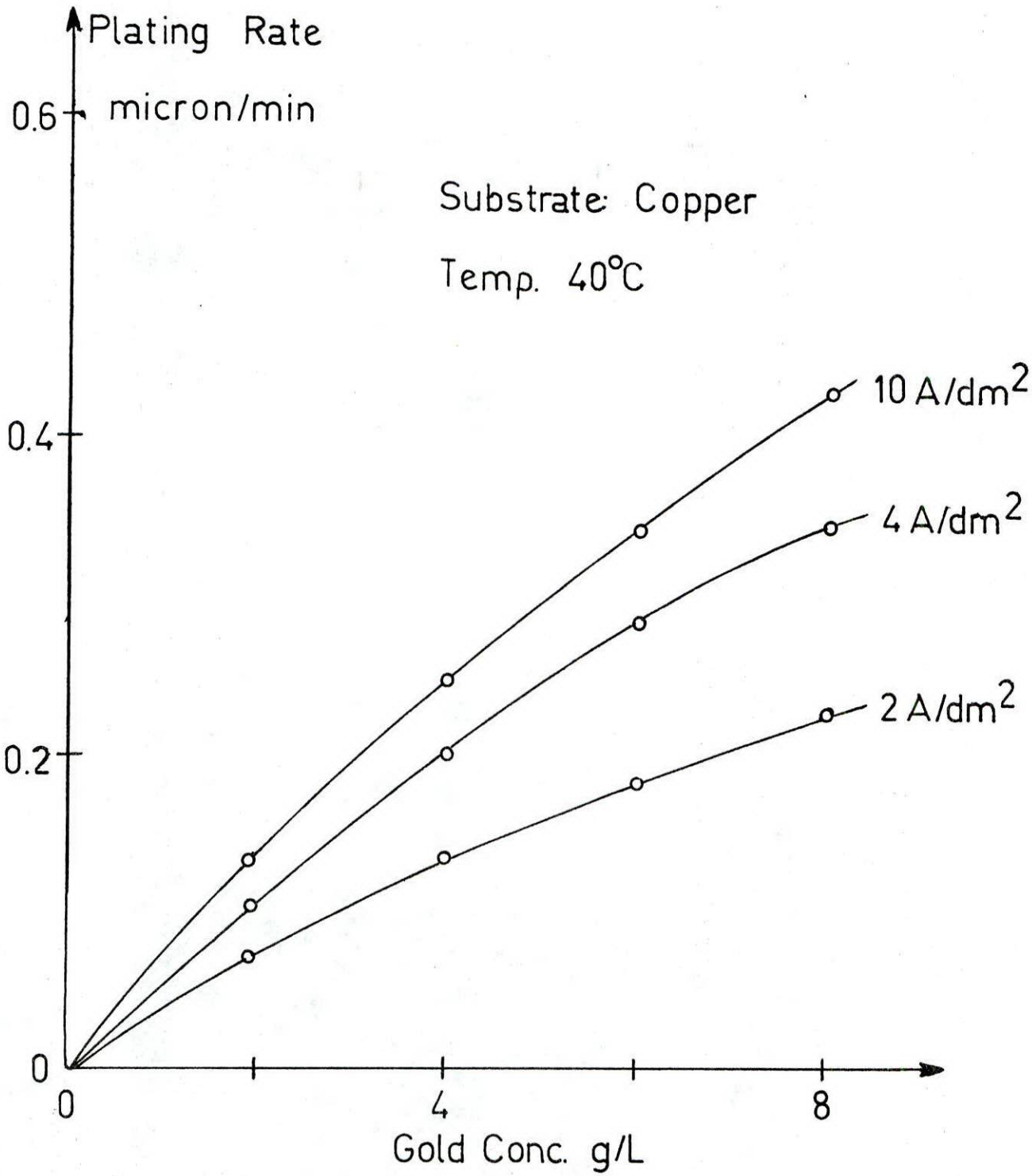
Plating Rate
micron/min
0.6
0.4
0.2
0
Substrate: Copper
Temp. 40°C
10 A/dm2
4 A/dm2
2 A/dm2
0
4
8
Gold Conc. g/L

FIG. 4

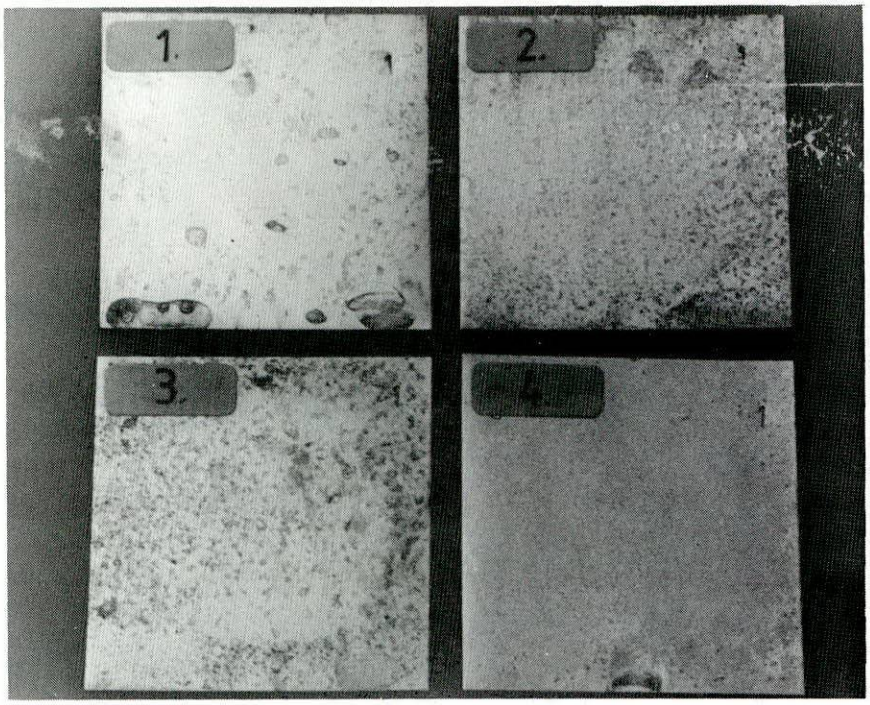

FIGURE 5a. WATER SPRAY, 55°C, 2 DAYS

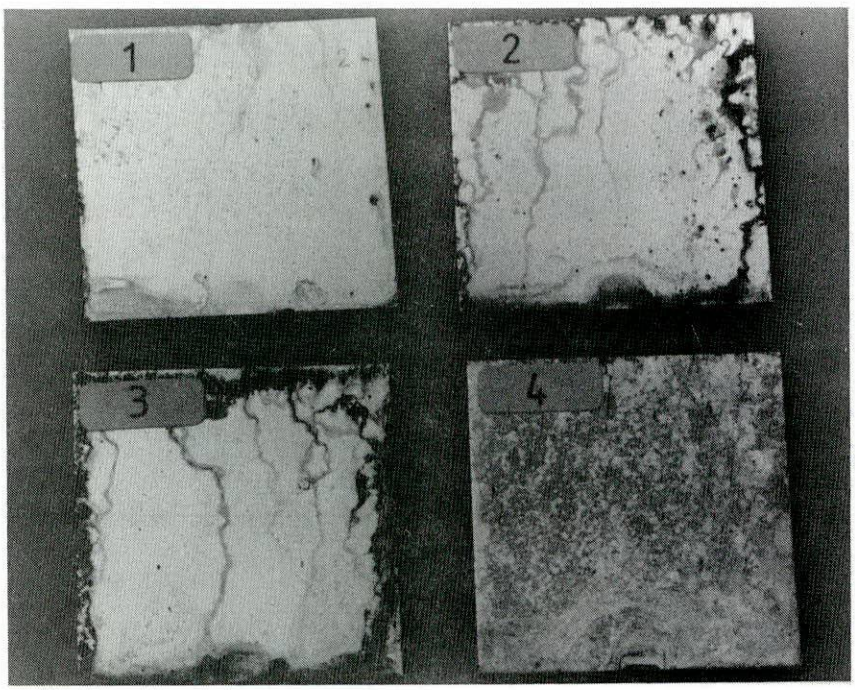

FIGURE 5b. SALT SPRAY, 35°C, 3 DAYS

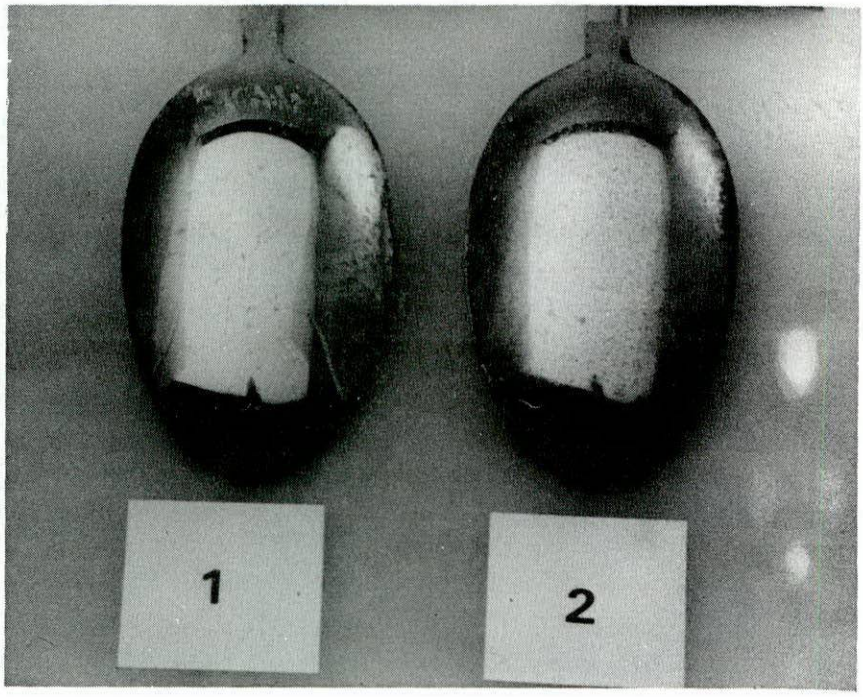

FIGURE 6a. WATER SPRAY, 55°C, 2 DAYS

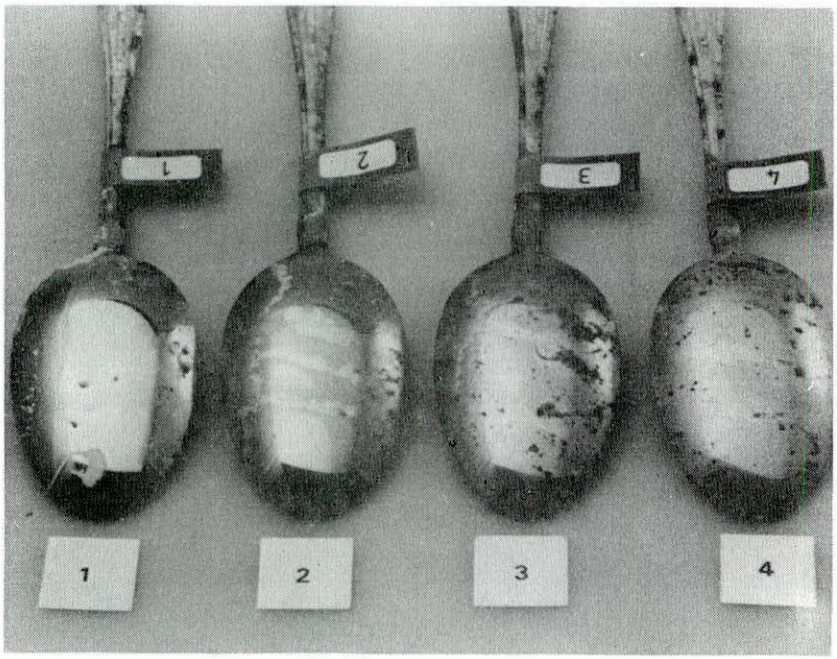

FIGURE 6b. SALT SPRAY, 35°C, 2 DAYS

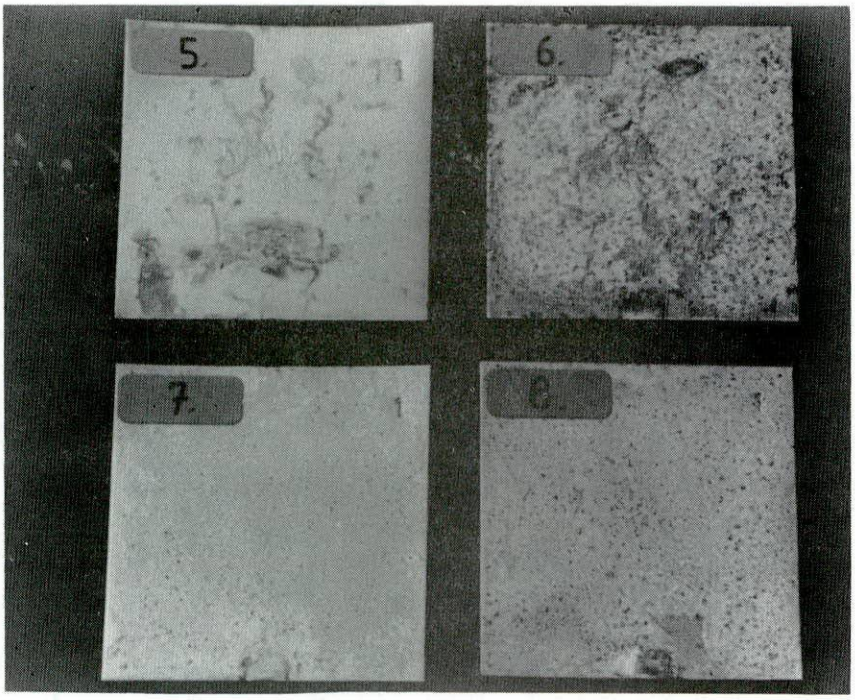

FIGURE 7a. WATER SPRAY, 55°C, 2 DAYS

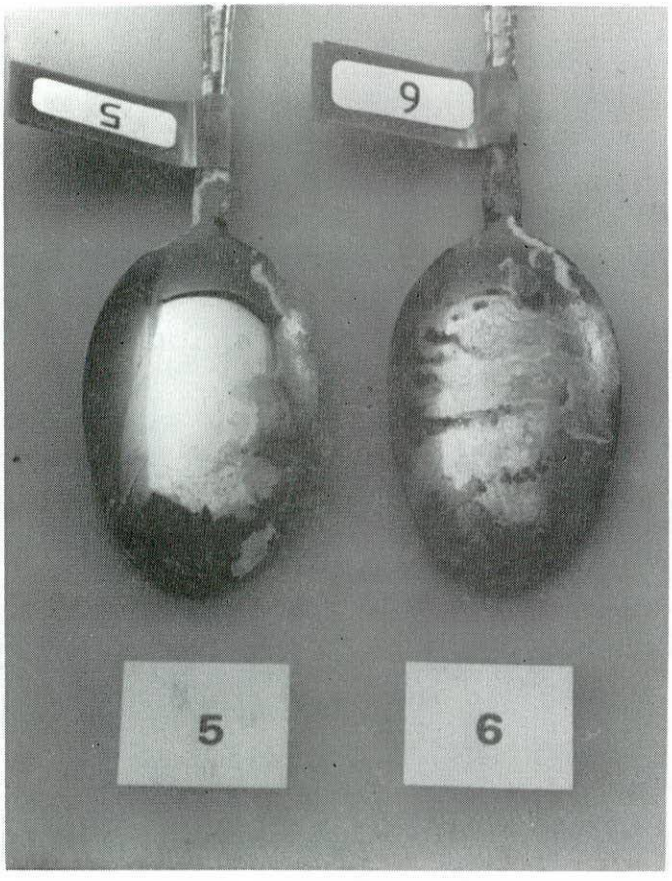

FIGURE 7b. SALT SPRAY, 35°C, 2 DAYS

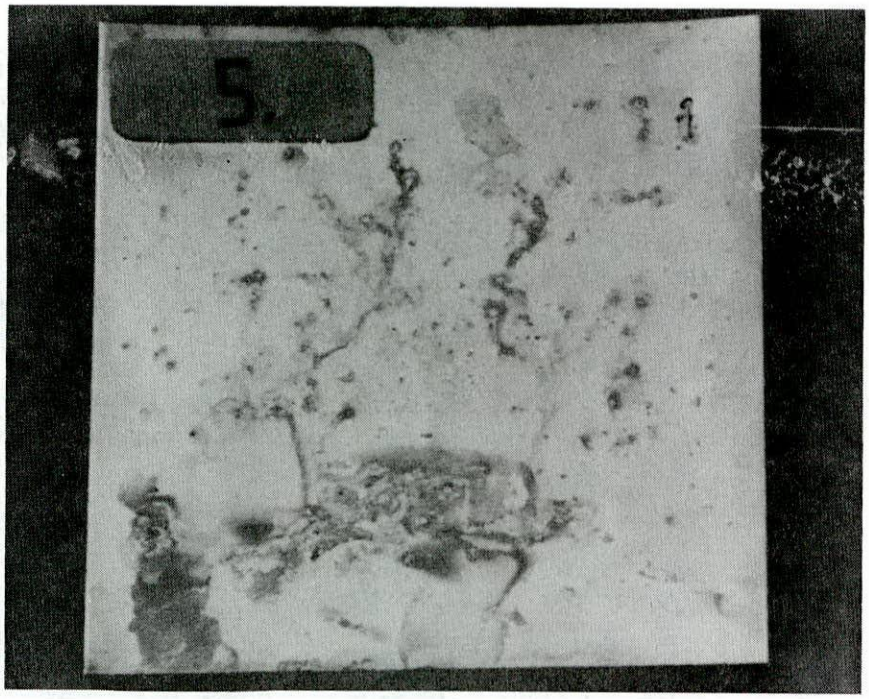

FIGURE 8a. WATER SPRAY, 55°C, 2 DAYS

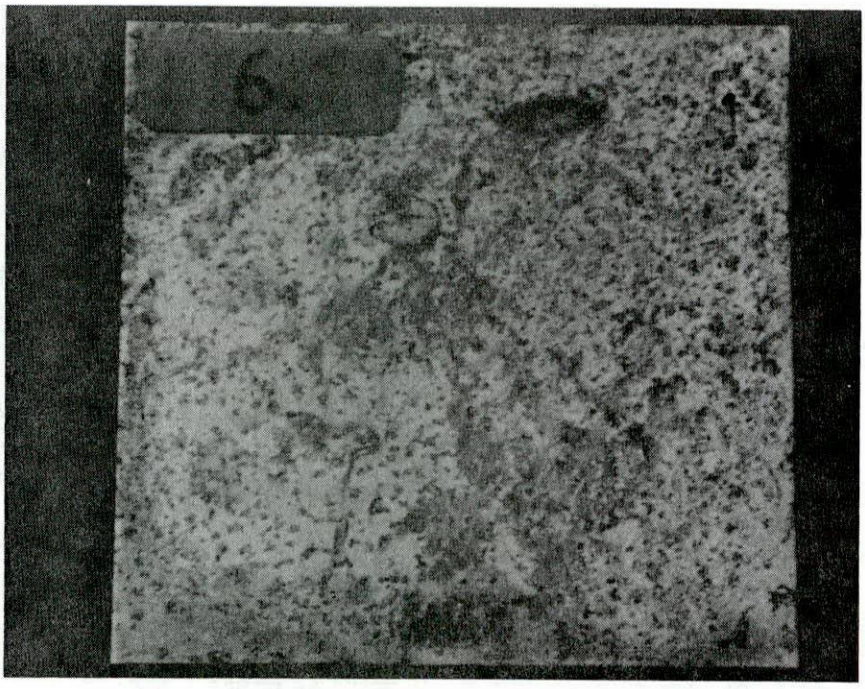

FIGURE 8b. WATER SPRAY, 55°C, 2 DAYS

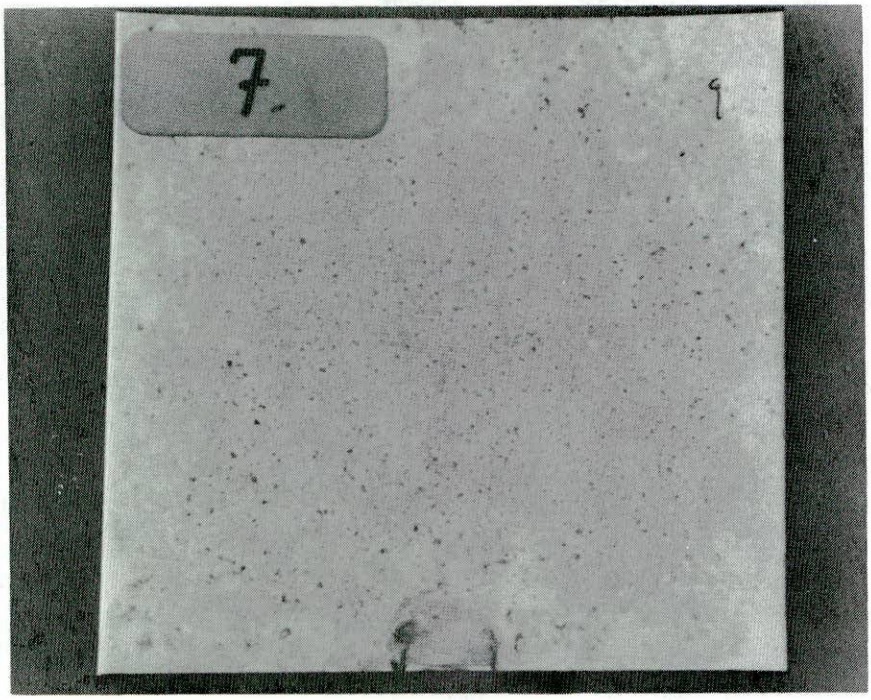

FIGURE 8c. WATER SPRAY, 55°C, 2 DAYS

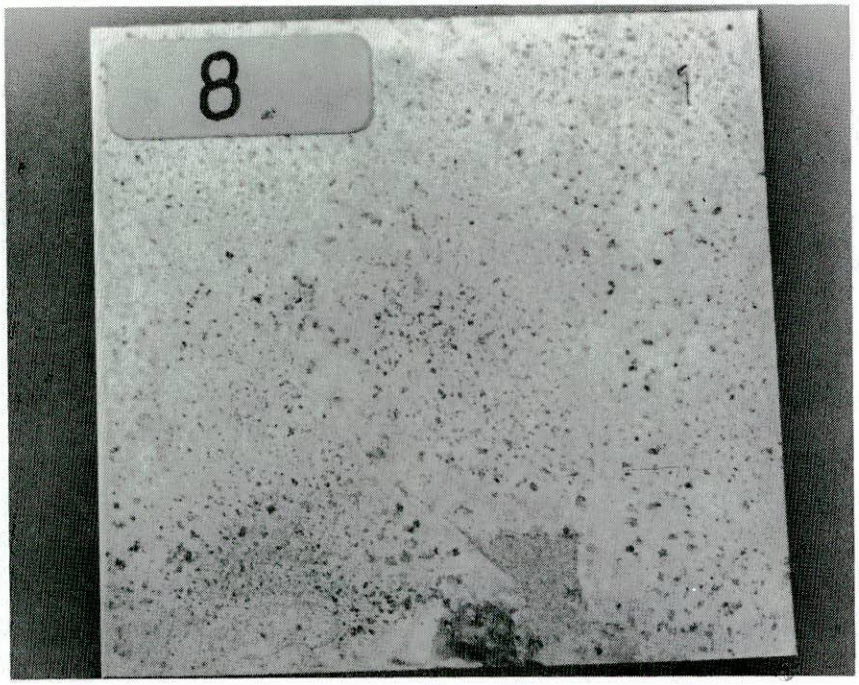

FIGURE 8d. WATER SPRAY, 55°C, 2 DAYS

G-4

Decorative II
Session G

Recent Applications of Acid Zinc Technology on a Commercial Scale

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RECENT APPLICATIONS OF ACID ZINC TECHNOLOGY ON A COMMERCIAL SCALE

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ABSTRACT

Acid zinc processes have captured the major share of the worldwide market for both decorative and functional applications. The two main types of electrolytes are based on either chloride or sulfate ions. Both types of electrolytes will be examined as to their operating parameters, advantages and disadvantages. Recent technical advances in terms of performance features and deposit properties corresponding to specific acid zinc systems will be presented.

Selected examples from a variety of commercial scale operations demonstrate the unique benefits of state-of-the-art acid zinc technology.

INTRODUCTION

Commercially viable, decorative acid zinc processes were introduced in the early 1970's and have steadily gained prominence displacing cyanide and alkaline zinc systems. The original acid zinc baths of the late 1960's[1] were highly chelated, hence, they were not widely accepted due to waste treatment and chromating difficulties. The first commercially successful acid baths were the ammonium chloride variety developed in Germany[2-4]. From these, the concept of a chloride complexed acid zinc spread throughout the industrialized world.

Since pollution control and meeting government effluent standards became of uppermost importance for the plating industry, the next generation acid chloride zinc baths developed were ammonia-free, potassium based systems[5]. The potassium systems grew in prominence and became the most important decorative acid zinc variety in the United States. However, a full five years passed before the next development occurred; namely, a commercially viable, all sodium chloride process[6], although mixed ammonium-sodium baths had been previously utilized. As with the potassium based baths, certain economic and commercial advantages were the driving force in these developments.

An older part of the acid zinc picture is the functionally oriented processes which have been utilized for years in large scale industrial rust proofing. Here the most popular process has been the acid sulfate based electrolyte, although chloride baths are successfully used as well, and mixtures of the two are also practiced. The functional market is currently enjoying a period of exciting development and resurgence[7] because of both the high cost of worldwide corrosion and the upcoming 5-10 year corrosion guarantees in the automotive industry.

In this paper, we will discuss the important technical features of both decorative and functional processes which have been demonstrated to be commercially viable.

PROPERTIES OF ELECTROLYTES

The six most important acid electrolytes for decorative and functional zinc plating are described in Tables I and II, respectively. Of course, minor variations of each type can be found in the industry. Following is a brief discussion of the properties of the various electrolytes.

Conductivity

The acid chloride electrolytes are the most conductive zinc baths known[8], providing considerable power savings to the user. As noted in Figure 1, the ammonium chloride is the most conductive, with potassium next, and sodium last. The difference is small though significant, if the plater has only a limited power supply and is changing from an ammonium to a sodium based system. It is important to note that some of the reported variations in conductivity on a commercial scale can be ascribed in baths using boric acid to the formation of insoluble polyborate salts on the zinc anodes and not to electrolyte differences. The formation of such polyborates is common and has been found to be related to the amount of boric acid in the bath, the bath pH, the bath temperature, and the amount of agitation available in the vicinity of the anodes. Recently, novel organic additives have been developed[9] that permit a reduction of standard boric acid levels and the elimination of the polyborate films.

Throwing Power

Throwing power is of utmost importance in decorative plating and especially for barrel applications of acid zinc. The various throwing power properties of different electolytes were explored at length in a previous AES publication[10]. More recently, R. Lash[8] reported on throwing power properties of sodium chloride systems. A comprehensive picture of the throwing power of acid zinc systems is given in Table III. These results, based on the Haring-Blum Method[11], show the decorative acid chloride systems to have the best throwing power properties and the functional sulfate with the least.

Cathode Efficiency

The results from prior work[7,8,10] are summarized in Table IV. It seems that the operating cathode efficiency of the various baths ranges between 90-99%, depending, of course, on the standard cathodic current densities used. Thus, we can conclude that acid zinc baths are highly efficient.

Electrolyte Comparisons

When comparing the advantages and disadvantages of an electrolyte, one must keep in mind the ultimate application. First, let us consider the various decorative chloride processes, starting with the properties of the salts used, as given in Table V. The various advantages and disadvantages of these baths are summarized below.

Ammonium Chloride Electrolytes

Advantages:

- Most conductive electrolyte
- Electrolyte provides its own buffer
- Electrolyte provides some detergency for cleaning
- Ammonium ion complex formation reduces the need for high brightener levels
- Most chloride per pound of salt
- Deposits have good chromating properties

Disadvantages:

- Salts lower bath temperature on dissolving
- Downtime attack on zinc anodes builds electrolyte
- Special waste control necessary
- Most expensive salt (U.S.)

Potassium Chloride Electrolytes

Advantages:

- Medium conductivity electrolyte
- Excellent high and low current density brightness
- No electrolyte volume building due to attack on anodes
- Simple waste control

Disadvantages:

- Some commercial salts contain clay anticaking agents, which absorb additives and clog filters
- No buffer capacity, separate addition agent needed
- Some processes prone to difficulty in forming yellow chromate conversion coating
- Most expensive salt in Far East and Australia

Sodium Chloride Electrolyte

Advantages:

- Lower make-up and maintenance costs
- Least expensive, most available, and clean salt
- Good ductility of thick zinc deposits
- Least corrosive chloride electrolyte
- Second most chloride level per pound of salt
- No electrolyte volume building due to attack on anodes
- Simple waste control
- Deposits have good chromating characteristics

Disadvantages:

- Buffer addition agent needed
- Least conductive chloride salt
- Highest brightener levels needed for low current density brightness

The corrosivity of the various plating solutions was measured by inserting a 2.5 x 10 cm mild steel panel in 500 cc of plating solutions prepared to similar conditions and held at 28°C for 500 hours. At the end of this period the weight loss of each steel panel was determined. The results shown in Table VI indicate that the chloride electrolytes are rather aggressive, particularly the potassium and ammonium based systems.

The functional acid zinc baths have other requirements and should be looked at from an applications point of view, taking into account the possible current density range, deposit properties, and whether one is plating discrete parts or continuous substrates.

Sulfate Electrolytes

Advantages:

- Least corrosive electrolyte
- Very ductile deposits
- Insoluble anodes can be utilized
- Medium plating rates up to 60 A/dm^2
- Commercial grain refining additives available[12]

Disadvantages:

- Little throwing or covering power
- Relatively low conductivity
- Good solution agitation necessary

High Speed Sulfate Electrolytes

Advantages:

- Very fast plating rates of 100 to 200 A/dm^2 are possible with proprietary additives
- Insoluble anodes such as lead or lead alloys can be used for constant cell geometry
- Amenable to continuous, high production equipment
- Lack of throwing power minimizes wrap-around on continuous steel strip
- Less corrosive electrolyte than chloride
- Good conductivity of electrolyte
- Ductile deposits

Disadvantages:

- No throwing power or covering power for complex shapes
- Relatively high solution agitation needed

Chloride Electrolytes

Advantages:

- Highly conductive electrolyte
- Moderate throwing power can be achieved
- Plating rates up to 50 A/dm^2

Disadvantages:

- Very corrosive electrolyte
- Limited to soluble, consumable anodes and, therefore, labor intensive to maintain in continuous, high production operations
- Deposits tend to be large-grained and dendritic
- Good solution agitation necessary
- No commercially viable additives

PROPERTIES OF DEPOSITS

Ductility and Adhesion

After appearance, the deposit property most quickly noticed when problems arise is of the adhesion of the coating. This condition is critical because a deposit with cracks and poor bond strength will separate from the basis metal and become useless in protecting the substrate from corrosion. Related aspects of this condition are the ductility and the internal stress. A comparison[17] showing the stress in deposits from sodium vs. potassium chloride bath can be seen in Figure 2. This result is consistent with the reduced tendency for flaking of deposits from a sodium chloride electrolyte in barrel operations. Such flaking, as shown in Figures 3 and 4, appears to be especially noticeable in potassium based baths, unless special addition agents are used to provide enhanced ductility and uniformity of the deposit.

However, since the flakes seldom penetrate to the base metal but are a zinc-from-zinc phenomenon, the deposits are widely accepted in the industry. Nevertheless, such flaking must necessarily reduce thickness and, therefore, in the long run, also corrosion resistance.

Hardness

The hardness of a zinc deposit is not a critical issue for most applications as zinc deposits generally are rather soft, especially when no additives are used. Commercial deposits with additives tend to be similar in hardness values as illustrated in Table VII.

Deposit Surface Properties

The results[8] of surface characterization via electron spectroscopy for chemical analysis (ESCA) are illustrated in Figure 5, and via ion scattering spectroscopy (ISS) in Figures 6 and 7. These data reveal some interesting features of bright deposits from sodium and potassium chloride electrolytes. The outer surface layer of the sodium based deposit has an appreciable amount of chloride which persists into the coating while sulfur and oxygen were noted on the surface of deposits from a potassium chloride bath. Whether these differences or others, such as codeposition of organic brightener films, influence yellow chromating characteristics of the potassium bath has not been determined yet.

Crystal Structure

Deposit microstructure has been shown[7] to vary with the electrolyte, type of additives, and the amount of solution agitation adjacent to the cathode. X-ray diffraction was used to obtain crystal orientation data for deposits from seven different acid zinc baths. The results[16], shown in Table VIII, indicate that the type of electrolyte and additives used exert a significant effect on the preferred orientation for crystal growth.

While the practical importance of these differences in crystal orientation is still being studied, one interesting observation is that a preferred orientation with the close packed direction of $(11\bar{2}0)$ has been correlated with improved corrosion resistance.

Corrosion Studies

The greatest factor influencing corrosion resistance in a zinc deposit is its thickness. As noted in Table IX, deposits 12.5 μm thick, without chromate or post-treatment, will develop 10% red rust in about 240 to 380 hours of ASTM B 117 Neutral Salt Spray Test. Generally speaking, these numbers are relatively close; however, their absolute values must be used with caution due to the inherent variability of such tests[18].

Corrosion results for industrial atmospheric (Chrysler modification of ASTM B 537-70) and marine conditions are underway and will be presented at SurFin '85. Generally speaking, the trend shown by the various decorative and functional deposits so far is quite similar and highly dependent on deposit thickness.

COMMERCIAL EXPERIENCE

The success of a process depends on how well it performs commercially. Wide operational margins, tolerance to periodic abuse, and ease of process control are just some of the prerequisities for a good commercial process. In the final analysis, the most economical and most consistent process will be the most popular on the market.

The successful economics of acid zinc can be easily illustrated by case histories from actual commercial experiences which can be found in Tables X through XIV and from a general cost comparison chart presented in Figure 8. The "LCZ" and "MCZ" abbreviations in Figure 8 denote low and medium cyanide zinc, while "ALK" indicates noncyanide, alkaline zinc. The last three columns are acid chloride zinc systems. The chart is formulated for barrel applications.

Production increases, power savings, and quality deposits have all played a significant role in the dramatic increase in acid zinc technology. Table XIII illustrates actual power savings experienced by commercial plating shops when converting to acid zinc. In addition, all these installations achieved energy savings due to cooling, with one as much as 65%, as well as production increases of up to 50%. All operations significantly improved the quality of the work. Also, new functional zinc operations, such as the conduit installation outlined in Table XIV are becoming increasingly popular because they are cost efficient, trouble-free, and provide increased production efficiency.

CONCLUSION

The increased market demand for higher productivity, energy savings and product quality has led to a number of significant advances in zinc technology. In decorative applications, the development of improved additive system has led to unprecedented performance levels for ammonium-free chloride electrolytes based on either potassium or sodium anions. These systems are now fully proven in large scale production. In functional applications, the recent advances in the additive technology for sulfate electrolytes has led to major improvements in the speed of plating coupled with improvements in the deposit properties. These developments have led to a new generation of high speed processes that are particularly well suited to the needs of continuous processing operations.

Acknowledgements

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References

1. R. P. Bellinger, Plating, 56 (10) 1135 (1969).

2. W. Immel, (Friedr. Blasberg), German Patent 1,263,445 (1968).

3. J. Korpium and H. J. Steeg (Max Schloetter), U.S. Patent 3,537,959 (1970).

4. H. G. Todt and G. Voss (Schering AG), U.S. Patent 3,594,291 (1971).

5. E. R. Jorczyk, Proc. AES Zinc Symposium, p. 6 (1977).

6. SPECTRALYTE® NX (sodium chloride process), OMI International, Warren, Michigan.

7. S. Martin, Proc. AES Fourth Cont. Strip Plating Symposium, p. K1, (1984).

8. R. J. Lash, Trans. IMF, 61, p. 25, (1983).

9. Patent pending (OMI International).

10. H. G. Creutz, and S. Martin, Plating and Surface Finishing, p. 681 (1975).

11. H. E. Haring and W. Blum, Trans. American Electrochem. Soc., 44, pp. 313-345 (1923).

12. Z-BRITE® USZ Process (acid sulfate process), OMI International, Warren, Michigan.

13. Handbook of Chemistry and Physics, 63rd ed., ed., R. C. Weast and M. J. Astle, CRC Press, Inc., (1982) pp. D-127,230,251,261.

14. Lange's Handbook of Chemistry, 12th ed., ed. J. A. Dean, McGraw-Hill Book Co., (1979), pp. 10-7, 15, 18.

15. R. J. Lash, "A New High Performance Sodium Chloride Acid Zinc Plating Process", IMF, Brighton, England, May 3, 1981.

16. D. R. Marx, Private communications, Sel-Rex Plating Systems, OMI International.

17. W. Verberne, Private communications, Udylite Plating Systems, OMI International.

18. T. S. Doppke and A. W. Bryant, Proc. 2nd SAE Automotive Corrosion Prevention Conference, #831815, p. 57, (1983).

TABLE I

Typical Decorative Acid Chloride Based Electrolytes

Decorative Ammonium Chloride	Decorative Potassium Chloride	Decorative Sodium Chloride
Zinc Chloride 45 g/L	Zinc Chloride 52 g/L	Zinc Chloride 52 g/L
Ammonium Chloride 180 g/L	Potassium Chloride 180 g/L	Sodium Chloride 165 g/L
pH 5 - 6.5	Boric Acid 30 g/L	Boric Acid 30 g/L
	pH 4.7 - 5.6	pH 4.7 - 5.4
Carrier	Carrier	Carrier
Brightener	Brightener	Brightener
Cathode Current Density 0.1-6 A/dm^2	Cathode Current Density 0.1-5 A/dm^2	Cathode Current Density 0.1-5 A/dm^2

TABLE II

Typical Functional Acid Zinc Electrolytes

Functional Sulfate	Functional High Speed Sulfate	Functional Chloride
Zinc Sulfate 200 g/L	Zinc Sulfate 500 g/L	Zinc Chloride 200 g/L
Conductivity Salts* 130 g/L	Sulfuric Acid 36 g/L	Sodium or Potassium Chloride 130-230 g/L
pH 1 - 5		pH 2 - 5.0
Proprietary Additives	Proprietary Additives	No proprietary additives
Cathode Current Density 5-50 A/dm^2	Cathode Current Density 20-200 A/dm^2	Cathode Current Density 5-50 A/dm^2

*Sodium Sulfate used most often, although mixtures of magnesium and sodium sulfate are common

TABLE III

Throwing Power* of Acid Zinc Processes

Bath Type	Average Current Densities (A/dm^2)		
	0.5	2	4
Decorative Ammonium Chloride	47%	40%	33%
Decorative Potassium Chloride	34%	27%	22%
Decorative Sodium Chloride	22%	16%	10%
Functional Chloride**	4%	-5%	-7%
Functional Sulfate**	N/A	-13%	-15%

*According to the Haring-Blum Method[11]
**Contains no additives

TABLE IV

Cathode Efficiency of Acid Zinc Processes

Bath Type	Utilized Cathode Current Density (A/dm^2)	Temperature (°C)	pH	Efficiency
Decorative Ammonium Chloride	3	27	5.5	99%
Decorative Potassium Chloride	3	27	5.2	99%
Decorative Sodium Chloride	3	27	5.2	99%
Functional Chloride*	50	50	4.0	95%
Functional Sulfate*	50	50	3.0	95%
Functional High Speed Sulfate	100	55	0.5	92%

*Contains no additives

TABLE V

Property Differences*

Property	Ammonium Chloride	Potassium Chloride	Sodium Chloride
% chloride, wt.	66.0	47.6	60.6
Solubility, Limit in water, g/L			
@ 100°C	758	567	391
@ 20°C	370	342	359
Heat of Solution, Kcal/mole (25°C)	3.53	4.12	0.93
Specific Conductance, mmho/cm 20°C at 124 g/L	220	170	140
Cationic Radius (Å)	5.8	1.33	0.95
Complexing Medium	ammonium ion/ chloride	chloride	chloride

*From References 13, 14.

TABLE VI

Corrosivity Comparison of Plating Solutions

Electrolyte	Weight Loss of Steel Panel
Zinc Chloride (Potassium), pH 5	393 mg
Zinc Chloride (Ammonium), pH 5	358 mg
Zinc Chloride (Sodium), pH 5	259 mg
Zinc Sulfate Electrolyte, pH 5	150 mg

TABLE VII

Hardnesses of Various Zinc Deposits

Deposit	Hardness**
Decorative sodium chloride	75 D
Decorative sodium chloride	69 R
Decorative potassium chloride	76 D
	69 R
Decorative ammonium chloride	80 D
	69 R
Functional HS Sulfate	78 D
	69 R
Functional Sulfate	72 R
Functional Sulfate*	68 R
Functional Chloride*	<63 R

*Contains no additives
**D-DPH 100g - R-Rockwell 15T

TABLE VIII

Influence of Additives and Electrolyte on Crystal Orientation

Deposit from Bath Type	Preferred Crystal Orientation	Peak Intensity**
Bright Sodium Chloride-Process I	$(10\bar{1}0)$	M
	$(11\bar{2}0)$	VS
Bright Sodium Chloride-Process II	$(10\bar{1}0)$	VS
	$(10\bar{1}1)$	S
Bright Potassium Chloride-Process I	$(10\bar{1}0)$	M
	$(10\bar{1}1)$	VS
Bright Potassium Chloride-Process II	$(10\bar{1}0)$	M
	$(10\bar{1}1)$	VS
Functional Sulfate* - Electrolyte A	(0002)	VS
Functional Sulfate* - Electrolyte B	$(10\bar{1}1)$	VS
Functional High Speed Sulfate with Additive	$(11\bar{2}0)$	VS

*No additives

Key:

**VS - Very Strong
S - Strong
M - Medium

TABLE IX

Salt Spray** Corrosion Comparisons of Deposits from Various Commercial Electrolytes

Electrolyte	Hours to 10% Red Rust
Sodium Chloride	378
Potassium Chloride	242
Ammonium Chloride	270
Functional Sulfate*	300
Functional HS Sulfate	324
Functional Chloride*	296

All deposits 12.5 μm thick, without passivation or post-treatment.

*Contains no additives
**Based on ASTM B 117 Neutral Salt Spray Test

TABLE X

Case History: Conversion from Low Cyanide Zinc to Acid Sodium Chloride

Equipment: Model C Barrel
Tank Volume: 15,000L
Plating Stations: 22

	Low Cyanide Zinc	Sodium Chloride Acid Zinc
Anodes	Zinc Balls in steel wire baskets	20% zinc balls in titanium baskets and 80% zinc slab
Tank Voltage	12 - 15 V	6 - 7 V
Tank Current	4000 A	2000 A
Machine Speed	45 barrels/hr	55 barrels/hr
Barrel Load	9 - 12.7 Kg	16 - 18 Kg
Chemical Usage per Shift	NaCN 3 Kg NaOH 32 Kg	NaCl 29.4 Kg H_3BO_3 6.8 Kg
Production per shift	3919 Kg	7484 Kg
Rework	>5%	<1%
Results:		91% increase in production

TABLE XI

Case History: Conversion from Potassium to Sodium Chloride Barrel Zinc

Equipment: 122 cm x 46 cm Automated Horizontal Barrel
Tank Volume: 11,400L
Anodes: Zinc Balls in Titanium Anode Baskets
Production Rate: 18 barrels/hr
Dragout: 1.9 L/barrel

	Potassium	Sodium
Make-up Cost per liter	$0.26	$0.20
Dragout cost per week (3 shifts per day)	$1,069	$820
Chemical usage per day (3 shifts)	KCl 184 Kg H_3BO_3 21 Kg $ZnCl_2$ 37 Kg	NaCl 135 kg H_3BO_3 18 Kg $ZnCl_2$ 37 Kg

Cost savings* in chemicals per year = $11,703
(47 weeks)

*KCl price used: $0.20/Kg
NaCl price used: $0.13/Kg

TABLE XII

Case History: Conversion from Potassium to Sodium Chloride For Parts Requiring Excellent Physical Properties of Zinc Deposit

Equipment: 46 cm x 91 cm Manual Cylindrical Barrel
Tank Volume: 11,400L
Anodes: Zinc Slabs
Barrels in Plating Tank: 6
Production Rate: 10 Barrels/hr
Plating Time: 60 Minutes
Average Current on Tank: 3000 A
Load Size: a) 102 Kg Fasterners
b) 54 Kg Stampings
Deposit Thickness: 12.5 µm average
Filtration: 22,700 L/hr Horizontal Plate Filter

	Potassium	Sodium
Average salts usage per shift	44 Kg	32 Kg
Requirement: No blistering upon welding	Not Passed	Passed
Filter Maintenance	Twice a week	Once every 4-6 weeks

TABLE XIII

Power Savings by Conversion to Acid Potassium Chloride Zinc

Customer	Equipment	Process Replaced	Voltage		Amperage		Annual Power Savings
			Before	After	Before	After	
Case I	Oblique Barrel	Alkaline Non-Cyande	13	8.5	2200	900	$1630
Case II	Horizontal Barrel	Alkaline Low Cyanide	15	8.5	5000	3000	$6900
Case III	Oblique Barrel	Pyrophosphate	12	7.5	3500	1300	$2940
Case IV	Rack	Alkaline Low Cyanide	7.5	4	6500	4500	$4900

TABLE XIV

Successful Acid Zinc Conduit Operation

Equipment	Conveyor Type
Bath Type	Acid Sulfate with Additives
Production	601,000 pcs/mo.
Conduit Length	3 - 3.7 m
Tank Current	75,200 Amperes
Average Cathode Current Density	7 A/dm^2
Conveyor Speed	1.5 - 3.5 m/min
Thickness	10 - 15 μm
Product Specification	3 cycles of Neutral Salt Spray test to white corrosion

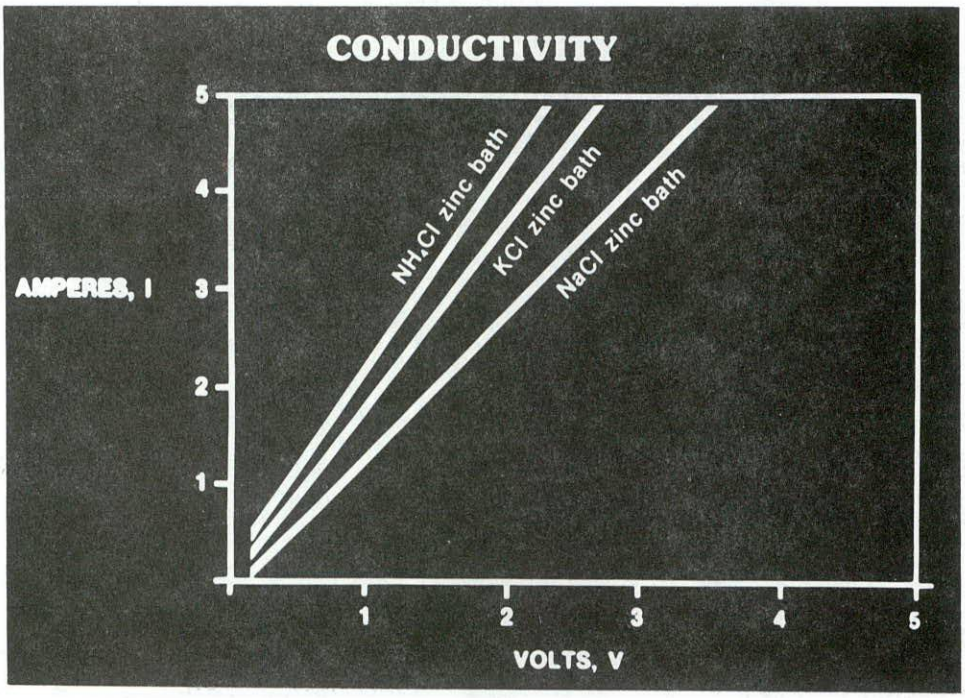

FIG. 1 CONDUCTIVITY COMPARISON OF ACID CHLORIDE ZINC BATHS

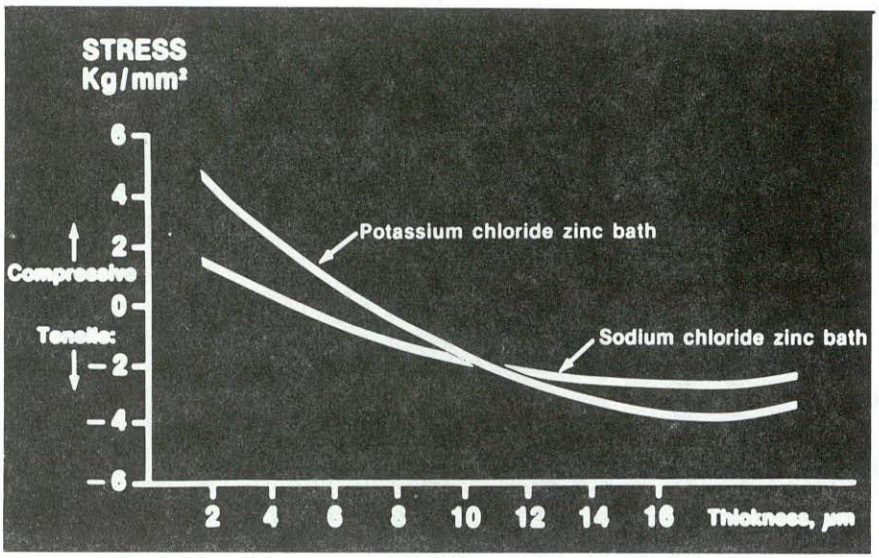

FIG 2 STRESS IN ACID CHLORIDE ZINC DEPOSITS[15]

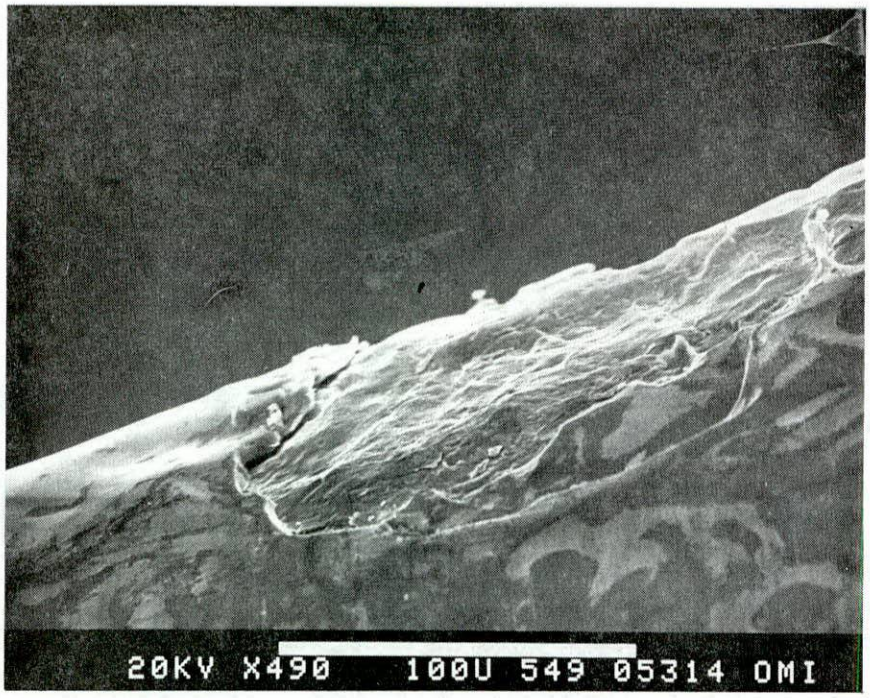

FIG. 3 SEM MICROGRAPH OF ACID POTASSIUM CHLORIDE BARREL ZINC DEPOSIT FLAKING PHENOMENON

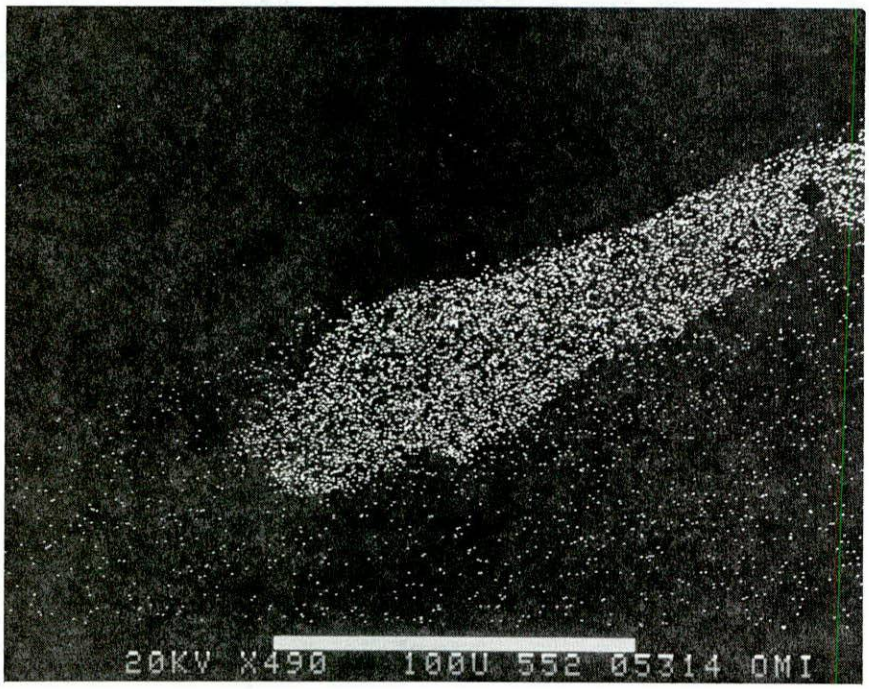

FIG. 4 EDS MAPPING OF IRON OF FIG. 3 WHICH INDICATES ZINC DEPOSIT THICKNESS

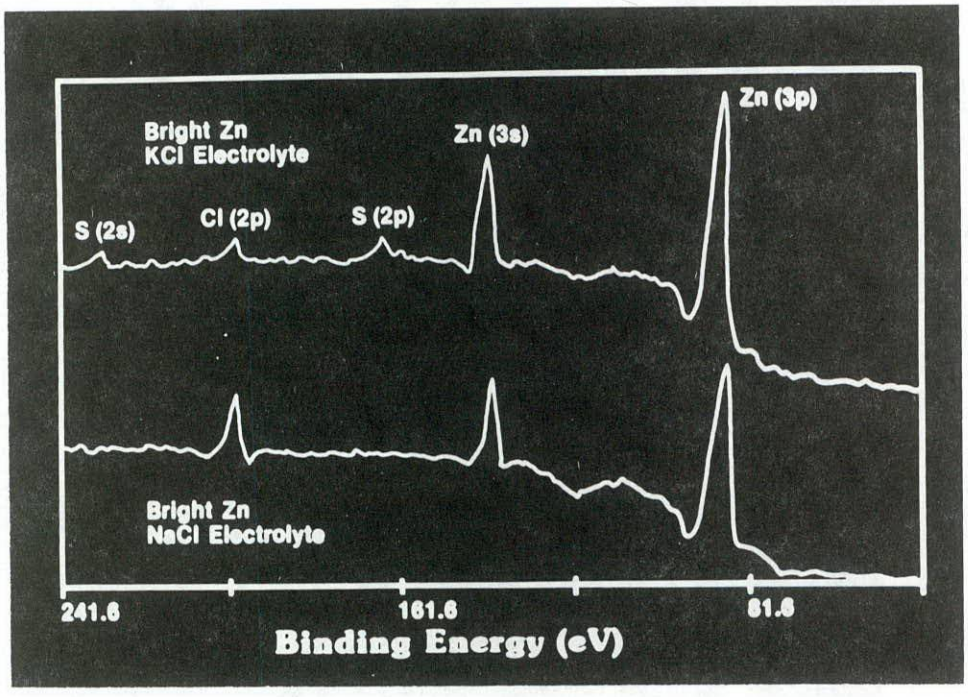

FIG. 5 ESCA SURFACE ANALYSIS OF SODIUM AND POTASSIUM CHLORIDE BRIGHT ZINC DEPOSITS

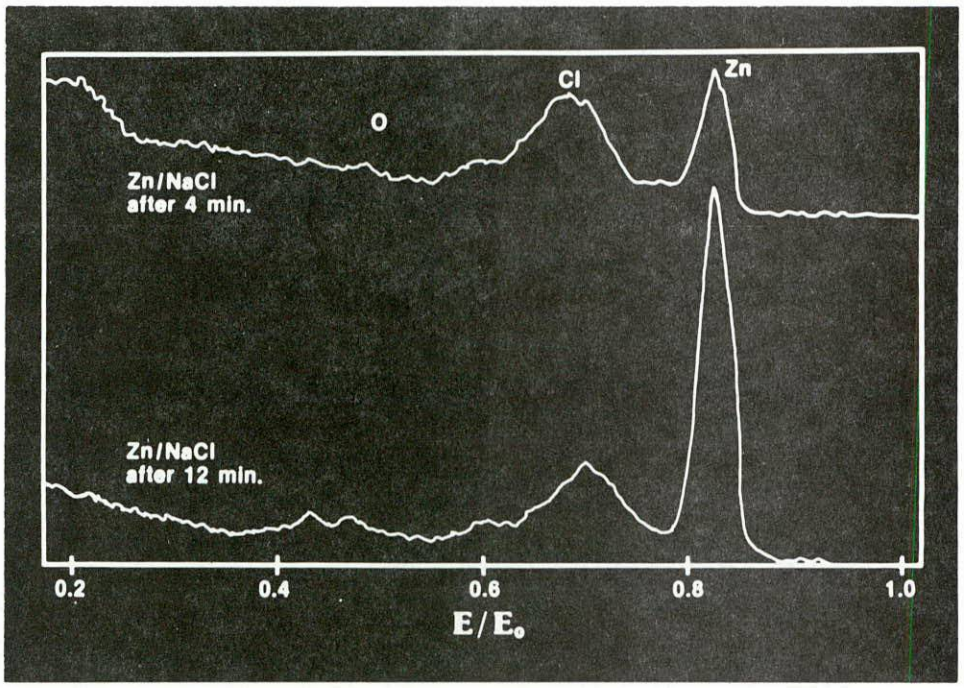

FIG. 6 ISS SURFACE ANALYSIS OF SODIUM BASED BRIGHT ZINC DEPOSIT

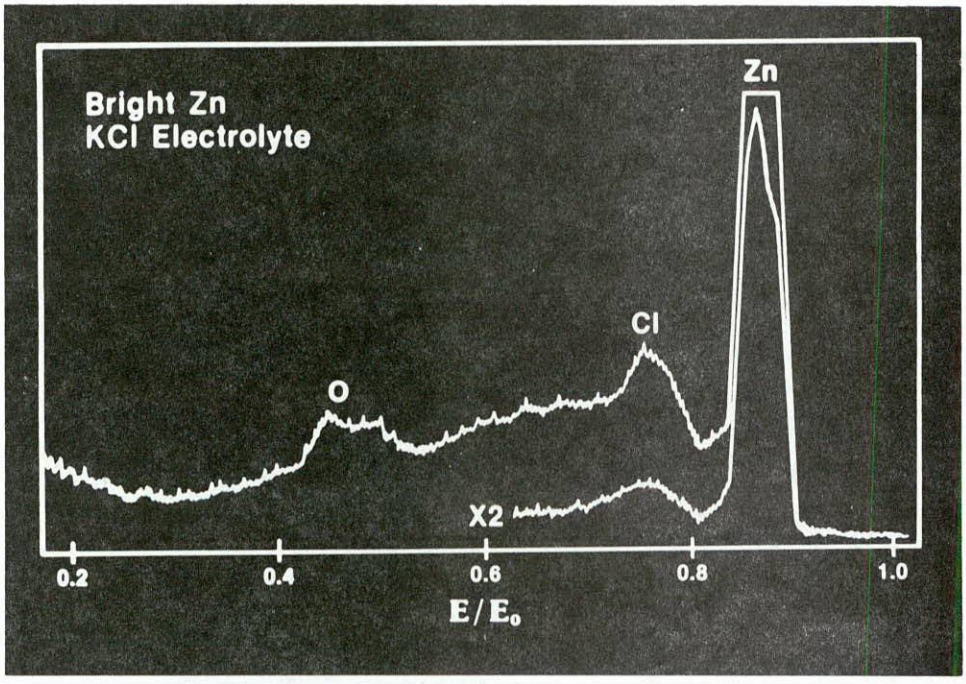

FIG. 7 ISS SURFACE ANALYSIS OF POTASSIUM BASED BRIGHT ZINC DEPOSIT AFTER SPUTTERING OF 10 MINUTES

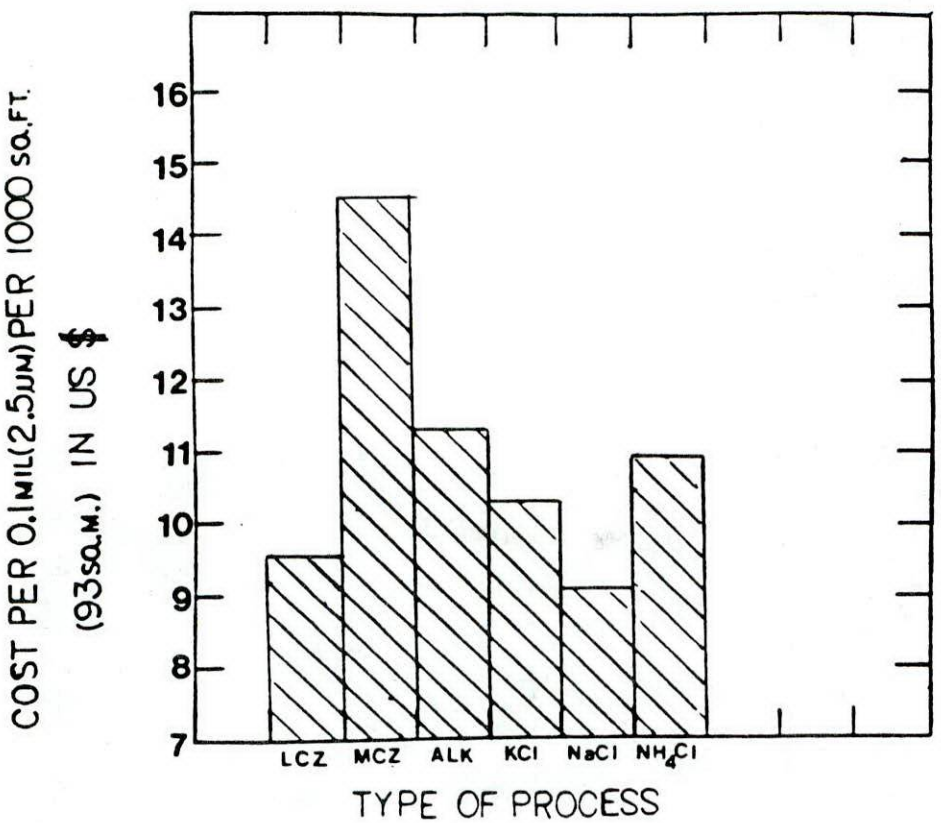

Fig. 8 COMPARATIVE OPERATIONAL COSTS OF DECORATIVE ZINC BATHS

BASED ON KNOWN CONSUMPTION RATES, EFFICIENCIES, AND SOLUTION DRAG-OUT OF 6 GAL. PER 1000 SQ. FT. (24 L/100 SQ. M.)

H-1

Environmental II
Session H

Recycling in the Japanese Electroplating Industry

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RECYCLING IN THE JAPANESE ELECTROPLATING INDUSTRY

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Introduction

The Environmental Administration of Japan has become increasingly more stringent since 1970. The First Oil Crisis in 1973 drew attention to the increased need to recycle resources. This paper covers the history of the environmental pollution control administration; present effluent regulations; the status of the electroplating industry; and reviews the basic treatment technology to meet the current effluent regulations.

Recycling and recovery technology will be discussed in this paper with examples of the Central Ion Exchange Regeneration Center (Resource Center) and common waste water treatment technologies of collective plating shops.

1. History of Environmental Pollution Control Administration and Effluent Standards

Pollution problems in Japan can be traced back to air and water pollution and ground sinking at mines or smelters due to large-scale growth of the mining industry in the late 1880's. A water pollution problem was first observed in the Ashio copper mine pollution incident in Furukawa near Tokyo. This incident is considered as the first pollution problem in Japan, because it contains such common factors as a suffers' movement which arose in response to the incident, and covers measures taken by the Government and private enterprises as a result of the incident.

Pollution problems until the early 1950's at the local level and were handled under the local government's regulations. And local goverments with large-scale industrial areas such as Tokyo, Kanagawa and Osaka enacted pollution prevention regulations.

In the late 1950's, pollution problems became more serious, extending over a wide area and could not be solved by regulations set by local governments. The public strongly demanded at that time that pollution problems be regulated by national laws. In 1958, two laws "Law regarding Preservation of Pubic Water Area" and "Law regarding Regulation of Plant Effluents" are enacted. These two laws established the basis of the Governments fight against pollution.

The enactment of the "Basic Law for Environmental Pollution Control" in 1967, which coverd the basic idea of pollution control and countermeasures, also opened the way to comprehensive pollution control measures. The Basic Law tightened the regulations and took a step forward towards the establishment of both incident settlement and a relief system of the suffers.

Two laws enacted in 1958; "Law regarding Preservation of Common Waterways" and "Law regarding Regulation of Plant Effluents", are integrated as the Water Pollution Prevention Law in 1970. This Law regulates not only water quality but also deterioration of water conditions such as color or temperature. A Law issued by the Prime Minister's Office, in order to regulate degrees of pollution (refer to Table 1), also sets the effluent discharge standards for plant effluents from a designated plant into public waterways. Plants discharging effluents must keep them within these standards: if they violate the Law, penal regulations are applied and a correction order is issued by the government. Another avenue is for local governments to set more strict standards (add-on regulations) than the national ones.

In 1971, the Environmental Agency was established to carry out more comprehensive and effective anti-pollution policies, and in 1978 the Water Pollution Control Law was amended to include the regulation of the total discharge volume. Concentrations of heavy metals were well regulated, but the control of organic substances, expected by the public could not be obtained. Therefore, the amended law considered not only effluent concentration but also the total amount of waste water emitted from housing or business areas. Total amount regulations are not applied through Japan. But are though, local regulatios for COD (BOD), applied to closed waterways such as the Seto Inland Sea, Ise Bay and Tokyo Bay, where water pollution is a severe problem. To prevent organic contamination, nitrogen and phosphrous compounds are to be regulated from April in 1985.

2. Outline of the Electroplating Industry and Present State of Waste Water Treatment in Japan

2-1 Outline of the Japanese Electroplating Industry

In Japan, about 16% of the total sales volume of plated products is occupied by captive shops. The remainder is occupied by plating job shops. Table 2 shows types of plating at job shops. From this table, about 75 % of the plating job shops handle decorative nickel and/or chromium, and zinc plating.

Table 3 shows the total sales volume by industries. About 50 % is comprised of automobile, motorcycle and electronic parts. Recent demand for automobile parts has not increased due to changes of raw materials. On the other hand, the sales volume for electronic parts have been growing year after year. The sales of electronic parts are now estimated to be greater than that of automobile parts.

Japanese electroplating job shops have a well-organized, nation-wide association on the local level and each local association is part of a parent organization of the Japan Electroplating Industrial Association. Table 4 shows the status of the industry as of the end of 1982. There are about 4000 job shops of which about 3,150 shops are members of the Association. The total number of employees of the members are about 42,000 and the average number of empoyees is 13.3. This means the Japanese electroplating industry is comprised on the whole of small enterprises.

An average volume of effluents per employee is calculated to be about 2.8m³/day. And the average volume per shop is about 37m³/day. The annual cost of waste water treatment is about $26,000 /shop. The operating cost of waste water treatment corresponds to about 6 % of the total sales volume.

2-2 Current State of Waste Water Treatment

In order to decrease waste water treatment load, many Japanese platers have made efforts of their own to improve the rinsing methods and processes, and to utilize recycling equipment such as ion exchangers, evaporators, reverse osmosis, electrodepositon, etc. for recovery purposes.

Typically they usually employ continuous treatment of oxidation and reduction and chemical precipitation before final discharge. Figure 1 shows a typical flow diagram of waste water treatment practiced at most job shops. As the figure shows, the waste water is segregated into chromium, cyanide and other wastes (acid and alkali). Chromium wastes are reduced to trivalent by a reducing agent (ex. sodium bisulfite). Cyanide wastes are destructed by an oxidizing agent (sodium hypochlorite). After the treatment, these wastes are mixed together with acid and alkali wastes, and added inorganic substances (ex. $FeCl_3$, $Al_2(SO_4)_3$, $Ca(OH)_2$, $CaCl_2$), then acid or alkali is added to adjust pH and finally poly-electrolytes are added to coagulate suspended solids in the solution.

After sedimentation, this supernatant solution is clarified by sand filter and discharged after pH adjustment. The slurry from the sedimentation process is pumped to the dewatering equipment (ex. filter press, etc.) for disposal. Dewatered sludges are sent to landfills designated by local governments.
Recently activated carbon is often added after sand filtration to remove organic substances. According to our estimate, about 20 to 30% of the existing treatment facilities have this carbon treatment. The dumped or aged concentrated solution are separately treated or are disposed of by a subcontractor.

3. Recycling and Recovery Technology

3-1 Econoback System

The Econoback System, introduced in 1971 to the Japanese electroplating industry was the results of a national project of principal technology development supported by the Agency of Industrial Science and Tchnology titled " Industrial-tion practice of chemicals and water recycle for plating processes". It was a culmination of the research and development works carried out since the late 1950's by the author, A. Yagishita, for the recycling and recovery of resources from plating processes.

The Econoback System, an economical recovery and recycling system for the reuse of rinse water and valuable chemicals, comprises of

1. Control and purification of plating chemicals.
2. Recovery of plating chemicals.
3. Recycling of rinse water and improved rinsing efficiency.
4. Regeneration center to recover resources from eluates.

Figure 2 shows an example of the Econoback System at plating shops. It utilized such equipment as oil separators and filters for clarification of pretreatment solutions, filters, ion exchangers, and electro-dialysis for purifying plating solutions. Rrcovery can be achieved using either an evaporator, ion exchanger, reverse osmosis or electro-diposition. Ion exchange and reverse osmosis are used for rinse water recycling. The best equipment which treats wastes economically must be selected carefully.

It is very important to consider the total energy balance when recycling resources. Following four recycling loops can be considered when overall conditions are considered. They are recycling

1. In a plating process.
2. In a plating shop.
3. In a regional group.
4. In an extensive area and/or an industry.

For example, in the chromium plating process, chromium is lost in the following way: About 10% for plating, 30% as mist, 60% as drag-out. In other words, 90% of the chemicals are wasted. The recovery rate of drag-out solution can be raised to about 40～50 % by installing one recovery tank. If an additional one or two tanks are added, the recovery rate is raised to about 65～80 %. After improving the rinsing efficiency by installing a rinse tank, an economical recycling process can be realized by a combination of recovery equipment as shown in Figure 2, and the recovery rate of the drag-out solutions can be raised to 95 %.

The most economical and efficient way of increasing the recovery in the System is to improve the rinse process. Based on counter-current rinsing, the addition of rinsing tanks decreases the concentration of the last rinse tank, thus leading to minimizing the size of the required recovery equipment. Generally it is economical if a dragged-out plating solution can be returned to the plating tank by means of concentration, but if impurities accumulate during the concentration process, it becomes necessary to purify the solution before returning to the original plating tank. Purification of process solutions extend the solution life, and therefore reduces the amount of aged solutions which may have to be disposed of.

The use of a Centralized Regeneration Ssystem (Resource Center System) for ion exchangers used in the plating processes is much more economical as compared with regeneration at each shop.

Segregation of waste water is a fundamental principle for this recovery method. If waste water is mixed together, recovery becomes difficult and uneconomical.

3-2 Resource Center System

The resource center system is a centralized regeneration/resource system for the recycling of rinse water for reuse by ion exchange and recovery of valuable metals. The center was established in 1976. Since then, the system has produced 24,000 m^3/day of water on site. The saturated cartridge ion exchange columns are transferred from customers to our center and 500 columns per month of ion exchangers are regenerated .

The resource center system has many variations as shown in Figure 3. The system has to be economically operated to meet condtions of such location. The variations (a)～(f) shown in the figure have all been in use and satisfactory results have been obtained.

Since central regeneration is the main purpose, ion exchangers must be easy to handle and transport and the construction must be simple for resin loading and unloading. The amount of resin in the columns are either 5, 25, 50 or 100 liters. Resin volume is calculated based upon the expected load on the system. Figure 4 shows general ideas of Resource Center System at our Inuyama Factory.

The columns transferred to the center are separated according to their application for regeneration. And eluates from a regeneration process (metal concentration is 20-50 g/ℓ) are converted into valuable resorces by either evaporation, electrodeposition or solidification.

About 50% of the regeneration is used by resins applied for chromium such as chromium plating or chromate conversion coating , 15～20% by copper plating (copper cyanide, copper sulfate baths), 5-7 % by nickel plating and the remaining by precious metal plating. Figure 4 shows these trends. The amount of nickel and copper recovered and returned to smelters are 1.5 ton/year and 2.0 ton /year respectively. The annual growth rate in the use of this recovery process of the past five years has been more than 20%.

4. Case Studies

4-1 Applied for Electroplating Industrial Complexes

Collective plating shops for purpose of common waste water treatment for effluents from small plating shops had been studied since 1960's in Japan when effluent regulations became stricter.

Small job shops have many difficulties in installing their own treatment facility due to the initinial investment costs and space requirements. Common waste water treatment facilities have many difficulties in sharing treatment costs and managing the facility, and local governments since the 1970's, have advised job shops to get together and take advantage of the common waste water treatment. Centralized waste water treatment systems have been adopted by the Japanese plating industry and are to be promoted in the future. Table 5 shows the common waste water treatment systems at such industrial complexes.

Advantages in Centralized Waste Water Treatment for Plating Shops

1. Reduction in waste water treatment cost and lowering of treatment facility investment for each plating shop.

2. Realization of efficient recycling and recovery due to an increase in treatment volume.

3. Ease of obtaining government finacial support for waste water treatment facilities.

4. Relocation of industrial areas in a city by transferring plating shops to an industrial complex in the suburbs.

4-2 A Successful Case of the Econoback System applied to Chuo Electroplating Industrial Park.

Chuo Electroplating Industrial Park was constructed with in the industrial area on a man-made island by Tokyo Bay in 1977. This industrial park consists of eleven electroplaters, one united company of eleven small job shops, related companies of one chemical supplier and one equipment manufacturer, the total number of employees is about 350. The total land area of the industrial park is about five acres. The total cost for construction of the park was about 16.6 million dollars including buliding and treatment facilities.

The government gave its support in obtaining a low interest loan for the construction of the park, and provided guidance for centralized waste water treatment and disposal of industrial wastes to the park.

The results of waste water treatment system in Chuo Electroplating Industrial Park is effective recovery and economical treatment performed at the right place in each plating shop and common treatment facility. Waste water is segregated into seven different waste water streams. And they are transferred by seven different 100 mm diameter pipes from each plating shop to the common treatment center. They are diffrent streams, and are cyanide, copper, nickel, chromium, chelated, acid, and alkali waste water.

Recycle and Recovery in Individual Plating Shops

The first stage of recycle and recovery consists of recycling of rinse water by portable ion exchangers, and recovery of precious metals and copper by electrodeposition in each electroplating process.

Waste water treatment processes at individual plating shops consist of electrolysis of cyanide waste and removing heavy metals from chelated waste before they are transferred to the common treatment center. This brings economic benefits and solves technical difficulties in treatment at the common treatment center. Counter-current rinses using stagnant rinse type is applied to most electroplating processes.

Nickel and chromium wastes, which are not economical to recover on site due to treatment volume, are stored at plating shops and pumped to the common treatment center. The waste, which has been partially treated at the plating shops is also pumped to the center.

Treatment at the centralized treatment center

The second stage of recovery for metals such as nickel, copper and chromium recovery as solution are performed at the treatment center. Oxidation of cyanide waste and reduction of chromium waste is also carried out.
Finally conventional chemical treatment, clarification and pH adjustment before discharge to the sewer are carried out. Typical neutralization and precipitation of chemical treatment is applied for acid and alkali wastes. Chelated waste water is pumped to the pH adjustment tank after removing heavy metals in the plating shops.

The portable ion exchangers which are used for recycling rinsing water at the last rinsing tank of each plating process, are brought back to the common treatment center for regeneration when saturated.

The total amount of waste water volume has been significantly decreased since utilizing this recycling and recovery system in this industrial park. Also water consumption is reduced to one tenth of the average water consumption of most Japanese electroplating shops, which calculated to be 0.3m³ per person.

5. Conclusion

The future points to even stricter regulation of industrial wastes by the Japanese environmental administratrion. For example the decision has been made to regulate nitrogen and phosphrous compounds from April, 1985.

The present expenditure for pollution control in the electroplating industry is 5-6% of the total sales amount (national average) and is expected to rise even further. In some areas, local governments or inhabitants strongly demand platers for zero discharge and some platers have already realized it. Under these circumstances, not only must attention be given to treatment processes, but also to economical treatment as well. It is very important to consider component equipment of the system to meet mandated requirements with close attention being paid to analytical techniques.

In the neighbouring countries of Korea, China and other southeast Asia countries, demands for environmental pollution control also have been rapidly growing. For example plating complex in Korea has adopted our unique recycling system and is expected to start operation in the coming spring.

Necessity and demand of recycle and recovery including extensive recycling loops will certainly grow with technical improvement and an increase in recovery benefits.

References:

1) Research report for finding a way out of the plating
Japan Electroplating Industrial Association, 1980
2) Research report for estimation of electroplating demands
Japan Electroplating Industrial Association, 1983

Table 1. Discharge Values (Waste Water Prevention Act, Article 3)

Harmful substances (Health Factor)			Living Environmental Factors		
Item	Concentration		Item	Concentration	
Cadmium	0.1	mg/ℓ	pH	5.8-8.6	
Cyanide	1	mg/ℓ	Total chromium	2	mg/ℓ
Chromium(Hcxa)	0.5	mg/ℓ	Coppcr	3	mg/ℓ
Lead	1	mg/ℓ	Zinc	5	mg/ℓ
Arsenic	0.5	mg/ℓ	Soluble iron	10	mg/ℓ
Total mercury	0.005	mg/ℓ	Soluble manganeese	10	mg/ℓ
Alkyl mercury	not decetable		Fluorine	15	mg/ℓ
Organic phosphate	1	mg/ℓ	Mineral oil	5	mg/ℓ
PCB	0.003	mg/ℓ	Animal fat & Plant oil	30	mg/ℓ
			BOD	160 (120)	mg/ℓ
			COD	160 (120)	mg/ℓ
			SS	200 (150)	mg/ℓ
			Phenol	5	mg/ℓ
			Colliforms	(3000)	

Table 2 The Percentage of Types of Plating of Job Shops [1]

Type of plating	(%)
Decorative Ni and/or Cr plating	42.8
Zinc plating	33.1
Precious metal plating	10.6
Hard Chromium plating	8.0
Others	5.5

Table 3 The Percentage of Sales Volume (1982) [2)]

Industry	Total sales volume	(%)
Automobile, Motorcycle parts	89.04	23.69
PCB, Leadframe, Computor parts	86.81	23.10
Screw, Tool, Pipe, Architectural fittings	45.76	12.17
Watch, Camera	34.19	9.10
Home electric apparatus	29.54	7.86
Flatware, Kitchen ware	23.46	6.24
Office fixtures	18.79	5.00
Reciever, communication equipment	15.88	4.23
Toys	10.50	2.79
Bicycles	8.14	2.17
Sewing machines, Knitting machines	3.21	0.85
Others	10.54	2.80

Unit: billion yen

Table 4 The Outline of Japanese Electroplating Job Shops [2)]
(The end of 1982)

Total members of Japanese Electroplating Association Japan Electroplating Industrial Association(JEIA)	3,144	
Total employees of JEIA members	41,777	
Number of non-members job shops (estimated)	790	
Average employees in each shop	13.3	
Average water consumption /employee	2.8	m^3/day
Average Annual waste treatment cost, Chemicals /shop	2,440,000	yen
Others /shop	4,040,000	yen
Ratio of waste water treatment cost to total sales volume	6	%

Table 5 List of Electroplating Complexes in Japan

#	Designed and installed by SANSHIN	Name of Complexes	Total number of companies	Number of platers	Total number of employees	Employees at plating shops	Date of completion	Total area of plating shops (m^2)	Building area of plating shops (m^2)	Collection tank at each plating shop	Collection tank at common treatment facility	Total amount of wastes/day (m^3)	Joint undertaking						
													Wastewater treatment	Welfare facilities	Purchase	Testing & analyses	Subleasing financing	Boiler	Order reception
1		Kita Nihon Electroplating Industrial Association	5	5	25	25	Jan. '78	2,815	1,500		○	15	(Corporation of all works)						
2		Takasaki Metal Industry Corparative Association	17	6	900	300	Feb. '68	30,000		○		1,300	○	○					
3	○	Takasaki Kagano Electroplating Industrial Association	4	4	75	75	July '71	7,950	2,868		○	352	○		○				
4		Ageo Electroplating Industrial Association	6	6	150	150	July '72	6,600	4,015		○	600	○		○	○	○		
5	○	Ichikawa Metal Finishing Industrial Association	6	4	122	95	Dec. '77	4,790	2,474		○	213	○	○		○		○	
6		Toukatsu Electroplating Industiral Association	3	3	40	40	Mar. '81	4,522	2,322		○	200	○						
7	○	Katushika Electroplating Industrial Association	8	3		256	Mar. '68		2,544		○	292	○	○		○			
8		Jyounan Electroplating Industrial Association	9	9	178	178	Aug. '75	4,675	4,464		○	266	○	○	○	○	○		
9	○	Chuou Electroplating Industrial Association	14	12	390	345	Dec. '78	12,996	11,660	○		90	○			○	○		
10	○	Keinann Industrial Association	18	4		150	Apr. '83	2,050	4,130	○		50	○			○			
11		Yamanashi Machinery & Metal Industrial Association	14	9	301	135	Sep. '74	26,302	8,759	○		300	○		○	○	○		○
12		Matsumoto Metal Industrial Association	10	5	166	58	Jan. '78	5,847	2,336		○	10	○	○	○		○		○
13	○	Sanjyoh Metal Finishing Center Industry Association	5	5	154	154	Mar. '76	7,833	6,050		○	230	○		○	○			
14		Ozeki Industrial Complex, Wastewater Treatment Association	9	9			Jun. '74	34,440			○	179	○			○		○	
15		Yoshida Metal Center Industry Association	22	3	649	168	Mar. '77	29,844		○		109	○	○		○	○		
16		Nagoya Nakagawa Metal Industry Association	11	2			Jun. '77	6,853	2,748	○		100	○		○		○		
17		Toyokawa Industrial Association	10	3	300	70	Mar. '81	4,500	3,688	○		200	○						
18	○	Yokkaichi Metal Finishing Industry Association	5	3	225	41	Apr. '81	8,403	5,497	○		250	○						
19		Himi Electroplating Industrial Association	4	4	60	60	Mar. '73	5,458	4,210		○	89	○		○	○	○		
20		Gold Plating Center	4	3		35	May '73	330	390		○	70	○			○			
21		Koube Electroplating Industrial Association	7	7	119	119	Mar. '75	3,157	4,174		○	380	○			○	○	○	
22	○	Fukuyama Metal Industry Association	11	7	267	170	Mar. '77	23,207	8,360	○		115	○			○	○		

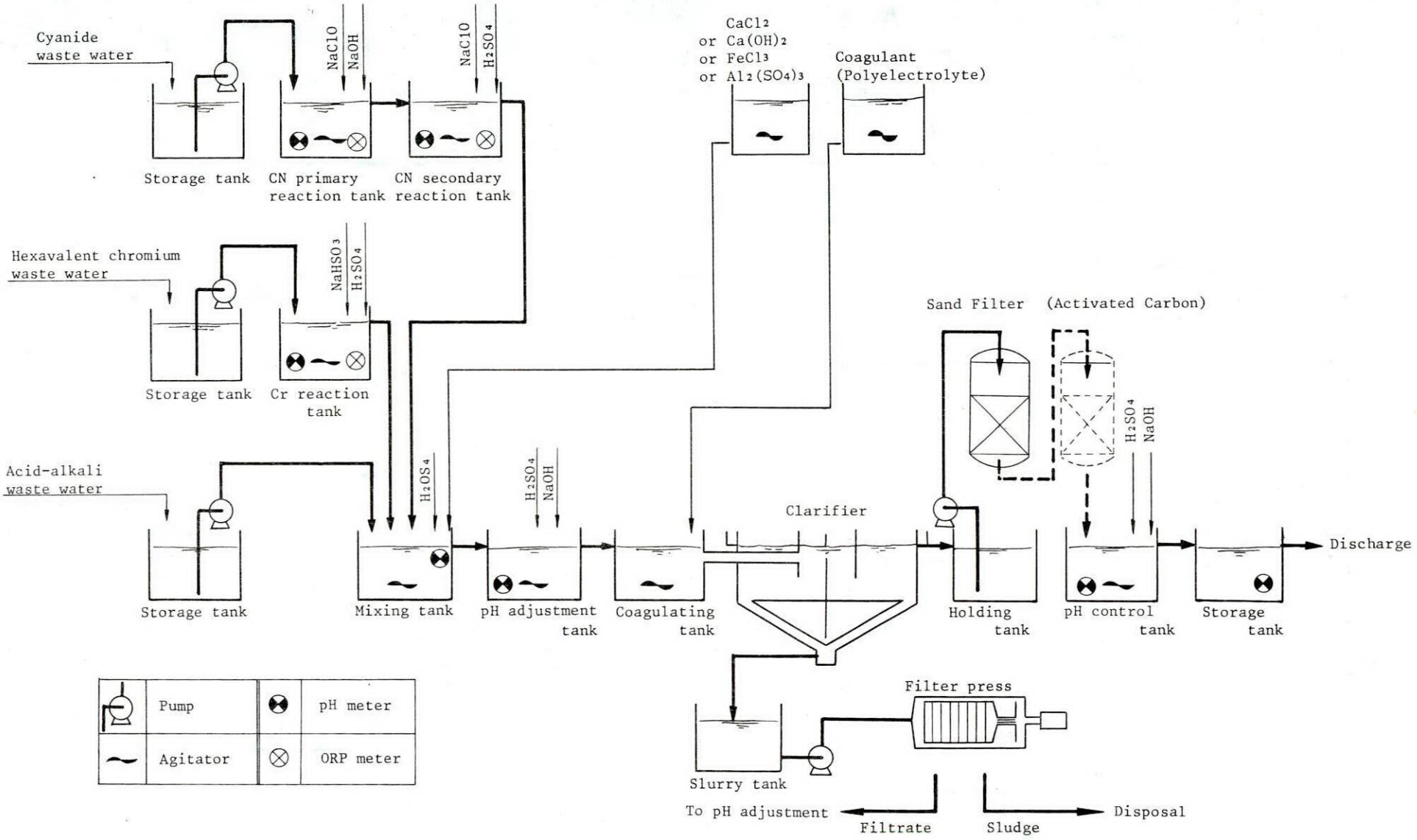


Figure 1 Flow Diagram of Wastewater Treatment System

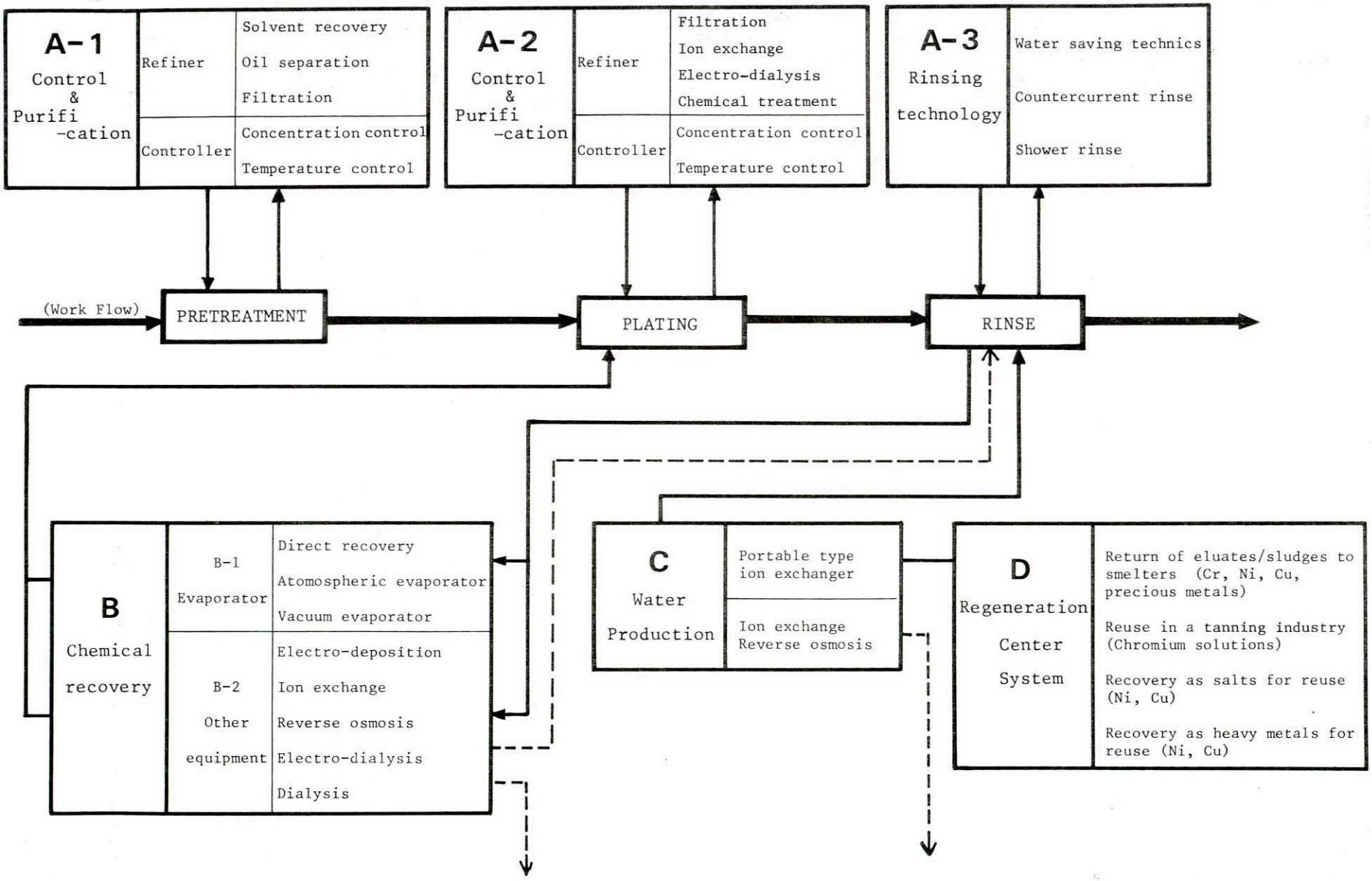
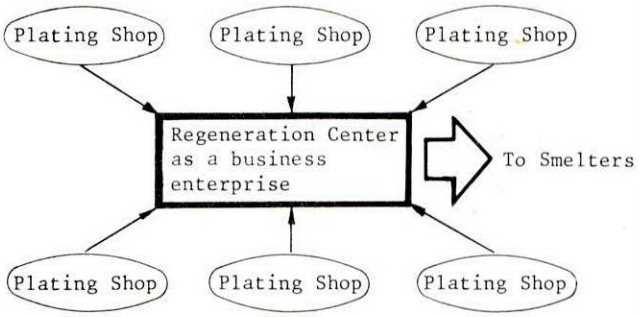
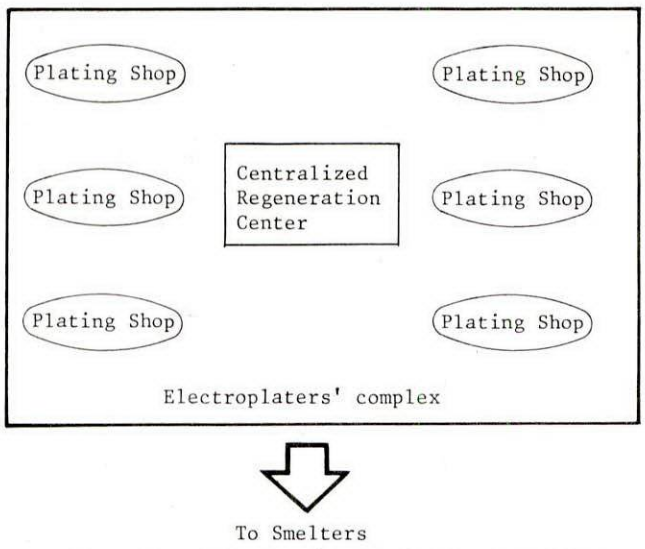


Figure 2 Recycling System at Plating Shops

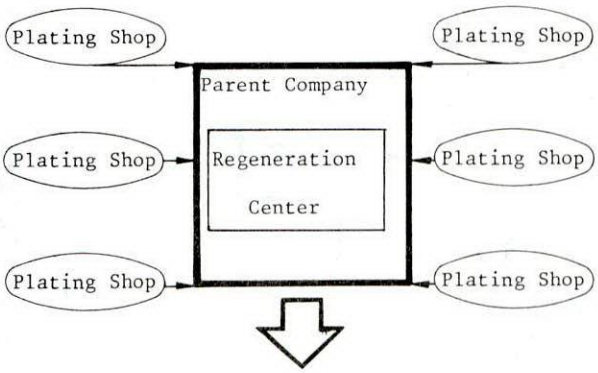


(1) Nation-wide scale
(2) Region-wide scale

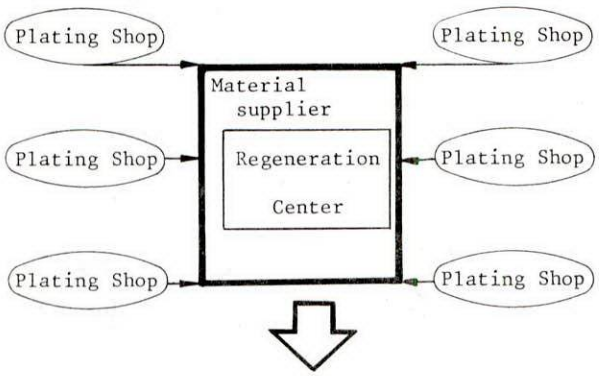
Type a. Business Enterprise Type



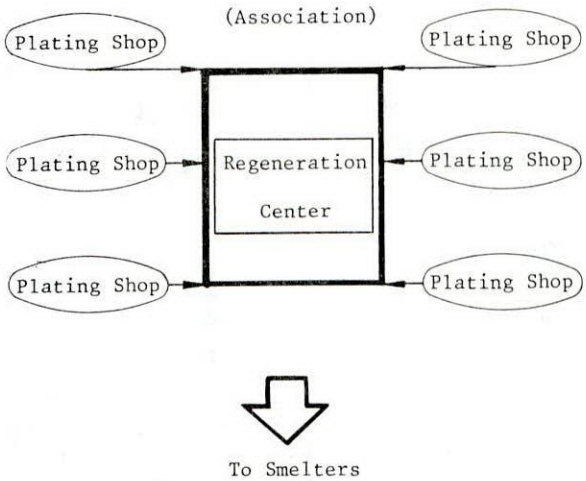
Type b. Electroplaters' Complex Type



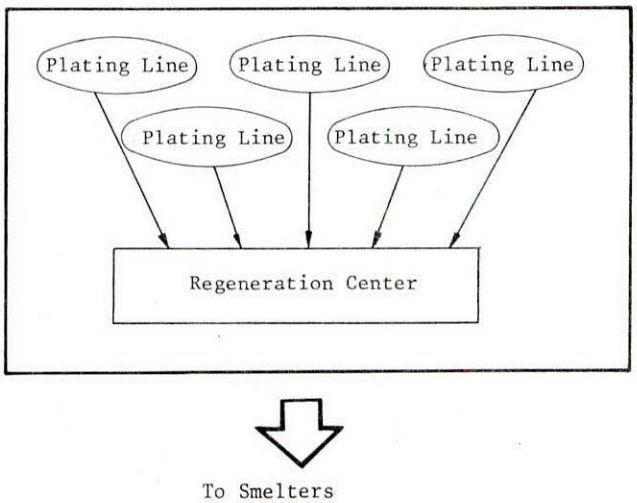
Type c. Parent & Affiliated Companies Type



Type d. Marketing Channel Type



Type e. Association Type



Type f. Factory-owned Center Type

Figure 3 Types of Regeneration Center

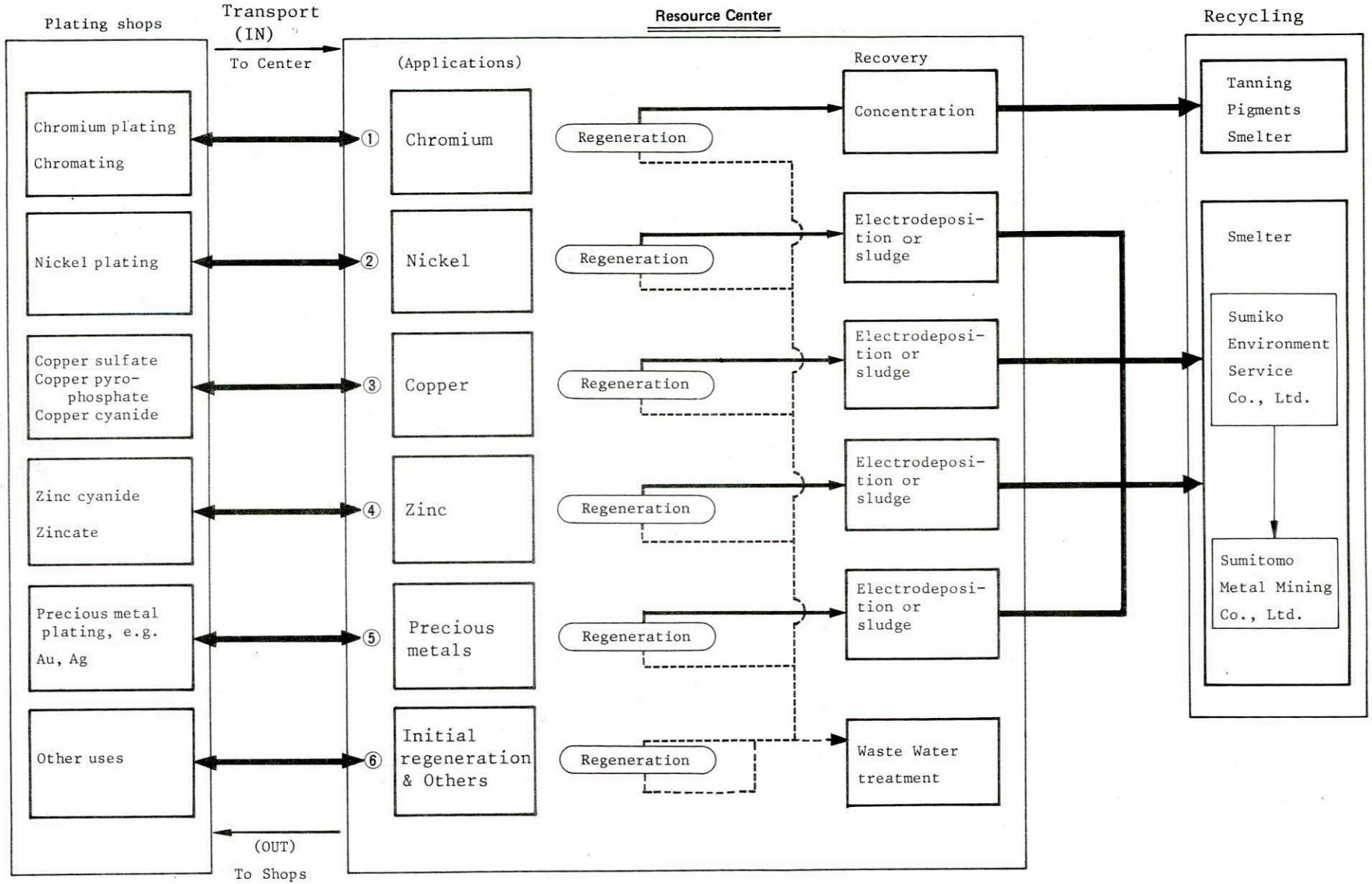
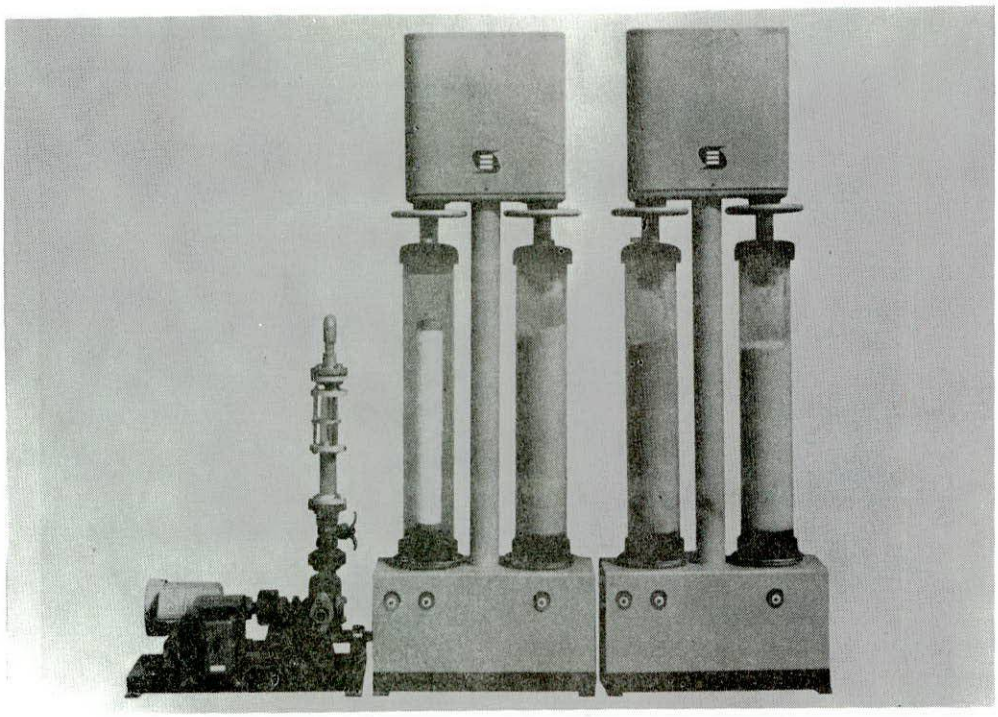
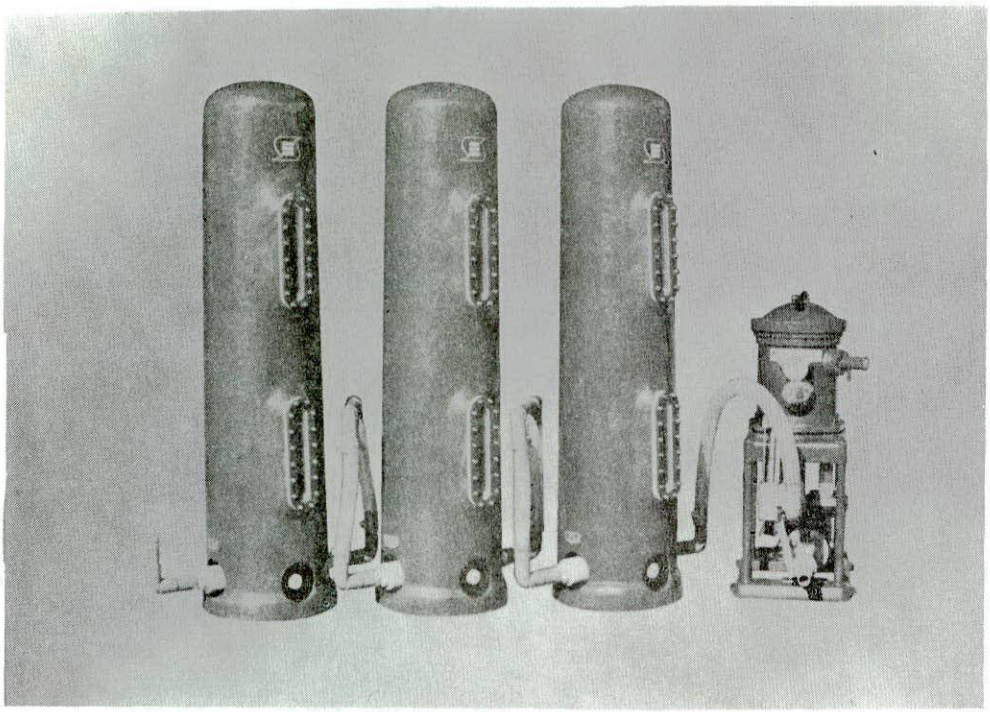


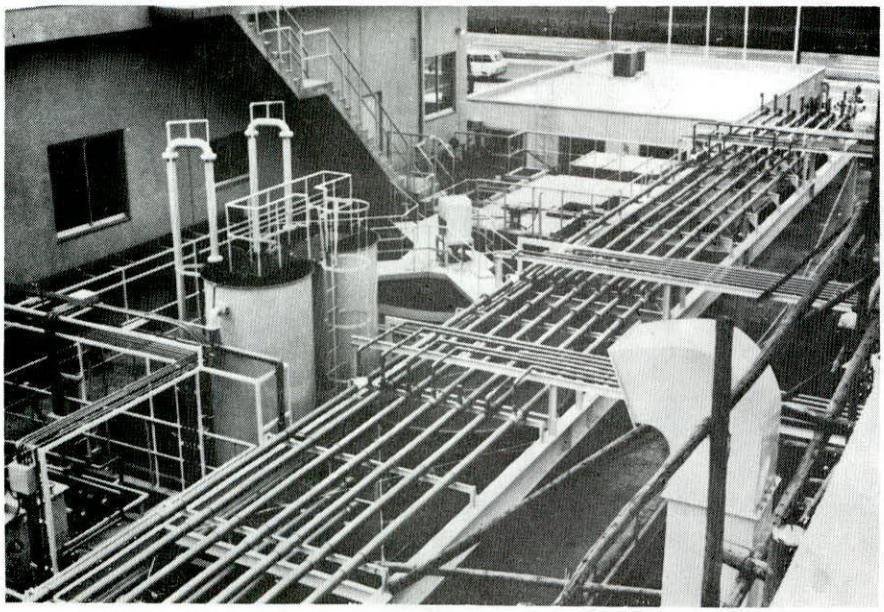
Figure 4 General Idea of Resource Center System



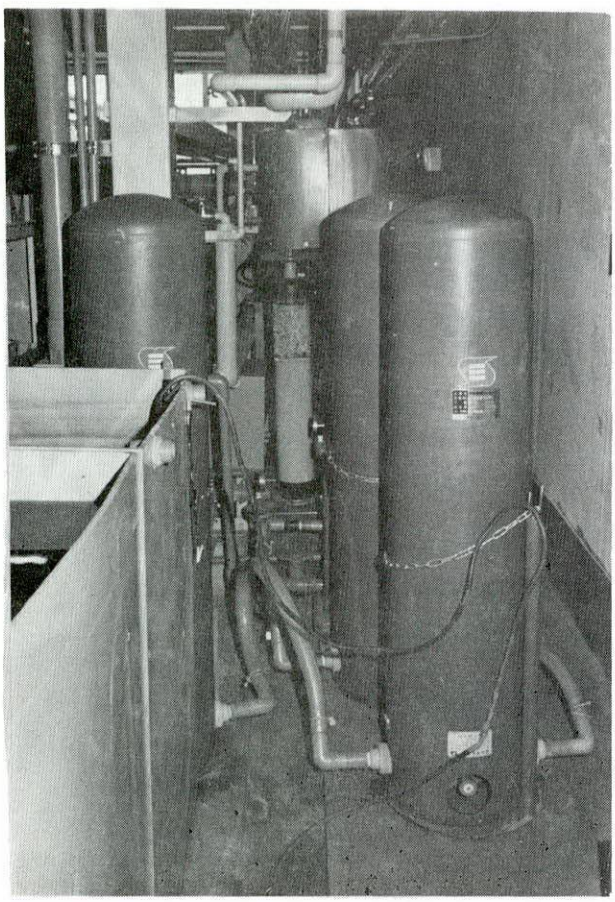
Ion Exchangers of Portable Type 5 liters Columns



Ion Exchangers of Portable Type 50 liters Columns



Chuo Electroplating Industrial Complex



Ion Exchangers of Portable Type

H-2

Environmental II
Session H

Plater Discharges to Country Club Stream

Richard J. Musil, CEF
National Mfg. Co.
Sterling, IL

Charles A. Forbes, P.E.
Lancy International
Zelineople, PA

PLATER DISCHARGES TO COUNTRY CLUB STREAM

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In June of 1983, National Manufacturing of Sterling, Illinois, decided to build a new plating department in a second plant located in Rock Falls, Illinois. The plating line was to be a large, fully automated rack machine capable of producing three different finishes, namely: nickel on steel hinges, nickel and brass flash on steel hinges, and zinc followed by chromate on threaded steel rod. The major drawback of the concept was that, unlike the main plant in downtown Sterling, no sanitary sewer was available at the Rock Falls location. In fact, the only option existing, if there had to be a discharge, was directly to a crystal clear stream which ran straight down the middle of a country club golf course.

Preliminary Design Considerations

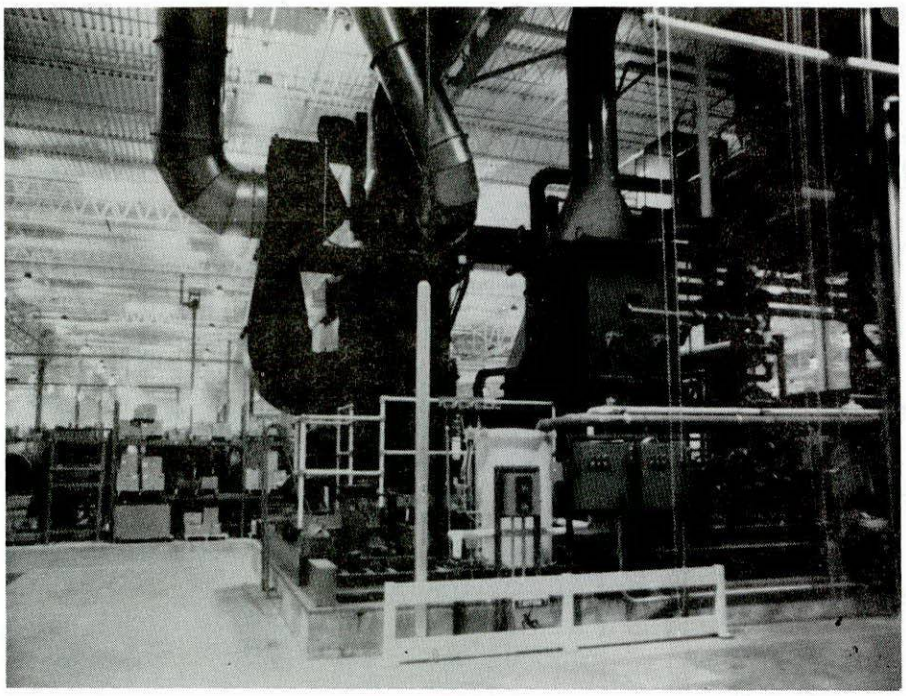
The first idea which was considered was the concept of "zero discharge." The best way to avoid the hassles and potential liabilities of a direct discharge to the environment is not to discharge at all. Present day "zero discharge" schemes were evaluated, but a number of flaws still existed in the systems. The unproven track record of these innovative ideas and the lingering problem of solids (salts) build-up in closed loop systems prompted us to look to another overall treatment scheme.

The second idea which we pursued was to look to the actual proposed plating line, use recovery technologies wherever possible and utilize conventional treatment for the remaining wastes.

If we would go to conventional treatment, it was further decided to add effluent safeguards, such as an advanced polishing system and final effluent holding tanks to catch the treated, polished effluent and test it before discharge. With this overall concept, we were as assured as possible that we would not damage the environment with any non-complying releases.

Atmospheric evaporative recovery was the chosen mode of treatment to handle some of the wastes coming directly off the proposed line. It was decided that, we would employ nickel and brass cyanide rinses since they had demonstrated at a number of facilities their ability to efficiently recover these chemicals. Atmospheric evaporative recovery was a good choice because of the simplicity of operation of the equipment and a good, proven record of consistent recovery. Also, nickel is very economical to recover by evaporation and the best way to deal with cyanide waste water is not to have to treat it at all. Both of these waste rinses were prime candidates for closed loop recovery.

Our experience with evaporative recovery on zinc chloride rinses produced some unfavorable results such as excessive foaming and equipment maintenance problems. We, therefore, decided it would be easiest to add this acid zinc effluent to the conventional waste treatment requirements.



Atmospheric Evaporation is a proven method for recovery of nickel and brass cyanide from dilute rinsewater.

Waste Material and Flow Minimization

Both waste water and waste material minimization techniques were utilized on the plating line. Four-stage counter current rinses were used after the nickel and brass cyanide baths to down size the evaporative recovery systems, maintain efficient rinsing, and minimize waste carry-over through the process. A deionization system was added to supply water to the rinses involved in the evaporative process to reduce unwanted natural salts build-up from the fresh water feed.

A three-stage counter current rinse system also followed the zinc plate and the chromate treatment. A three-stage counter current rinse system that followed the acid treatment was in turn counter flowed over to another three-stage counter flow rinse system following the caustic cleaners. Air knives were designed right into the plating rack hoist system which directed air flow downward on the racks to blow down dragged out material as the parts were raised from the tanks. At the same time, top sprays were utilized to wash down the racks as they were lifted from the baths. The result of all these minimization efforts was the need for only 120 gph evaporative recovery units and a total conventional treatment flow from a large plating line of only 12-14 GPM.

Conventional Scheme

After reaching a decision on the type of waste which would be treated and flow rate to a conventional treatment system, a general flow scheme was developed and equipment was investigated (ATTACHMENT 1). The general flow pattern involved catching the waste water in trenched, fiberglass tanks installed at the plating line. This waste water was pumped from the plating line through overhead piping to a treatment site approximately 300 ft. away.

At the treatment site the waste water, (containing zinc waste, acid-alkide waste, reduced chromate waste and final hot water rinse and some stripper rinse) was collected in a 6500 gallon cylindrical fiberglass equalization tank. Dual 20 GPM pumps, which could work combined @ 40 GPM or independently at 20 GPM, were set up to pump the waste water up to a set of fiberglass pH adjustment tanks with mixers, chemical feeds and probes designed for a maximum flow of 40 GPM. Two pH adjustment systems were used (both independently sized for 40 GPM) to assure a constant pH of 9.5 - 10 even with high pH fluxes of incoming waste water. From the pH adjustment systems the waste water continued to flow into a third, small fiberglass tank where polymer and recycled sludge would be added to create a good floccing situation. A variable speed mixer was planned for this flocculation tank so the speed of mixing could be adjusted to the flocculation process.

From the flocculation tank the flow is directed to an oversized 100 GPM clarifier which is an advanced design incorporating sludge blanket filtration and inclined tube modules for high rate separation combined in a minimal space design. Even though the whole system is designed for only 40 GPM, the clarifier was rated at more than twice the needed capacity to assure us of top quality, low solids effluent to the polishing filter.

The effluent continues from the clarifier to a 40 GPM advanced duplex filter system which utilizes sulfide treatment chemistry and media adsorption with the capability to further treat and polish the effluent to the highest possible quality; to meet even the most stringent stream discharge standards. (At this time we had no idea how strict the EPA would get with our discharge limits so we designed the best treatment capability which we could into the system). This polishing filter system has the ability to add just the minimal amounts of sulfide required as measured by an elaborate probe type controller. The filters in this polishing system have the expandable finger elements which are precoated with a proprietary media which enhances the polishing effect on the entire process. The sulfide chemistry, the adsorptive capability, and the proprietary precoat allow the system to respond to almost anything from slight chelate problems which may result with our stripper rinse water to any metals which escaped the conventional hydroxide precipitation.

The combined treatment and polishing system is designed to create a crystal clear effluent with metal concentrations below 0.1 PPM across the board. This system has definitely kept us in compliance with all of our stream discharge limits since we began treating in August of 1984. The

reasons for adding the specialized effluent polishing system were:

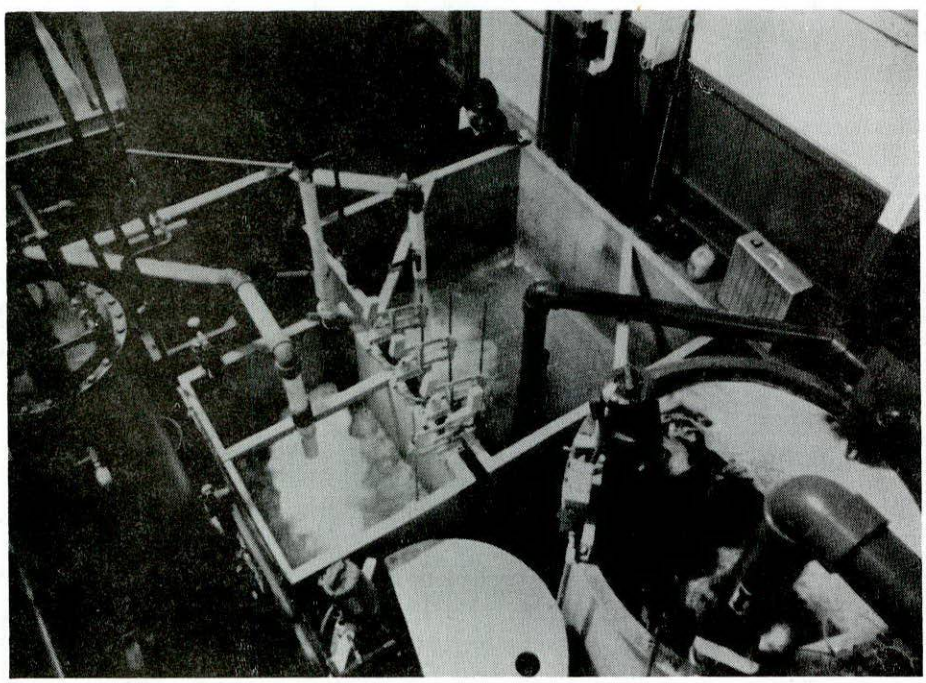
1. To assure us the lowest possible heavy metal concentrations in our effluent because of the very high quality of the creek we would discharge into.

2. The possibility of the creek going into very low flow at certain times of the year; which would require our effluent to be near pure stream quality.

3. To assure top quality effluent even if the clarifier fails to do its job completely or chelation comes into play.

4. To allow for even more stringent effluent limitations in the future.

5. To create good public relations with the community to assure them that this company has gone all the way to assure no harm will result from our discharges.



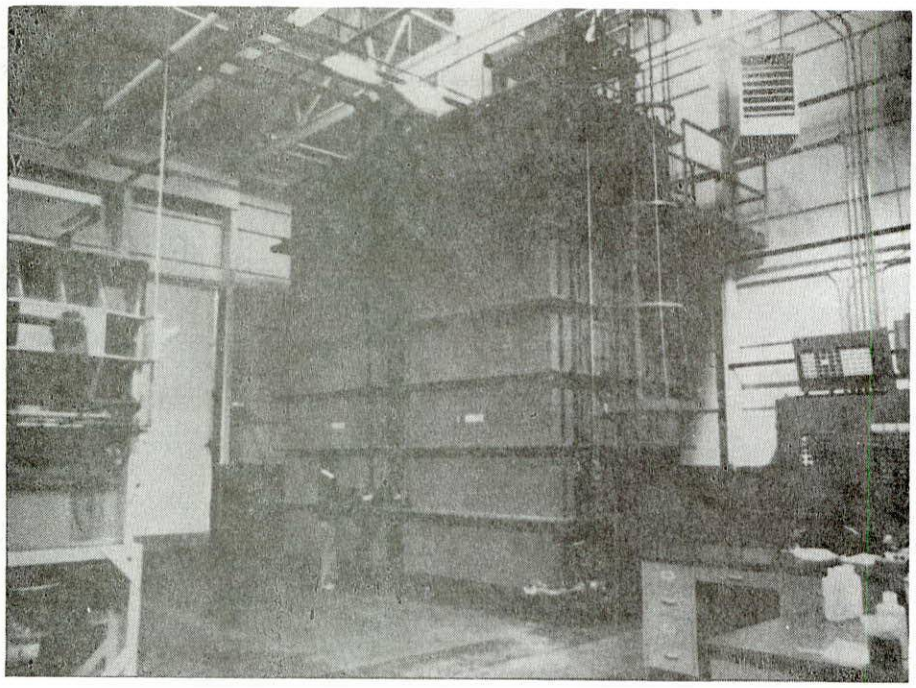
An elaborate effluent polishing
filter is an entire system in itself.

Then to complete the whole design, and in keeping with company management's demand for total assurance of effluent quality, the polishing filter effluent is adjusted to a neutral pH of 7 - 7.5 and discharged into one of two 8000 gallon holding tanks. A sample from every batch of treated water is fully tested for total compliance. Discharge to the creek will not

occur without direct authorization from the control laboratory. Even after the order to discharge is completed, the operator must open two valves--one electric, one manual, before water will be released. This makes the operator think just a little longer about what he is doing.

If, on the other hand, the effluent in these tanks is "off-spec," the order is given to retreat. At this point, pumps connected to these final holding tanks will pump back the "off-spec" effluent into the system for further treatment.

National Manufacturing Co. is committed to preserving our Rock River Valley environment, and has gone to the limit with this system to get as close to 100% assurance of direct discharge compliance as possible. We were just not satisfied with a conventional continuous discharge system because when a composite sample is analyzed from the previous day's operation the release has already occurred, good or bad. With the safeguards designed into this system, after the fact testing of a bad discharge cannot occur.



Ultimate Control -- "all" treated water is caught and held, sampled and tested "before" any discharges can occur. "Off-spec" effluent is recycled back into the system for further treatment.

Solids Handling

The solids handling system consists of a 1600-gallon sludge-thickening holding tank, with an automatic sludge pumping system. The pumping system has one pump to recycle sludge "for seeding" back to the flocculation tank and another to automatically periodically pump sludge from the clarifier to the holding tank to be dewatered. There is also a 10 cubic foot capacity filter press. In addition, seven 3-cubic yard dump boxes collect and store the dewatered sludge until a transportation load size of 20 cubic yards is reached. At this point, the dumpsters are emptied into a truck and hauled off to a secure landfill site.

Batch Treatment Scheme

The batch treatment system conists of a 2000-gallon fiberglass tank to hold cyanide wastes, a 2000-gallon fiberglass tank to hold concentrated acid-chromate wastes, a 4500-gallon fiberglass tank to hold concentrated alkali wastes and a 2000-gallon fiberglass tank with a decant pipe and mixer to batch treat any waste. All tanks are vented with the exception of the alkali hold tank. All tanks are also air agitated. (In addition to high pressure air supplied by the main plant, the treatment system has its own low pressure air system).

The purpose of this batch treatment system is two fold. One purpose is to act as a back-up treatment in case the evaporators at the plating line fail. (Pumping systems are set up for this type of situation.) A second purpose for this batch treat system is to independently treat concentrated wastes and keep them out of our dilute continuous treatment system. In this manner, concentrated wastes such as floor spills, filter clean-outs, acids and chromate batches can be treated, filtered through the filter press to remove the majority of the conentrated solids and have the remaining filtrate retreated in the continuous treatment scheme. It should be noted that the concentrated alkali wastes produced in this process cannot be treated in this system due to tests showing too high of a BOD for the creek to handle. The BOD of these wastes would go right through our chemical treatment plant and, could have caused problems in a concentrated sense. In tracking then with this idea, the alkali holding tank is merely a storage system. When the alkali reaches a certain level, it is pumped out into a stainless steel tank used to transport it to an outside chemical treatment contractor. Air diaphram pumps with stainless steel welded parts are used where possible to make waste transfers from tank to tank. The reason for using this type of pump is ease of operation and maintenance and consistent good performance.

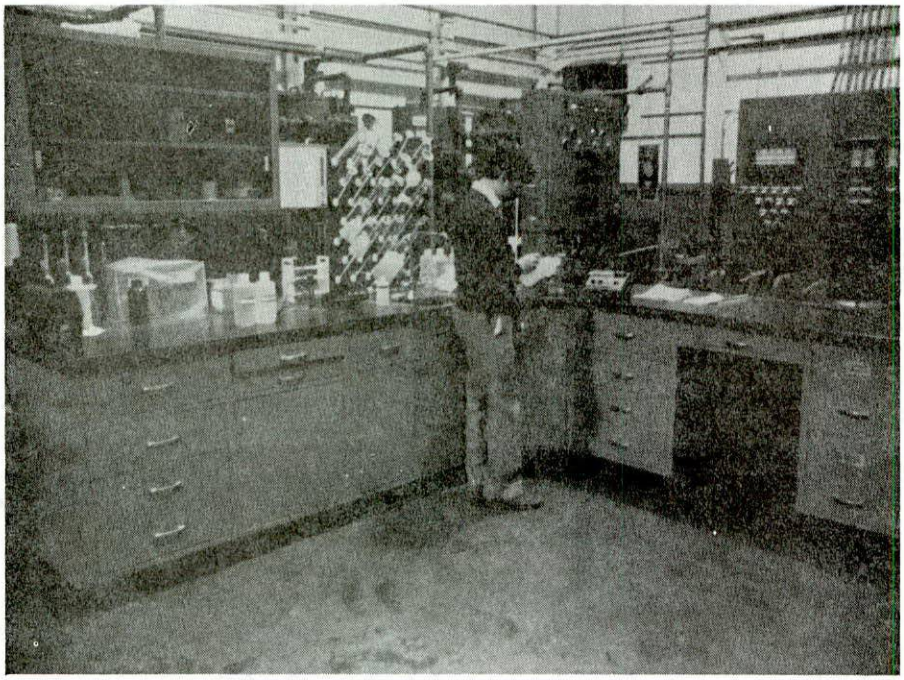
Process Controls

A variety of safeguards and controls have been designed into the entire process scheme. The main control panel contains a number of different control functions; including motor switches, tank level control indicators, pH meters and both audible and visual alarms. The entire system has its own independent microprocessor to coordinate all the various functions. In addition, the polishing filter and deionization system are also controlled by microprocessors. All of these microprocessors are tied into a small

central computer which transmits visual messages back to a CRT at the Sterling plant control lab. This allows us to also monitor the whole process during and after hours from an off-site location. Float-type alarm control switches have been installed throughout the whole process to function as alarms on sumps where liquid might collect, indicating high levels in tanks, and control pumps. All these small, independent alarm-control switches are also tied into the microprocessor in the main panel of the treatment plant.

In addition, there are visual indicator panel systems both in the waste treatment area and at the plater which light up in the event of an alarm situation and indicate to the operator what the problem is.

As for an effluent control, there is an on-site lab designed to do many preliminary analytical checks. Also, the main plant in Sterling has a control laboratory which is completely equipped with such advanced instrumentation as an atomic absorption spectrophotometer to do complete analytical checks according to approved E.P.A. methodology and N.P.D.E.S. requirements.



"On-site" laboratory control is a vital tool to optimum treatment operations.

The whole plating and treatment process is presently manned by one supervisor who splits his time between the plater and the waste treatment system. Future plans call for an additional plating line, and handling this additional load has been designed into the treatment plant capacity. When

the additional plating line goes into operation, we may plan to place a full-time operator in the waste treatment plant and add atomic adsorption instrumentation to the existing lab for quicker, more efficient on-site analytical control.

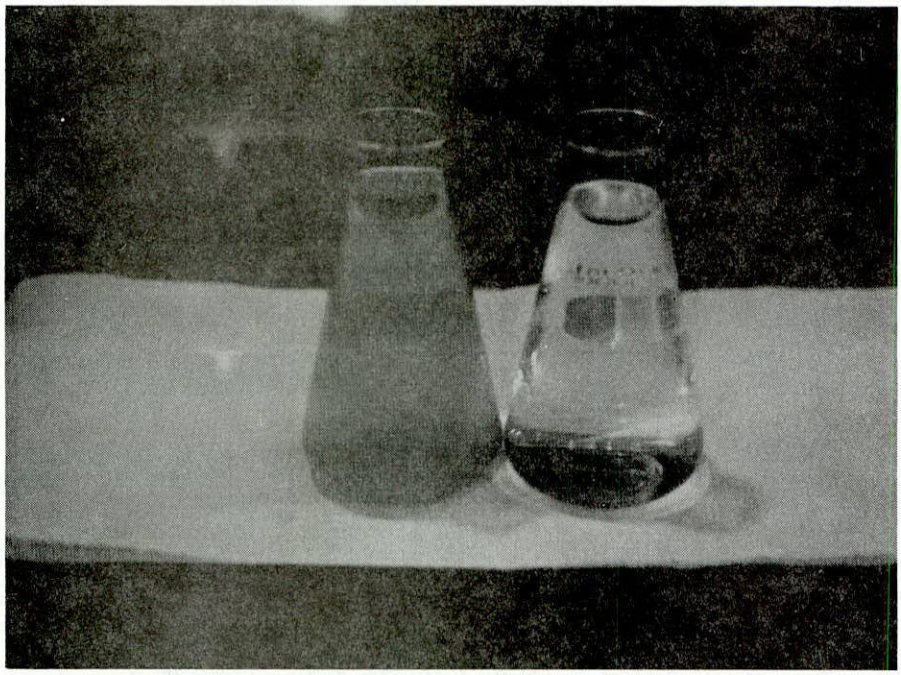
Miscellaneous Design Control Features

There are a number of miscellaneous design features which add depth of control to the whole system. The plating filter systems, which are situated next to the line, are all sitting in large steel diked trays to catch and contain any concentrated spills or leaks; keeping them away from the continuous treatment system. The entire plating line is totally enclosed in a diked area completely lined with acid resistant brick. All cyanide operations are independently diked and segregated. The entire treatment plant sits on a foundation which is totally diked, sumped in the center and alarm monitored. The entire plating line is ventilated with an extensive "push-pull" air system. The treatment plant building is also totally ventilated with large, wall-mounted ventilation fans and large electrically operated louvered openings which could add abundant fresh air, if required.

The hexavalent chrome reduction system was one of the last components designed into the system. National Manufacturing Company, along with a number of vendors, tried very hard to develop a trivalent chromate which would meet all of our plating needs. The attempt failed and a 10 G.P.M. system, consisting of a small fiberglass tank, mixer, ORP and pH controls, and sulfuric acid and sodium metabisulfite chemical feed tanks, was designed to be placed right at the plater. This treatment location was chosen because the treatment plant was already laid out and it was just as convenient to reduce the hexavalent chrome at the plater and let it transfer over to the treatment plant as part of the general acid-alkali wastestream.

Summary

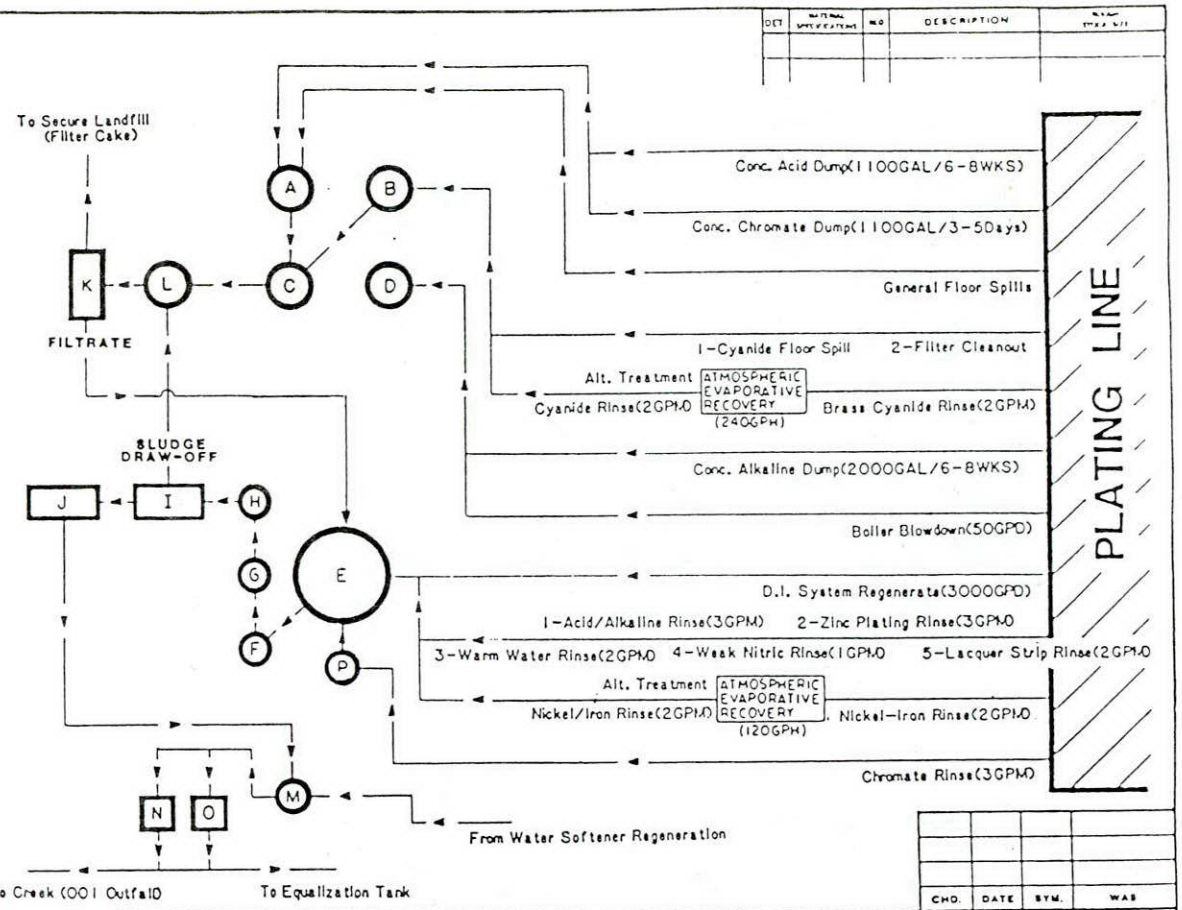
National Manufacturing Company has a long-standing reputation in the community for protecting the environment. What began as an idea in June of 1983 became a reality only 12 months later, including obtaining Corps of Engineers, air pollution and N.P.D.E. S. permits. Total environmental regulation compliance was achieved at a cost to National Manufacturing Company of about three quarters of a million dollars. It was a fast paced, concentrated, yet thorough effort by a company genuinely concerned in doing the proper thing. However, the considerable investment has paid off with a system which consistently meets all compliance standards for direct discharge to a natural surface water. (ATTACHMENT 2)



What comes in doesn't go out!
Note the crystal clear effect
of "polished" effluent.

--COMPONENT LIST--

A- ACID HOLDING TANK
B- CYANIDE WASTE HOLDING TANK
C- BATCH TREATMENT TANK
D- CONC. ALKALINE HOLDING TANK
E- EQUALIZATION TANK
F- pH ADJUSTMENT TANK
G- pH ADJUSTMENT TANK (BACK-UP)
H- FLOCCULATION TANK
I- CLARIFIER
J- POLISHING FILTER SYSTEM
K- FILTER PRESS
L- SLUDGE HOLDING TANK
M- FINAL pH ADJUSTMENT TANK
N & O- FINAL EFFLUENT HOLDING TANKS
P- CHROME REDUCTION TANK



DET		NO	DESCRIPTION	

CHD.	DATE	SYM.	WAS

NATIONAL MANUFACTURING CO.
ONE FIRST AVE. P.O. BOX 577 STERLING, IL 61081

TOOL NAME: LINE FLOW DIAGRAM

TOLERANCE		
.000	±	
.00	±	
.0	±	
ANGULAR	±	

DRAWN: CAVE TRUEBLOOD — DATE
CHECKED — DATE
SCALE: NA
A | B | C | D | E
SHEET OF

PRODUCT NUMBER: BLDG 22
PRODUCT NAME: ROCK FALLS PLANT
PART NAME: WASTE TREATMENT
PART NUMBER: DEPT. 21
DWG. NUMBER: 5845 B

ATTACHMENT 1

ATTACHMENT 2

TYPICAL MONTH EFFLUENT DATA

(October, 1984)

PARAMETER	Average Effluent Concentration (PPM)**	N.P.D.E.S. Limits (PPM)
Total Chromium	- (.01)	1.0
Hexavalent Chromium	- (.01)	0.10
Total Cadmium	- (.01)	0.07
Total Nickel	0.02	1.0
Total Zinc	0.34	1.0
Total Lead	- (.01)	0.20
Total Copper	0.04	0.50
Total Cyanide	- (.01)	0.10
Total Suspended Solids	0.67	15.
Average pH	7.8	6-9
Average Flow (MGD)	0.010	-

* - ( ) denotes a less than.

** it should be noted that these concentrations were used without the use of sulfide chemistry and utilizing only the adsorptive precoat media in the polishing system. At present, it is planned to begin using the extra feature of the sulfide system and even lower effluent contaminant concentrations are expected.

H-3

Environmental II
Session H

Removal of Heavy Metals from Waste Streams with Novel, High-Affinity, Selective and Regenerable Media

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DeVoe-Holbein (Canada) Inc.
175 Bouchard Boulevard, Dorval, Quebec

REMOVAL OF HEAVY METALS FROM WASTE STREAMS WITH NOVEL, HIGH-AFFINITY, SELECTIVE AND REGENERABLE MEDIA

L.G. Neiringck and B.E. Holbein

DeVoe-Holbein (Canada) Inc.
175 Bouchard Boulevard,
Dorval, Quebec

Current Environmental Protection Agency regulations and impending rulings on effluent discharge and sludge disposal have forced industry to re-evaluate their processes in terms of their short and long term environmental hazards. The discharge of toxic heavy metals is by no means an exception, and has become subject to stringent guidelines and intense scrutiny by authorities. Although much of this type of pollution can be reduced through increased process control, and by new and more efficient techniques, these measures will never eliminate heavy metals from waste waters. Pollution abatement has thus become an immediate concern of virtually every industry where aqueous metal laden wastes are generated and discharged to waterways.

Since traditional methods of dilution and discharge of heavy metal wastes from industry are now regarded as unacceptable, there is a need to implement some form of waste water treatment technology. The technology must not only be effective in reducing metals to the required limits but must also achieve this goal economically. The metal finishing industry, according to available statistics[1], is responsible for about 57% of all metal discharged in effluents. A variety of waste treatment technologies have previously been utilized in the metal finishing industry [2] with varying degrees of efficiency for metal extraction, cost effectiveness, and potential long term benefits. This paper describes a recently developed technology the "DeVoe-Holbein Technology", which has been found to have distinct advantages over existing technologies for the treatment of certain waste waters arising from the metal finishing industry.

Development of the DeVoe-Holbein Technology

The DeVoe-Holbein (D-H) technology consists of a series of new and unique synthetic media (compositions) and processes for their use in the management of metal containing waste water. This technology grew from the basic research of Drs. DeVoe and Holbein, both biochemists specializing in metal metabolism of biological systems. Using biological metal sequestering mechanisms as models, DeVoe and Holbein began in 1980 to create synthetic mechanisms which would accomplish similar high efficiency metal extraction. The end result was a non biological product designed to be as selective and efficient as those utilized by living cells to sequester essential metals.

A family of compositions has since been synthesized . Each composition

was designed to obtain the necessary degree of selectivity that is required in order to efficiently capture a metal or group of metals from aqueous solutions in the presence of competing metals.

Nature and Characteristics

All D-H media are relatively inert and insoluble materials. They are generally granular and irregular in shape with a particle size distribution which is dependent on the type of composition and nature of the intended application. A variety of inert support materials may be used depending on the application. All D-H compositions share certain characteristics which reflect the uniqueness. These characteristics are:

(i) Efficient Metal Capture

The D-H media demonstrate an effective metal capture efficiency of 99.9% plus and are effective for the treatment of effluents of both high and extremely low metal concentrations. Table 1 describes the capture efficiencies that can be achieved with actual complex industrial wastewaters. Efficiencies such as those described in the table are achieved both at the laboratory and field scale. High efficiency uptake is a very desirable quality when recovering highly toxic metals such as mercury or cadmium, and a mandatory requirement when treating radioactive metallic wastes. Additionally the very rapid exchange kinetics that are offered by these materials enables high efficiency capture at high flow rates (up to 50 bed volumes per hour). The ability to be effective at high flow rates gives these media a distinct advantage over other commerically available media currently used in industry.

(ii) Metal Selectivity

Many of the D-H compositions display high levels of selectivity for the metals or groups of closely related metals for which they were designed. This latitude of product selection permits design of water treament systems where only one or very few metals are removed during treatment. Other metals which may not pose hazard or which are of no economic value are simply passed through the system. Design simplification and operational economy are the result. Table 2 describes the high degree of selectivity that can be achieved with DH 573 treatment of a complex incinerator scrub waste water. With their high selectivity,DH media avoid the problems of saturation and interference from competing cations which can seriously limit the effectiveness of ion exchange materials and zeolites (see Figure 1).

(iii) Regenerability

DeVoe-Holbein media are regenerable. The metal is easily displaced in concentrated form from the composition with small volumes of regenerant (1.5 to 4 bed volumes). This feature coupled with selectivity offers a net volume reduction which can be orders of magnitude greater than existing technology. Following regeneration the composition can be reused without significant loss in efficiency or capacity. Table 3 describes the regenerative quality of DH 524 for hexavalent chrome extraction from a plating operation effluent. Unlike many traditional systems, the regenerant

TABLE 1

THE EFFLUENT CAPTURE OF SOME TOXIC HEAVY METALS USING DEVOE-HOLBEIN MEDIA

Source	Target Metal	Influent Concentration (ppm)	Effluent Concentration[1] (ppm)	Volume Reduction per cycle[2]	Capture Efficiency[3] (%)
plating effluent	Zn	1070	0.01	13	> 99.99
plating effluent	Ni	670	< 1.0	33	> 99.99
plating effluent	Cu	221	< 0.01	45	> 99.99
photographic effluent	Ag	10	< 0.1	1500	> 99.5
horticultural waste	Ag	20	< 0.1	500	> 99.5
plating effluent	Cr(III)	144	< 0.1	34	> 99.5
plating effluent	Cr(VI)	3.8	< 0.4	3000	> 99.5
cooling tower bleed off/ boiler blowdown water	Cr(VI)	694	< 1.0	21	> 99.5
high volume incinerator srub water containing trace heavy metals	Hg	(a) 0.9(ppb) (b) 100	(a) 0 (b)<0.001	(a) 252 (b) 117	> 99.5
contaminated groundwater	Hg	0.123	<0.001	254	

[1] Effluent concentration at or below normal detection limits using either radioactive tracer or atomic absorption determinations

[2] typically 100 cycles can be expected

[3] capture efficiency determined as % reduction in influent concentration; values are greater or equal to those shown due to detection limits of effluent metal concentration.

TABLE 2

Selevtive Removal of Mercury from Incinerator Scrub Water Effluent by DeVoe-Holbein Composition DH 573

Metal	Untreated [a] Influent (ppm)	Treated Effluent (ppm)
Hg	14.0	0
Mg	2.8	2.8
Sr	0.17	0.17
Si	33.7	34.1
Ca	2.0	2.5
B	9.5	8.0
Na	~63000.	~63000.

[a] pH of Influent was 8.3

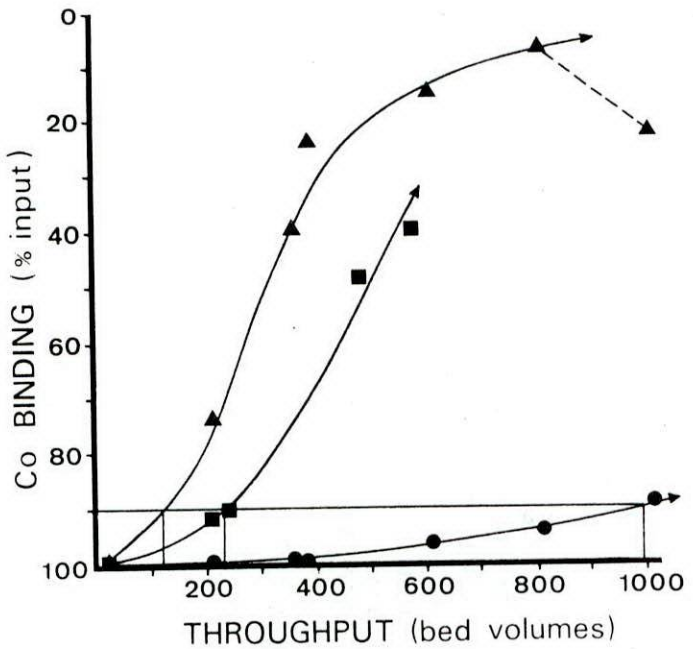


Figure 1
Removal of Cobalt (Co) from floor drain rad waste. DH 571 (●); strong cation exchanger (■); 4 and Co specific zeolite (▲). Rad waste chemistry: Na, 174 ppm; Ca, 91 ppm; Mg 23 ppm; and Co, 0.9 ppt).

used in the DeVoe-Holbein process can often be recycled thus reducing regenerant costs and further concentrating metals . The ease of regeneration affords some distinct advantages in the closed loop recovery of metals. Small volumes of regenerant containing concentrated recovered metal are readily available to either primary metal recovery, waste immobilization or secondary metal recovery as a mineral acid salt by-product.

TABLE 3

Regenerability of DH 524 for Hexavalent Chrome (500 ppm) Capture

Cycle	Residual Chrome in Effluent (ppm)	Capture Efficiency (%)	Capacity mg/cc of DH 524
0	< 0.1	>99.5	17± 1.5
1	< 0.1	>99.5	17± 1.5
10	< 0.1	>99.5	17± 1.5
60	< 0.1	>99.5	17± 1.5
100	< 0.1	>99.5	13± 1.5

pH of influent is 4.0

(iv) Capacity for Metal

Compositions have the ability to achieve high capacities before saturation occurs, while still maintaining high capture efficiency. The capacity of a composition for a metal at saturation, is dependent on the metal being captured, the composition being used, and the chemical make-up of the effluent. Typically, capacities are in the range of 5 grams to 30 grams of metal per kilogram of composition per cycle, or regeneration. As much as 60 grams of lead per kilogram of composition per cycle has previously been captured with a D-H medium.

(v) Mechanical Stability/Durability/Fouling

D-H media, because of the substrates employed, are resistant to relatively harsh treatments from acids and bases, abrupt changes in pH levels, temperature changes and high dose exposure from radioactive sources. These media offer good mechanical and dimensional stability, show no adverse aging characteristics and are readily sluiced during handling procedures. Furthermore these media offer excellent resistance to fouling by organic agents or soluble oils.

TABLE 4

Bed Volume (Litres of D-H Media)	L/D[a]	Metal[b]	Influent Concentration ppm	Effluent Concentration ppm	Flow Rate[c] B.V./h	Flow Rate[c] L/h	Capture Efficiency
0.002	1	Cr(III)	312	<0.03	25	0.05	>99.9
0.05	4	Co	0.9 ppt[d]	0.03 ppt[d]	50	2.5	99.
10.0	2	Ag	20	0.10	50	500	>99.
20.0	3	Ag	10	0.10	30	600	99.
25	1.1	Cr(VI)	500	<1.0	96	2400	>99.8
80	3.8	Cr(VI)	500	<0.05	19	1500	>99.9
140	2.5	Cu	500	<0.01	16.5	2300	>99.9

[a] L/D=length / diameter ratio

[b] target metal; often present in complex solution with potentially competing metal ions.

[c] typically maximum flow rates could not be attained due to mechanical limitations of the pump

[d] parts per trillion

THE DEVOE-HOLBEIN PROCESS

DeVoe-Holbein media are used in a manner not unlike classical ion exchange (see Figure 2) . The media is contained as a fixed bed and the metal laden solution is passed through the media during the service cycle. As the solution travels through the media, the metal is captured. Saturation of the media with metal occurs from top to bottom. Following complete saturation of the media, the bed is backwashed and the metal can be displaced by passing the appropriate regenerant through the media in the same direction of flow as the service cycle. This sequence would then be the equivalent of a co-current fixed bed ion exchange system. For reuse the D-H media would be rinsed, conditioned with an appropriate reagent and finally put back into service. Counter-current fixed bed systems have also been employed, but with limited value added to the DH metal extraction process for base metals.

Scale-up testing from the laboratory scale has involved the use of a variety of fixed bed dimensions. The results from some of these tests are desribed in Table 4, and indicate that column dimensions (length: diamter) are not critical to the performance of the media significant pressure drops can result when length: diameter ratios and flow rates are high. Since the DeVoe-Holbein process does not require a high pressure process, care must be taken in the sizing of the bed.

A typical and basic D-H system would utilize commercially available valves, fittings, piping, and controls as well as vessel with regeneration control valve head. Some design parameters are:

1. Robust construction, as exemplified by a plastic-coated steel vessel, glass-filled engineering plastic control head containing no motor driven parts, and diaphragm actuated, pilot operated valves.

2.Convenient field adjustments and servicibility. Routine maintenance, adjustments and rebuilding would be performed with simple hand tools without disturbing piping. Replacement costs as a percentage of capital costs would be extremely low.

3. Microcomputer - based automatic controls could be easily integrated with the system.

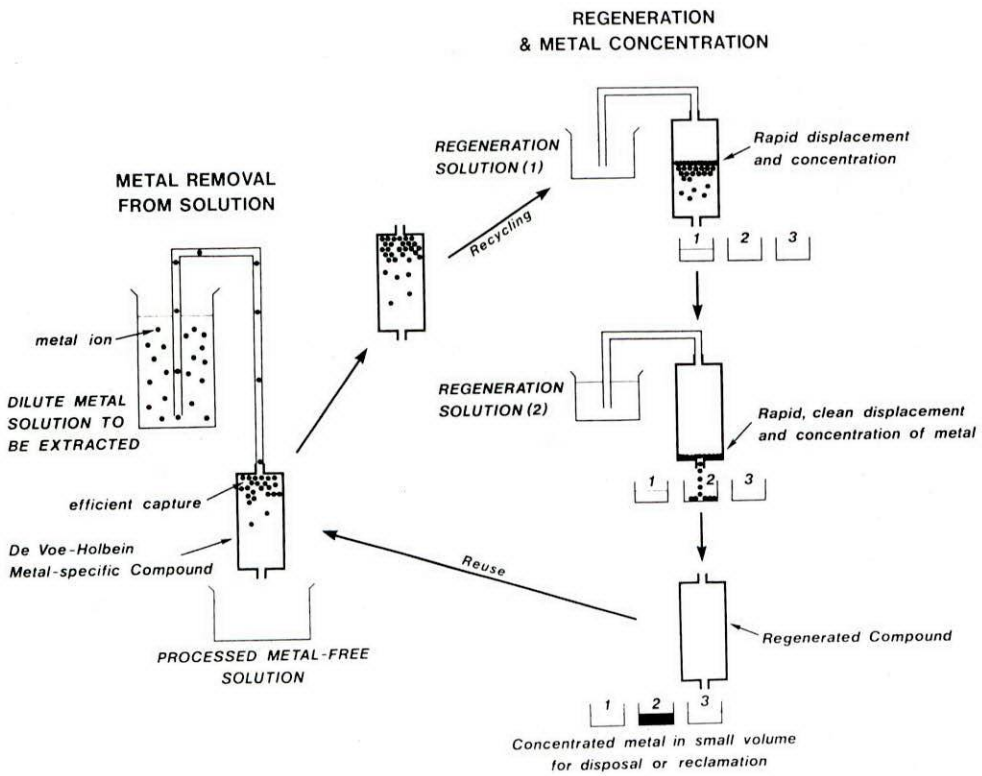
The basic system can easily be expanded to include several vessels in parallel or in series . In the latter case vessels may contain media of differing selectivity which allows sequential recovery of a single metal from a complex solution of metals.

UTILITY OF D-H MEDIA IN THE METAL FINISHING INDUSTRY

The utility of D-H media has previously been described for nuclear [3],[4] as well for some non-nuclear applications [5]. Emphasis, in this report, has been placed on the usefulness of these media for the extraction of metals from effluents being discharged by the metal finishing industry.

Figure 2

The DeVoe-Holbein Process for Metal Capture and Recovery



D-H media have been used to capture and recover both positively charged metal ions (cations) such as Ni++ or Zn++ and negatively charged metal ions (anions) such as Cr(VI) from a variety of metal plating waste effluents. Typically the media used for plating waste streams are relatively non specific and are used to treat rinse waters prior to their integration with other streams arising from the same plant. The treatment of final plant effluents is less attractive from a technical point of view, due to, the complexity of these streams, the hourly fluctuation in chemical make-up, and the potential of premature saturation of a bed with a metal (s) which are not considered hazardous.

A variety of plating rinse waters containing either zinc, nickel, copper or anionic chrome have been successfully treated with D-H media and the results are described for some of these in Table 1 of this report. The residual metal content of the effluent was in all cases, well below acceptable limits. In addition effluents containing trivalent (cationic) chrome, zinc phosphates or rinses containing more than one hazardous metal (Table 5) have been successfully treated. The working pH range for D-H media useful for anion extraction is from about 1.0 to 10.0 with an optimum capture efficiency at pH 4.0. For cationic species the range is from 2.0 to 11.0 with the optimum efficiency range being 5 - 9.

Cyanides are still widely used in the plating industry and are found in rinse waters as complexes with the metal intended for plating. Two of the most common are cadmium and zinc cyanide baths. The D-H media used for metal plating rinse waters have shown relatively low capacity but high efficiency for such cyanide complexes. This low capacity can be overcome by subjecting the cyanide to a destruct process. Following the oxidation of cyanide with chlorine using a batch method both cadmium and zinc were captured with very high efficiency (99%) and with capacities in excess of 12 grams of zinc or cadmium per litre of D-H media. Effluents bearing silver complexes such as thiosulfate or cyanide complexes do not require destruction of the cyanide or complex prior to extraction of the metal from solution. Using a selective and regenerable D-H media the silver can be efficiently (99.99%) removed from solutions to concentrations less than 10 parts per billion. Although the capacity of this medium for silvers is somewhat dependent on the nature of the effluent, capacities as high as 20 grams of silver per litre of media have been realized.

TABLE 5

Capture of Copper and Nickel from a Nitric Acid Rinse Water Using D-H 558

Target Metal	Influent Conc. (ppm)	Effluent Conc. (ppm)	Capacity Bed Volumes
Copper	381	0.5	14.0
Nickel	316	0.24	12.1

pH of influent was 2.2

Although iron can be found in many different types of plating wastes streams, this metal is not toxic and has little value attached to it. Iron does however present itself as a problem in the plating industry as a contaminant of plating and pickling baths. Iron gradually builds up in these baths to the point where their contents must be either partially or completely replaced with fresh chemicals. A D-H medium, which was designed specifically for very high efficiency iron capture has been found to have utility in the capture and recovery of iron from mixtures simulating electroplating baths. For example, Fe^{3+}, which is present at relatively low concentrations (50 - 500 ppm), could be selectively eliminated from a zinc electroplating bath solution formulation containing a second species of iron, Fe^{2+} (2,500 ppm), and zinc (61,000 ppm). This D-H medium proved not only to be highly selective at pH values as low as 1.5 but also highly regenerable under the conditions tested.

In conclusion, the novel media described in this report have application potential which could either complement existing technology or provide a unique alternative to existing waste treatment technologies.

References

1. EPA February 1982. Assessment of the Impacts of Industrial Dischargers on Publicly Owned Treatment Works. NTIS No. PB - 153958.

2. Cherry, K.F. 1982. Plating Waste Treatment. Ann Arbour Science Publishers Inc., U.S.A.

3. DeVoe-, I.W. and B.E. Holbein. 1983. New Technology for the High-Affinity Capture of Radioactive Metals from Water. 4th Annual Conference of the Canada Nuclear Society, Vol 2, P. 125.

4. Greer, C.W., D. Brener, E.N.C. Browne, I.W. DeVoe, B.E. Holbein and R.Ek. 1985. Vitrokele TM Compositions: Novel, High Affinity, Metal Selective and Regenerable Media for the Removal of Radioactive Metals from Aqueous Nuclear Waste Streams. In Press.

5. Holbein, B.E., I.W. DeVoe, L.G. Neiringk, M.F. Nathan and R.N. Arzonetti. 1984. New Technology for Closed-Loop Source Reduction of Toxic Heavy Metal Wastes in the Nuclear and Metal Finishing Industries. Proc. Mass. Hazard. Waste Source Reduction Conference. p. 66.

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Environmental II
Session H

RMA-Closed Loop Waste Water Treatment and Recycling System

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RMA-CLOSED LOOP WASTE WATER TREATMENT AND RECYCLING SYSTEM

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Currently, companies in the electroplating industry have to comply with new water discharge guidelines enforced by the Federal EPA as well as by local authorities dealing with effluent discharge.

Looking for methods of waste water treatment, most of the available techniques are based on chemical destruction and precipitation of pollutants in the process water. Only a few plating companies operate a central ion exchange system for the purification and reuse of their rinse water.

All these so called conventional waste water treatment systems generate a sludge that has to be disposed of in EPA approved sites which are quickly becoming scarce. Alternative waste water treatment systems should enable the operators to recycle the waste water and valuable chemicals and to recover metals in order to get rid of the sludge problem.

The RMA-system (recovery of metals from waste water) offers all companies of the electroplating and printed circuit board industries rinse water purification combined with the reclamation of metals by means of ion exchangers. This system was started in 1979 as a pilot project in West Germany, sponsored by the Federal Ministry for Research and Technology. About sixty plating companies were connected to a special service company, which handled the waste control problem. During this project, the first central recovery facility (CRF) was founded.

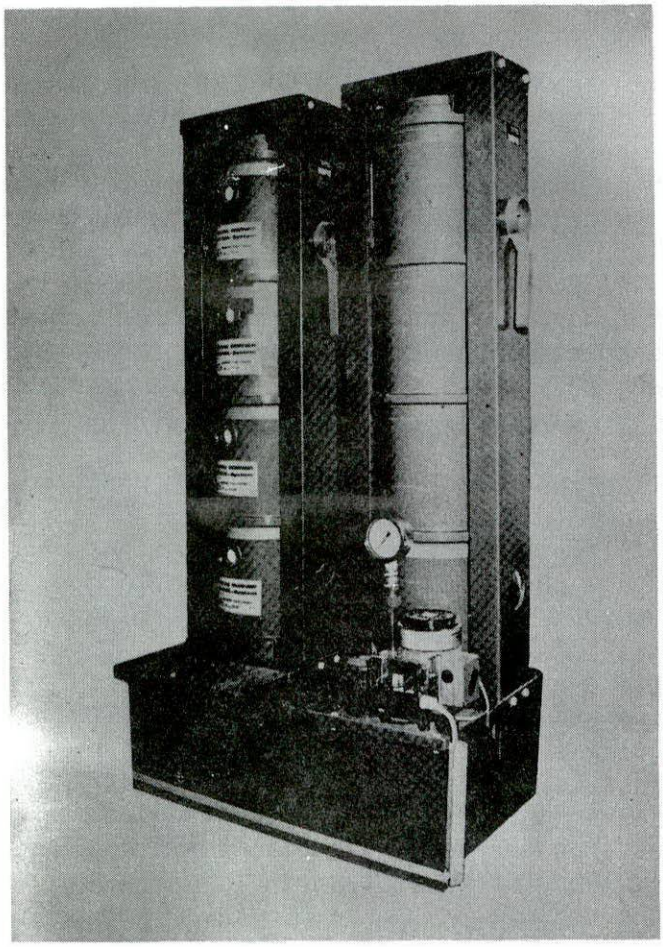
A company with a large electroplating facility located in Minneapolis, MN, installed an RMA system following an exhaustive study of all available systems. Because there is no CRF present, this company built their own regeneration and recovery plant.

Description of the system:

The RMA System utilizes a column, or series of columns, each consisting of four cartridges or cannisters containing a resin through which water from a rinse tank is pumped to absorb metals as well as non-metallic substances (see picture No. 1).

The number of columns required for the resins to absorb the metallic and non-metallic substances and return deionized water to the system is governed by the flow rate of 0 ÷ 6 gallons per minute pumped through the cannisters. Thus, it is a retention time in the cannisters that determines the purity of the water at the discharge point.

To be assured of good deionized water, the flow rate in the single column can be no greater than 3 gallons per minute. A second column would permit increasing the flow rate to 6 gallons per minute and a third column would accommodate 9 gallons per minute.



Picture No. 1: *RMA columns*

Two basic types of resin are used for the ion exchange: a cation resin to absorb the metals and a anion resin to absorb the non-metallics.

In addition, there is an indicator resin which can be observed through a window in the cannister. The indicator resin for the cation resin changes from brown to red when the cannister is loaded. The indicator resin for the anion resin changes from blue to creamy-white.

The basic resins, unlike the indicator resins, do not change color and may be used over and over again.

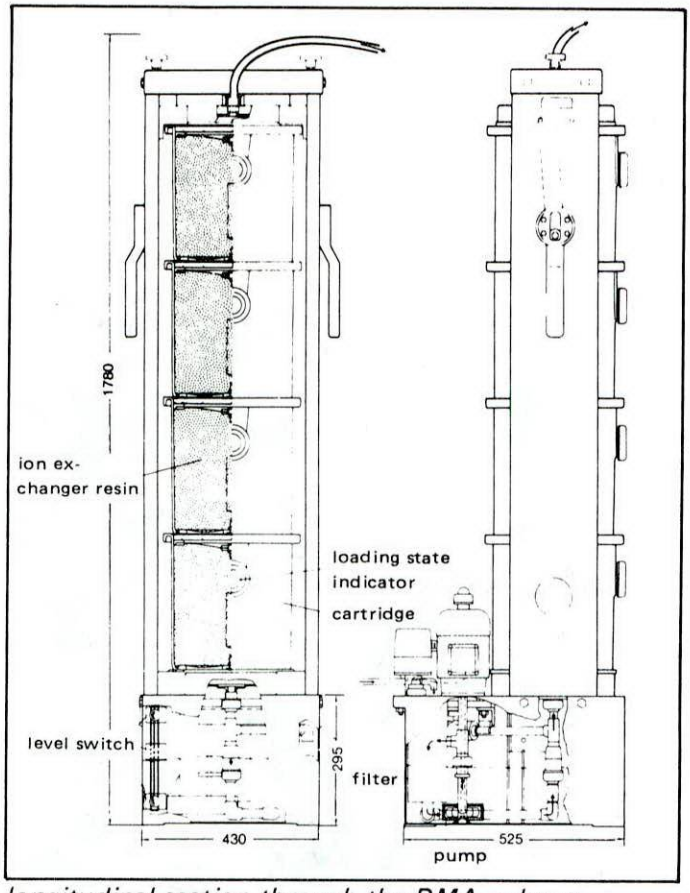
Using a single column as an example, there would be two cannisters for the cation resin and two for the anion resin. In each case, the bottom cannister would become loaded first and removed for regeneration. The top cannister would take its place and a regenerated cannister would be added.

Assuming the metals are to be reclaimed, a column (or columns) is required adjacent to the rinse tank for each metal. If the metals were mixed within the same cannister they would not be reclaimable.

The resins in the cation cannisters are regenerated by running an acid

(sulphuric acid or hydrochloric acid) through the cannisters to dissolve out the metal.

Regenerating the anion cannisters results in sodium salts being formed (sodium chloride, sodium sulphate, sodium acetate, etc) and they may be discharged down the sewer.



Picture No. 2: *longitudinal section through the RMA column*

The regenerants can now be used as:

- metal sulphate solution (i.e. Nickel, Copper) to replenish the plating baths.
- chromate solutions for the recovery of chromic acid.
- bulk solutions for the electrolytic metal recovery.

The other effluents, coming from the plating lines, can be treated as follows:

- rinse waters from acids, activators, cleaners can be mixed in a neutralization tank, pH-adjusted and discharged into the sewer.

- dump solutions (pretreatment baths, plating baths) should be collected and detoxicated in a batch treatment tank (i.e. cyanide oxidation).

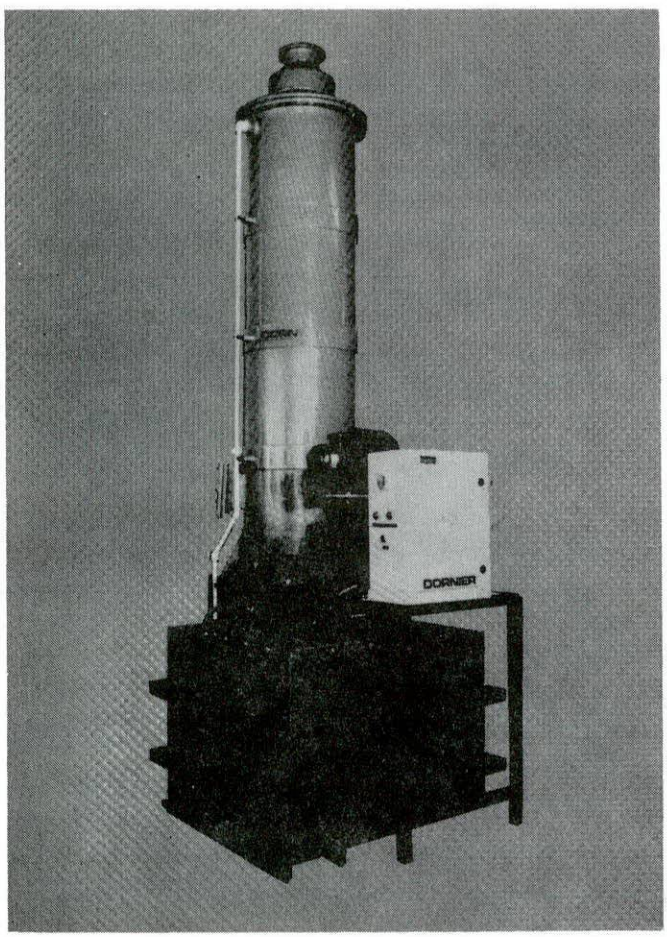
- solutions from rack strip tanks can be used for the electrolytic metal recovery.

All metal containing regenerants and metal precipitants generated in the batch treatment process can be used for the electrolytic metal recovery.

The flow scheme of the RMA-Closed Loop System is shown in picture No. 4.

In addition to the rinse water treatment, the RMA-system takes care of stagnant rinses containing diluted plating solutions.

A special spray tower was developed (see picture No. 3) that works on the principle of evaporation, with ambient pressure and a feed temperature of



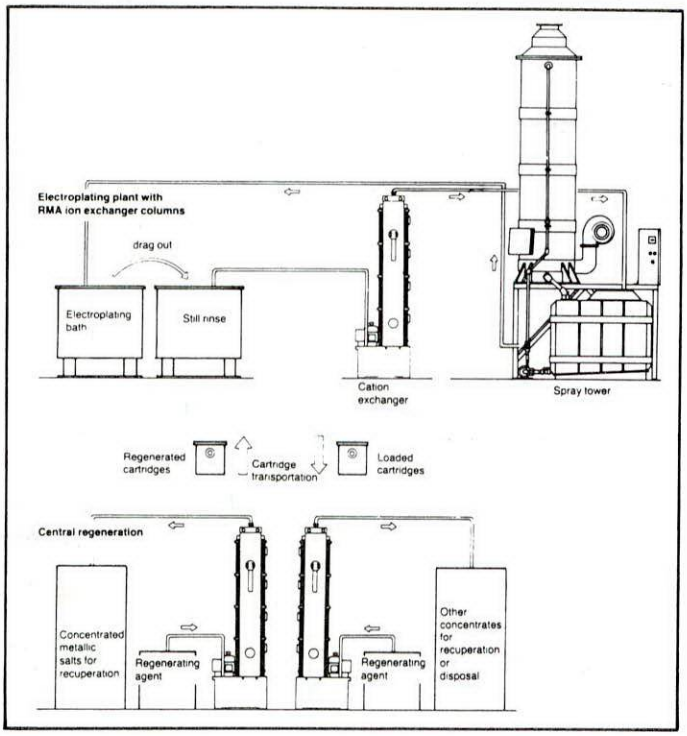
Picture No. 3: *Spray tower RT 500*

140° F for the solution to concentrate. From a storage tank in which the heating system is installed (electric heating coils or heat exchanger for water/vapor heating) the solution is pumped to the top of the tower onto a

spraying system. Via a packing column, the solution trickles to the bottom of the column and from there back into the tank.

By means of a blower, air is blown in the opposite direction, i.e. from the bottom to the top, through the packing where it is saturated with water vapor. A demister separates the droplets still included in the exhaust air.

The components (blower, packing, piping, pump, heating coils, etc.) are all made of appropriate plastics to assure resistance to chemicals also under higher loads. A temperature control with overheating protection guarantees that the given operating conditions are observed.



Picture No. 5: *Functional diagram of the RMA-system*

The spray tower works in batches, i.e. after filling or filling up of the storage tank, the solution circulates until the requested concentration level is reached (see picture No. 5).

The spray tower, 126 in. high (up to the exhaust air flange), needs only a basic surface of about 51 in. x 41 in. Mounting is extremely simple. In addition to an electrical connection (20kW), only an exhaust air tube (flange connection DN 150) must be mounted.

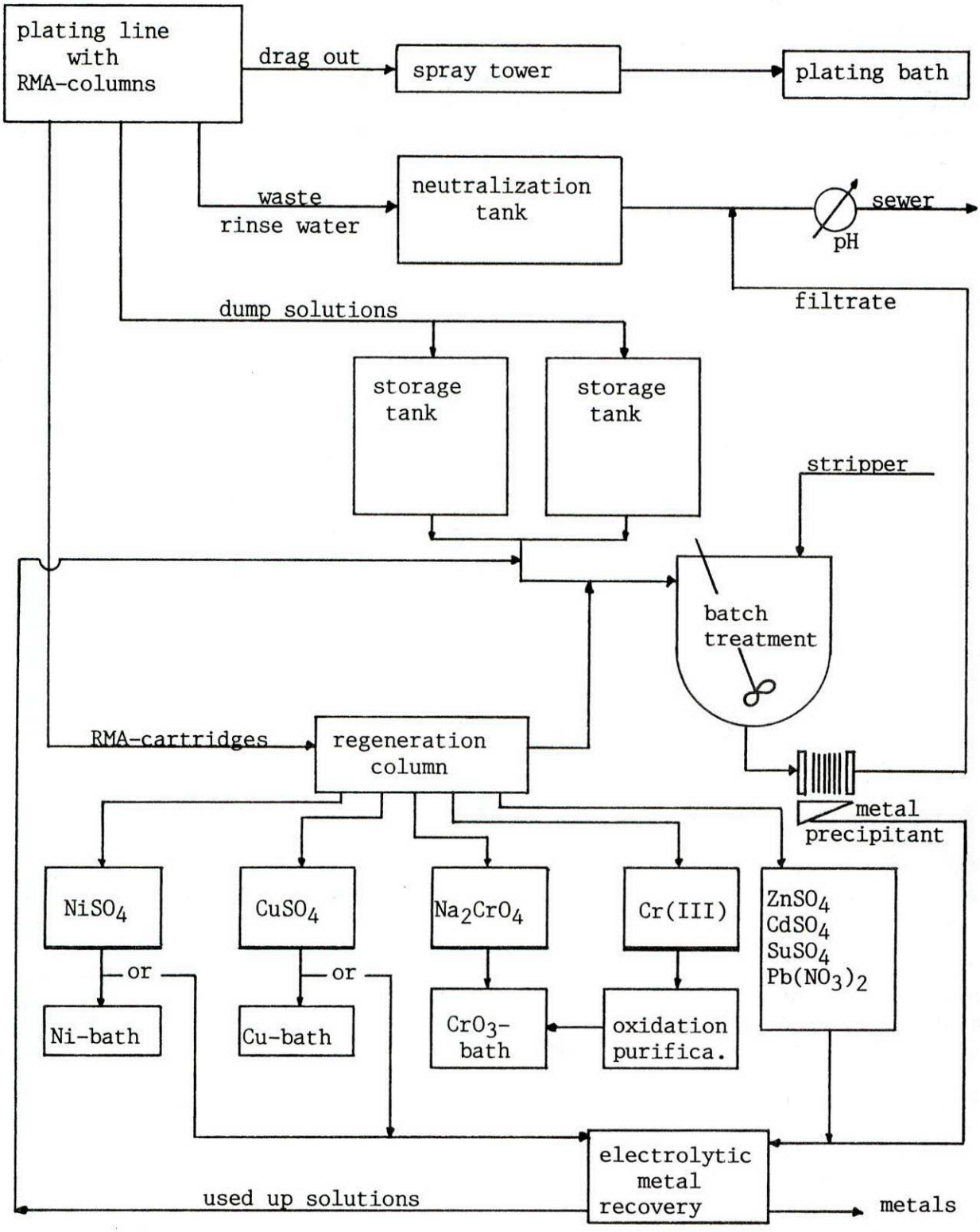
Primarily, the RMA-system can be used for the following processes:

- reclamation of metals in a central facility of a service company (see picture No. 6).

- reclamation of metals in a regeneration and recovery plant of a plating

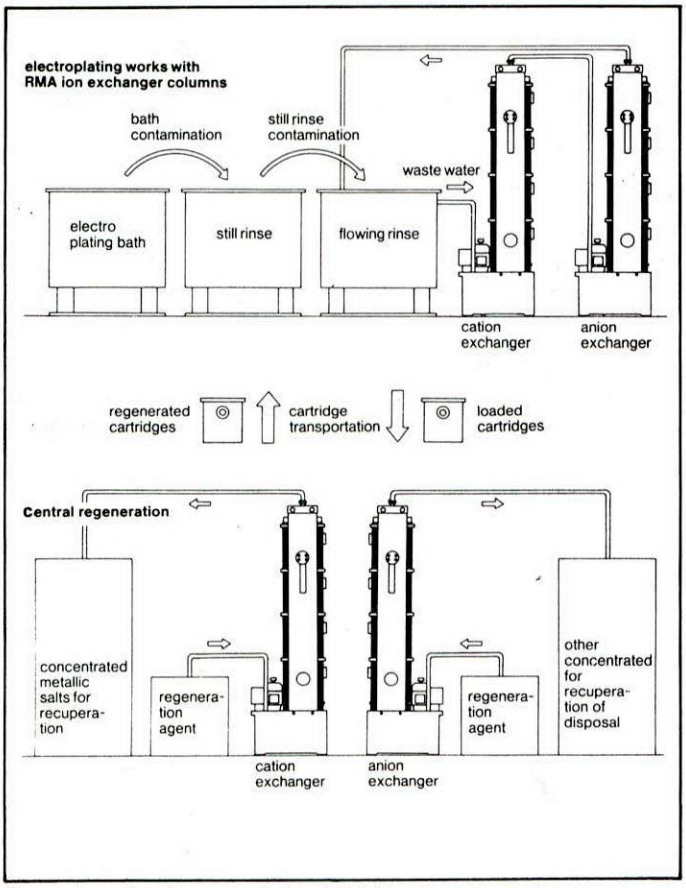
Picture No. 4:

Flow scheme of the RMA-Closed Loop System.



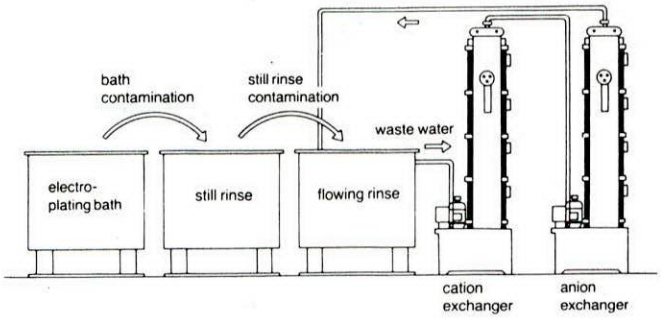
company.

° rinse water purification in plating shops for compliance of EPA standards.



Picture No. 6: *functional scheme of the RMA-system*

° rinse water circulation with ion exchangers (see picture No. 7).



circulation system for rinse waters

- water circulation system
- separate treatment of heavy metals (e.g. cadmium)
- metal recuperation

Picture No. 7:

- purification and recycling of plating baths in connection with an evaporative system.

- purification of chromate solutions for reuse.

- waste water detoxification in plating companies by elimination of pollutants (i.e. Cadmium, Cyanides, Complexes).

In contrast to conventional waste water treatment plants the system presents the following advantages:

- Modular design:
  - RMA columns can be connected to every plating line. This allows electrolytic metal recovery without mixed metal solutions.
  - If there is a change in the plating process (i.e. different plating baths or a new process sequence), the RMA columns can be integrated into the new plating system without any problem.
- Small space requirement:
  - Convenient handling and high safety in operation.
  - Because of the load indicators, there is an opportunity to exchange only fully loaded cartridges, that means high efficiency.
- Cost efficient:
  - In case of water circulations the company can save the sewer charge.
  - Because of the rinse water treatment and the reclamation of metals, there is no sludge to dispose of.
- Compliance of EPA standards.
  - Because of the technical design of the RMA-units (see table 1) the effluents meet the EPA standards.
  - In West Germany the RMA-units are well accepted by the Waste Management Boards for the rinse water circulation and waste water treatment in plating plants.

Efficiency and Capacity

Primarily the effectiveness factor is dependent on the mass transfer in the ion exchange resin bed. Chemical reaction engineering of heterogeneous catalysis shows, that

- a small size of catalyst particles,

- a relative high retention time, that means a well balanced ratio of

reaction volume and flow rate of reaction solution and

- a high ratio of chemical reaction rate and diffusion resistance

lead to a high efficiency of the overall chemical reaction in a fixed bed column.

	cartridge	column
flowrate	0 ÷ 6 gpm	
volume of resin	0.5 cub. ft.	2 cub. ft.
capacity of resin	up to 20 equiv.	up to 80 equiv.
maximum of specific flow rate	25 gals/h per	25 gals. of resin
height of resin bed	9.8 inches	39.3 inches
cross-section of flow	86,2 sq. inches	
retention time		70 seconds
weight (filled with resin)	30 lb.	225 lb.
floor space		3.2 sq. ft.

table 1: operational data

Two examples may point out the optimal design of the RMA-columns:

- rinse water circulation tests in plating plants were carried out at a metal concentration of 100 ppm. The analyses of the effluents showed a concentration of less than 1 ppm.

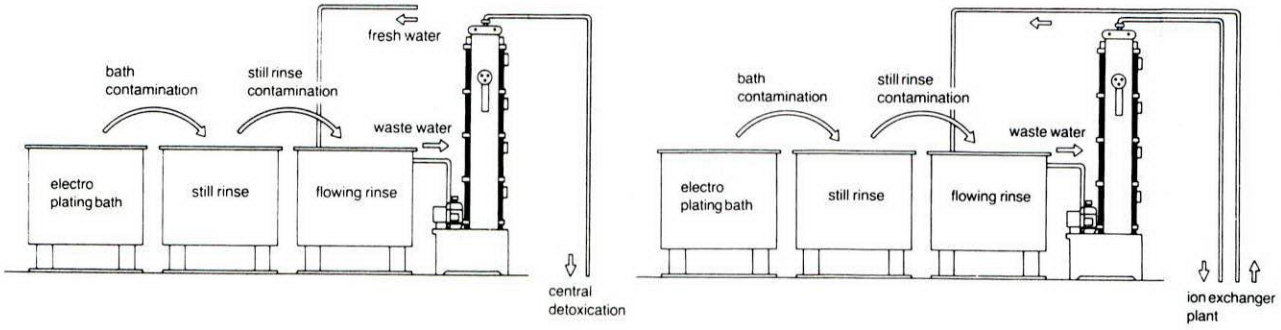
- a cartridge, filled with 0.5 cub. ft. of cation exchangers is able to absorb about 20 oz. of heavy metals. If there is rinse water with a load of 25 ppm treated in the RMA-column, one cartridge will purify about 6000 gals. of rinse water.

Variations in practical operation

Because of the flexibility of the RMA-units, the ion exchange columns can be adapted to various plating processes:

- Rinse water circulation can be carried out with one or two RMA-columns.

° A single column can operate as a bypass system in existing ion exchange systems or in existing conventional treatment facilities for the elimination of metal ions:



bypass system in existing detoxication system

- separate treatment of heavy metals
- metal recuperation

bypass system in existing ion exchanger system

- separate treatment of heavy metals
- metal recuperation

Picture No. 8:

° precious metals (i.e. gold, silver)

° toxic metals (Cadmium)

° metals that possibly unfavorably influence the following waste water treatment process (i.e. generation of metal complexes).

Experience of practical application

The RMA system, while new to the United States, has been in use throughout Europe since 1979 where there are more than 600 highly successful operations.

From the plating companies who operate the RMA-system, the following results can be summarized:

° All operating units stood the test in rinse water purification and reclamation of heavy metals (i.e. Cadmium, Copper,Nickel) and precious metals (i.e. Gold, Palladium, Silver).

° Waste water treatment using the RMA-system assures compliance with governmental pollution standards.

° In order to increase the operating time of RMA-cartridges, it can be useful to operate a stagnant rinse with an electrolytic metal recovery unit.

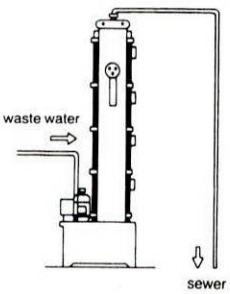
° According to the economical operation of ion exchange resins, the platers appreciate the load indication at the cartridges.

° More than 60% of all plating companies are operating the ion-exchange

resins for more than four years without any loss of efficiency.

° The enrichment of surfactants in the rinse water can be avoided by the use of special RMA-cartridges filled with absorber resins that remove the surfactants from the circulating process water.

° Many small companies operate the RMA-columns as a final monitoring system:



waste water purification

● RMA as a final monitoring system for the final waste water purification before it enters into the sewer.

Picture No. 9:

The use of special chelating resins guarantees waste water concentrations that meet the EPA standards.

° Several companies are recycling electrolytes from their stagnant rinses with the RMA-spray tower. This successful operation is carried out under economic aspects for the recovery of Nickel and Copper electrolytes and for chromic acid.

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Environmental II
Session H

Stockpiling of Metal Values in Metal Process Wastes Using Chemical Fixation and Solidification Techniques

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STOCKPILING OF METAL VALUES IN METAL PROCESS WASTES USING CHEMICAL FIXATION AND SOLIDIFICATION TECHNIQUES

by

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Technical Director

and

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Many processes in the chemical and metal process industries produce solids, sludges and liquid or semi-liquid wastes which contain large metal concentrations. In most cases it is not now economically feasible to recover these metal values, but it is becoming increasingly evident that dwindling mineral resources in the U.S. and the rise of mineral cartels elsewhere are going to change the economics of metal recovery. Today's waste may, in fact, become tomorrow's "ore."

This paper describes the application and use of chemical fixation and solidification (CFS) technology that can solve the problems of waste treatment and disposal, as well as metal waste stockpiling. By properly applying CFS technology, it is possible to convert sludges and other liquid wastes into non-hazardous solids. These solids can then be "stored" in special depositories either at the generation site or elsewhere, at low cost and with complete environmental safety. Further, the manifest and permitting requirements of the Resource Conservation and Recovery Act (RCRA) already provide a permanent inventory mechanism for hazardous wastes.

The environmental safety of the technology has been proven in more than ten years of use in the U.S. on metal-bearing waste streams, especially those from the metal-producing and -using industries. In terms of current waste disposal costs, this technology is inexpensive and is available on a competitive basis. By proper application, volume increase is minimized (for most economical storage) and CFS technology itself should not be detrimental to future recovery techniques.

Introduction

The issues involved in resource recovery of metals from wastes have been exhaustively addressed before, as have the increasing shortages of important minerals in the United States. For the first time in 20 years the U.S. is reviewing and updating its

stockpile of strategic minerals, including cobalt, aluminum, manganese, nickel, tantalum, titanium, vanadium, chromium, and the platinum group metals (Reference 1). As the costs of metal ores rise, and as waste disposal costs increase even faster, financial incentives will encourage greater use of recovery techniques. Already in the steel industry, for example, of the approximately 16.6 million tons of pollution abatement residues produced in 1974, 9.1 million tons were recycled. Most of this was in the form of dusts, scale pit sludge and other high metal content wastes. (2)

Most sludges and other wastes from the metal industries, however, contain much lower metal concentrations, and are complex mixtures of metals along with other contaminants which may cause difficulties in recycling or recovery. At present, these wastes are seldom reused and instead pose a significant disposal problem because of the toxicity of many of the metals. Arsenic, barium, cadmium, chromium (especially in the hexavalent state), lead, mercury, selenium, and silver are of specific concern under RCRA, while the Clean Water Act regulates disposal of copper, nickel, zinc, and antimony. Iron and manganese create esthetic problems. In addition, these wastes may contain phenol, cyanide, fluoride salts, and other toxic contaminants.

In the iron and steel industries, the primary residue metals are lead, zinc, copper, manganese, nickel, chromium, other alloying ingredients and, of course, iron. Arsenic, cadmium, lead, zinc, copper, chromium, antimony, nickel, and mercury are the principal hazardous constituents in the non-ferrous smelting and refining residuals, except in the case of the aluminum industry where very little toxic metal is found in the wastes. Table 1 (3) gives the estimated quantities of potentially hazardous wastes in this industry for 1983.

From a process standpoint, pyrometallurgical processes, such as blast furnaces, primarily produce slags which are highly utilized in construction and other areas. Sludges make up only 10 to 15 percent of those residues. On the other hand, electrowinning processes, using metals such as copper and zinc, generate mostly sludges. The "residual factors" (kilograms of waste per metric ton of product) for various processes are compared in Table 2 (3).

The predominant disposal methods used in the past by the metal-producing industry have been lagooning and open dumping; lagooning, sometimes with subsequent dredging and disposal in sanitary or special-purpose landfills, is most widely used for sludges.

In metal finishing, the metals of primary interest are copper, chromium, nickel, zinc, and cadmium. Sludges constitute the largest waste type produced in metal finishing. Precious metals are mostly recovered, and direct recovery is being practiced more and more in this industry, but the quantities of waste sludges are still large.

It was estimated that about 50,000 metric tons (dry weight) of sludge was produced in 1983 from independent job shops, while the tonnage from captive shops associated with other industries is much greater, probably by a factor of ten. These sludges contain solids in the range of 2 to 20 percent, so the wet tonnage is about ten times the above figures.

Table 3 (4) gives the estimated breakdown of aggregate sludge composition by metal in 1973. Nickel is most prevalent, followed in order by zinc, copper, chromium, and cadmium. While there is considerable potential value in the metals in these wastes, it should be noted that the concentrations given are on a dry-weight base. The actual aggregate composition of nickel, for example, in a wet sludge is only about 2 percent, not 20 percent.

The metal-producing industry relies on land disposal for its waste. Most job shops send their filtercakes and similar waste directly to landfills, while lagooning is more frequently used by captive shops.

Waste streams from other industries may also contain high metal concentrations. For example, a lagooned sludge from the ceramic pottery industry contains 25 to 75 percent basic lead carbonate (white lead); the electronics industry, too, generates a considerable amount of concentrated metal waste.

It is evident that substantial portions of the metals produced and/or used in the U.S. end up as general waste. However, because of low metal concentrations in these wastes, the recovery of these metals is not considered economically feasible at this time. Experience indicates that this current view of economic feasibility is changing for several reasons:

- .The increasing cost of needed metals;
- .Their diminishing supply, and
- .Improved and more economical recovery technology.

Effective Waste Storage

Until all the conditions for cost-effective waste metal recovery are met, the problem remains one of safely and economically storing such potential resources for the future. A method of keeping track of these potential resources is one aspect of this. From an institutional standpoint, RCRA provides a partial

material inventory mechanism in the form of its cradle-to-grave manifest system. Unfortunately though, most of the metal-bearing wastes which are disposed of each year do not, and will not, come under this system because they are non-hazardous by EPA definition. Presently, no other material inventory mechanism exists for locating these disposed-of wastes, although some states may have partial inventories based on state disposal permitting procedures for general industrial wastes.

The other key ingredient in a waste storage program is an effective, economical technology. Chemical solidification and fixation provides that technology and is commercially available now. In 1979 a USEPA study (5) arrived at the following conclusion: "The most secure final form of treated waste is a monolithic mass which has good dimensional stability, freeze-thaw resistance, low permeability, a high bearing capacity, and resistance to attack by biological agents. An end product such as this could be used as a foundation for buildings or roads, or simply buried and covered over in a landfill. The ideal fixing process does not require extensive heat-treatment nor large amounts of energy-intensive reactants. Also, the sludge materials should be reclaimable by some reasonable technique as some of the sludge contaminants (for example, manganese and chromium) are predicted to be in a critical supply in the future". (Emphasis is ours.)

Since this EPA study in 1979, concern for adequate supplies of certain metals has heightened. In March of this year, Congress' Office of Technology Assessment issued a report (6) that looks at alternatives that could protect U.S. industry from disruptions in the supply of chromium, cobalt, manganese, and platinum-group metals, in particular. Again and again the OTA report, "Strategic Materials: Technologies to Reduce U.S. Import Vulnerabilities," suggests that the government increase its emphasis on the development of new metal recovery technologies and recycling systems.

The report holds out little hope for much immediate progress, however, unless the situation either gets much worse or federal aid is offered as an incentive for change.

As long ago as 1972, the Commonwealth of Pennsylvania realized the potential for metal recovery in an electronics plant waste (see Table 5 for analysis) and the usefulness and environmental safety of using a solidification process to treat the waste for storage. An excerpt from the permit letter (7) reads: "It was concluded that the treatment to be provided will result in material that can be disposed of by on-land deposition with moderate precautions to prevent erosion of the earthy material. Since it has some potential value as a source of metal it should

be kept in a large mass separate from municipal refuse. Therefore, if it is sent to the ------- landfill, a separate area should be selected and used rather than incorporating it in the trash fill. This has the added safety feature of not subjecting the material to the intensive reducing conditions in contact with the organic material. Final slope of the pile should be such that it can be covered with soil and revegetated. A relatively thin soil cover should be adequate to establish vegetative cover that would control erosion. The earthy stabilized waste should have some available moisture capacity to help support vegetation. The usual soil restrictions on waste with putrescribles are not necessary for this stabilized waste which from the information we now have is non-hazardous."

CFS: A Short History

As recently as ten years ago, the words "chemical fixation" and "solidification" were not part of the environmental engineer's vocabulary. With only a few exceptions, the history of these systems dates from about 1970. Exceptions include the solidification of relatively small amounts of radioactive waste in drums, cemented backfill in certain mining operations, and the production of stabilized base courses for road construction using lime-flyash systems. In a few instances, waste residue generators, especially waste disposal site operators, have used cement, lime, flyash, soil and various combinations of these materials to solidify liquid waste for disposal in non-secure landfills. These early commercial uses of solidification were concerned with solidification only, and rarely, if ever, were subsequent leaching tests or other technical evaluations conducted. The only published work dating from this period on leachability, environmental degradation, or any other performance characteristics of solidified waste are internal studies done at various nuclear installations and government nuclear regulatory agencies.

In the early 1970s, several companies began applying scientific principles to the fixation and solidification of various waste materials. One used a lime-flyash process which incorporated sulfates from the waste to contribute to strength development in the final solid. This process was aimed primarily at the sludges expected to be produced by lime/limestone scrubbing of flue gases to remove sulphur oxides.

The other CFS system is a patented process based on soluble silicates and silicate setting agents, primarily sodium silicate solution and Portland cement. This process aimed at a wider variety of sludges, especially those resulting from manufacturing and metal production containing large concentrations of the polyvalent metals which are considered toxic. The company offered a mobile service which brought

treatment units to the generation or storage site, then removed and treated the waste over a period of days or weeks.

About 1975 CFS systems began attracting attention from the government, waste generators, and consulting engineering firms. The EPA's Office of Solid Waste Management initiated a series of projects to evaluate various solidification processes, to explore other possible systems and to develop testing and evaluation criteria.

While new processes and variations of old ones are being announced constantly, and a rather bewildering array of processes, systems and chemicals has appeared on the market, in fact the number of systems which chemically differ from one another substantially is really quite small.

CFS Systems

Solidification systems are of three basic types: (1) non-chemical, such as absorption; (2) organic systems, and (3) inorganic systems. Absorption-type systems do not use chemical fixation/solidification, but rather a different technology which has other uses. Organic systems, due to cost and other considerations, are not particularly applicable to metal-bearing waste storage. Rather it has been the inorganic systems that have really been developed and used to date for this purpose.

The most important inorganic CFS systems at present are lime-pozzolan, Portland cement-pozzolan, Portland cement-lime and Portland cement-sodium silicate. There are other systems, but for industrial wastes, the Portland-cement-based processes are the most widely used. A cement-flyash process works well with certain types of waste but, like the lime-flyash process, it requires large amounts of solidifying agents and results, therefore, in very large volume increases. This characteristic is generally undesirable from both storage and cost points-of-view. The Portland cement-sodium silicate process usually involves only moderate volume increases, but does not make use of waste products such as inexpensive flyash.

CFS chemistry forms products similar to rock, clay, concrete, brick, glass and other such materials known to be among the most stable physical forms on earth. The treated waste is not affected by ultraviolet radiation; it is non-biodegradable, and has a high resistance to ground or surface water. These characteristics, together with our knowledge of the kinetics and thermodynamics of these materials, mean that waste properly treated with correct CFS formulations will change only very slowly in the ground--on the same time scale as natural rocks

and minerals. The possibility of a sudden or catastrophic change in such materials--such as reversion to its original waste form--is almost non-existent.

In addition to the basic siliceous components of the chemical solidification system, various minor components can be added and/or adjusted to adapt a basic system to the particular waste treated and also to the processing mode in which the solidificaton is carried out. Certain additives can insolubilize and precipitate specific waste components, especially the toxic metals. The insoluble component can then be entrapped in the inorganic polymeric matrix and completely immobilized.

Principal attributes of CFS systems include:

- .Relatively low cost;
- .Long-term physical and chemical stability;
- .Documented use on various wastes for at least ten years;
- .General availability of chemical ingredients;
- .Non-toxic nature of chemical ingredients;
- .Ease of processing (ambient temperature and pressure);
- .Relatively low volume increases (with some processes);
- .Inertness to ultraviolet radiation;
- .High resistance to biodegradation;
- .Low water solubility;
- .Relatively low water permeability, and
- .Good mechanical and structural characteristics.

Stability

Stability is the ultimate test of any CFS system. The treated waste must remain where it is placed and must be environmentally safe. The economics of disposal and of storage for later recovery dictate outdoor storage in nearly all cases. This means exposure to water, biological activity, and ultraviolet radiation. Biological activity and ultraviolet radiation affect inorganic systems very little. The primary concern is with the leaching effects of rain, surface and ground water.

Leaching tests can be used which attempt to predict, and in some cases simulate, the effects of water on treated waste stored in the natural environment. Presently, the leaching tests most frequently required by regulators are:

(1) EPA EP Toxicity Procedure (40 CFR Part 261.24);
(2) EPA Multiple Extraction Procedure (MEP)-used for "delisting" tests, and
(3) ASTM Proposed Method A Water (or Acid) Shake Extraction Procedure.

The EP test is the accepted test at the moment, but ASTM is developing standards which may come into use in the future.

Column tests are very good for simulating actual, specific storage conditions, but currently have no regulatory standing.

Evaluating a material for leachability usually means comparing the concentration of the hazardous constituent in the leachate to that in the original waste. This indicates what proportion of the constituent dissolved out during the test. If test conditions can be expressed in terms of a time-related number, such as equivalent years of field exposure to rainfall, then leachability can be expressed in true rate terms. A way to express this is in pounds of constituent lost per year, or percent-of-original-quantity lost per year. This latter number is especially important when stockpiling metal values.

Tables 4-7 show what results to expect from leaching tests on typical metal-bearing waste sludges. The waste pickle liquor sludge (Table 4) from a steel mill contains about 1.5 percent chromium. The iron content is not shown, but would typically be 8 to 15 percent. Using the standard EPA EP Test, only about one part in 700[1] of chromium leached out during the test. From experience with other long-term leaching tests simulating 50-100 years of water leaching, about the same results would be attained. Thus, the loss of metal during any reasonable storage period would be minimal, even insignificant.

Delivery Systems

CFS technology can be used to treat waste using mobile facilities or on-site units which may be either permanent or portable.

Mobile solidification service is offered by several companies for one-time, periodic, or occasional treatment of impounded waste. Because such a service requires no capital investment from the waste generator, it is for some an economical way to handle waste-treatment needs.

Mobile equipment can process more than 100,000 gallons of waste per day, and the treated waste can be pumped to either temporary or permanent storage areas. In one project, about four million gallons of solidified liquid waste was pumped into a conical "hill" 35 feet high. If permanent, on-site storage were required, the hill could have been left intact. To prevent erosion, it probably would have been covered with a membrane, or with a thin layer of soil to provide the substrate for a ground cover such as crown vetch. This solid form has good structural integrity and is resistant to leachng by rainfall, surface, or ground water.

When solidified waste must be moved from a temporary curing area to a permanent storage location, its strong, clay-like structure

handles well with earth-moving equipment and can be compacted into a dense fill at the permanent storage site. This was, in fact, what happened to the 35-foot conical hill discussed above.

When impoundment is not feasible, waste can be treated by on-site systems, either permanent or portable. These systems are available in all sizes and can be owned and operated either by the waste generator or by a treatment contractor.

Chem-Technics, for example, designs, engineers, constructs, installs and starts up fixed units for use at waste generation sites, central hazardous waste management facilities, or in mobile treatment services. Units available range in through-put rate from several hundred to 300,000 gallons per day, batch or continuous, for a variety of waste forms. Depending on user preference and project requirements, options may include:

.Design and construction of the facility. The owner then assumes operation under a process license;

.General design and specifications as part of the license fee. Owner constructs and operates the facility.

.Purchase of proprietary chemicals which includes the use license and technical support.

CFS Treatment Costs

The cost of CFS treatment varies with the waste, location, type of solidification system, volume, and end-product specification. Mobile solidification service for metal-bearing, aqueous sludges and cakes typically costs $.15 to $.30 per gallon on jobs of one million gallons and more. Large-scale, permanent systems treating high-solids cakes may cost as little as $.05 to $.10 per gallon.

For smaller-scale installed systems, purchase of proprietary chemicals is often the simplest approach. Cost will typically range from $.20 to $.50 per gallon, but capital investment is small and technical support is included.

In addition to the solidification cost, dredging or other removal of the waste from an impoundment may add from $.01 to $.05 per gallon. Finally, if the solid must be transported and landfilled, charges for this must also be added.

Metal Value Recovery

CFS systems are designed to offer a high degree of insolubility of metals when exposed to normal, relatively mild, natural conditions. However, to recover these metals, the CFS process should ideally create a product similar to that of the naturally-occurring ores, because the main technology of metal production will continue to revolve primarily around ore as the starting material. Natural ores are oxides or hydroxides

(aluminum, chromium, copper, iron, and manganese), sulfides (cadmium, copper, lead, nickel, and zinc), and carbonates (cadmium, copper, lead, and manganese). Metal compoounds in solidified wastes are predominantly hydroxides (or hydrated oxides) and silicates, sometimes complex mixtures of the two.

The greatest differences between the stored wastes and natural ores will usually be the low metal content and high water content of the waste products. Water content is a problem, especially in pyrometallurgical processes, because of the energy needed to vaporize the water. In addition, technical and safety considerations arise with the sudden generation of large volumes of water vapor.

Low metal content is, of course, essentially an economic problem, and, as mentioned earlier, is the real reason these wastes are not being recovered at present. Once the economic situation dictates the need for a change, existing smelting and refining processes will likely be adapted to recovering metal from stored, solidified wastes without development of major new technology. For example, much steel industry waste could now be slowly bled into furnace feed with no fundamental process changes.

The biggest unknown is the effect of minor waste constituents on product quality and on the processing itself. If this becomes a problem, it can probably be solved with relatively minor technological adjustments, or by the selective use of recovered waste metal in non-critical products.

Conclusions

The technology that permits the safe, economical stockpiling of metal-bearing wastes already exists. In commercial use for more than ten years, this chemical fixation and solidification system of treatment and storage has already proven to be environmentally safe. Furthermore, the regulations dictated by the Resource Conservation and Recovery Act (RCRA) provide both the impetus and the initial inventory mechanism to begin this stockpiling.

In terms of present-day waste disposal costs, this technology is inexpensive and competitively priced. With proper application, the technology minimizes volume increase to achieve optimum storage economy. Finally, the chemistry employed to treat the waste streams should not be detrimental to future recovery techniques.

FOOTNOTE

[1]The concentration in the leachate is actually 1.0 mg/L. The final leachant volume is 2 L, which therefore contains 2 mg of Cr. Since the sample size was 100 g, it contained about 1400 mg of Cr (specific gravity = 1.1). Therefore, on a mass-balance basis, about one part in 700 was leached out.

REFERENCES

1. Buildup of Strategic Materials Resuming. Chemical and Engineering News, 8, March 23, 1981.

2. PAT Report, Steel Industry Sludge Is Being Reused. Environmental Science and Technology, 9:624, July 1975.

3. Calspan Corp., Assessment of Industrial Hazardous Waste Practices and the Metal Smelting and Refining Industry. USEPA, Washington, DC, 1975.

4. Hezir, J. S., Impacts of New Water Pollution Regulations on Solid Waste Management: New York City. USEPA, Office of Solid Waste Management Programs, Washington, DC, 103 pp., 1973.

5. U.S. Army Engineers Waterways Experiment Station, Survey of Solidification/Stabilization Technology for Hazardous Industrial Wastes. National Technical Information Service, Springfield, VA, 1979.

6. Protection of Critical Metals Supply Probed. Chemical and Engineering News, 29, January 28, 1985.

7. F. G. Loughry, Chief, Soil Science Unit, Commonwealth of Pennsylvania. Private communication re: waste disposal permit, 1972.

TABLE 1

SUMMARY OF ESTIMATED LAND DISPOSED AND POTENTIALLY HAZARDOUS WASTES UNITED STATES SMELTING AND REFINING INDUSTRY, 1983 (METRIC TONS)

Industry Category	Total Disposed Or Stored	Total Hazardous Constituents
Primary copper, smelting and tire refining (SIC 3331)	6,415,004	102,219
Primary copper, electrolytic refining (SIC 3331)	6,937	260
Primary lead, smelting and refining (SIC 3332)	542,400	61,200
Primary electrolytic zinc smelting and refining (SIC 3333)	51,081	12,662
Primary pyrometallurgical zinc smelting and refining (SIC 3333)	185,370	34,858
Primary Aluminum (SIC 3334)	502,766	78,575
Primary Antimony (SIC 3339)	8,313	157
Primary Mercury (SIC 3339)	21,425	109
Primary Titanium (SIC 3339)	5,100	2,170
Primary Tungsten (SIC 3339)	N/A	253
Secondary Copper (SIC 33412)	153,300	6,635
Secondary Lead (SIC 33413)	164,500	5,037
Secondary Aluminum (SIC 33417)	588,870	1,771
National Total		

N/A- Quantity of Total Disposed Not Available

*Partial Quantity- Total Quantity of Sludge Not Known

TABLE 2

RESIDUAL FACTORS FOR METAL SMELTING AND REFINING [1]

Metal Category	Type of Residual	Residual Factor(kg/MT of Product)
Primary Copper Smelting and Fire Refining	reverbatory slag	3000
	acid plant sludges	2.7
	dusts	17
	miscellancous slurries	17
Primary Copper Electrolytic Refining	miscellaneous slurries	2.4
Primary Lead	blast furnace slag	410
	slag fines	30
	acid plant sludge [2]	40
	sinter scrubber sludge [2]	19
Primary Zinc, Electrolytic	acid plant sludge [2]	17
	miscellaneous sludges [2]	9.1
Primary Zinc,Pyrometallurgical	retort residue [2]	1050
	acid plant sludge [2]	122
	retort residue ("blue powder") [2]	10
	cadmium plant residue	1.8
Primary Aluminum	rodding room dust	5
	pot line scrubber, sludge [2]	29.3
	pot line skimmings [2]	5.5
	spent potliners [2]	53
	cast house dust	2.5
Primary Antimony, Pyrometal-lurgical	blast furnace slag	2800
Primary Antimony, Electrolytic	anolyte sludge	210
Primary Mercury	kiln or retort residue	207,000
Primary Titanium	chlorination sludge	330
Primary Tungsten	digestion residue	50
Primary Tin	smelting slag	915

1.) Residuals immediately recycled to process (e.g. dusts) are not included.

2.) May be recycled after storage periods of months to years.

TABLE 3

ESTIMATED AGGREGATE ELECTROPLATING SLUDGE COMPOSITION

Compound	Dry Weight %	Metal	Dry Weight %
$Cu(OH)_2$	12.3	Cu	8.0
$Cr(OH)_3$	14.8	Cr	7.5
$Ni(OH)_3$	39.1	Ni	21.0
$Zn(OH)_2$	17.1	Zn	11.0
$Cd(OH)_2$	1.7	Cd	1.0
Impurities	15.0	Non-metals	51.5
Total	100.0	Total	100.0

TABLE 4

LEACHING TEST RESULTS

SOLIDIFIED NEUTRALIZED WASTE PICKLE LIQUOR SLUDGE

Constituent	Consentration Of Constituent in Untreated Waste	Concentration of Constituent Leached From Solidified Waste	
		Laboratory	Field
Arsenic	0.140	0.0013	< 0.5
Barium	27.4	3.17	0.22
Cadmium	2.91	0.054	0.021
Chromium, total	15950.	0.364	1.00
Chromium, hexa.	6.86	--	--
Lead	88.8	0.50	0.399
Mercury	0.260	0.0017	0.003
Selenium	2.6	0.0007	0.006
Silver	7.28	0.080	0.021

All results in mg/L
< = less than
- = not analyzed
ND = not detected

The above data reflects the analyses of leachates prepared according to the USEPA Extraction Procedures (40 CFR 261.24, Appendix II, Federal Register, May 19, 1980). All analyses were completed according to EPA methodologies. Organic analyses data are based upon retention time on a single column only and these results have not been confirmed. Values reported as "less than" indicate the working detection limit for the particular sample/parameter. Values reported as "less than or equal to" indicate that the particular sample may contain at least trace quantities of the particular parameter.

TABLE 5

LEACHING TEST RESULTS

WEATHERING TESTS

SOLIDIFIED ELECTRONICS MANUFACTURING SLUDGE

Constituent	Concentration of Constituent in Untreated Waste	Concentration of Constituent Leached From Solidified Waste - Column Leaching Test* 100 inches of Leachate	
		Original Testing of Field Product Samples	Testing of Field Product Samples After 10 months Weathering
Aluminum	500-5000	< 0.10	< 0.10
Total Chromium	100-1000	< 0.10	< 0.10
Cyanide	-	< 0.10	< 0.10
Copper	5-100	< 0.10	< 0.10
Iron	5000-50,000	< 0.10	< 0.10
Nickel	5-100	< 0.10	< 0.10
Phenol	-	< 0.10	< 0.10
Zinc	100-1000	< 0.10	< 0.10
Manganese	500-5000	< 0.10	< 0.10
Cadmium	10-100	< 0.10	< 0.10

All results in mg/L
< = less than
- = not analyzed
ND = not detected

*The above data reflects the analysis of leachate prepared according to Chem-Technics' Standard Column Leaching Test using distilled water as the leachant.

All analyses were completed according to USEPA methodologies in effect at the time of analysis.

TABLE 6

LEACHING TEST RESULTS

SOLIDIFIED CHEMICAL PLANT WWT SLUDGE

Constituent	Concentration of Constituent in Untreated Waste	Concentration of Constituent Leached From Solidified Waste Column Leaching Test* 100 inches of Leachate
Lead	6100	2.7
Copper	1.2	< 0.10
Total Chromium	38	< 0.10
Iron	1700	< 0.25
Nickel	14	< 0.10
Zinc	520	< 0.10
Cadmium	33	< 0.10

All results in mg/L
< = less than
- = not analyzed
ND = not detected

*The above data reflects the analysis of leachate prepared according to Chem-Technics' Standard Column Leaching Test using distilled water as the leachant.

All analyses were completed according to USEPA methodologies in effect at the time of analysis.

TABLE 7

USEPA MULTIPLE EXTRACTION PROCEDURE (MEP)
SOLIDIFIED ELECTROPLATING SLUDGE

	Concentration in Leachate (mg/L)						
MEP STEP	C6*	Cr	Ni	Total Cn	Free Cn	Initial pH	Final pH
1 (EP)	3.0	4.6	.54	.25	.07	12.1	5.10
2	.9	.95	<.05	<.05	<.05	10.2	10.9
3	.7	.8	<.05	<.05	<.05	10.2	10.5
4	.5	.5	<.05	<.05	<.05	10.0	10.5
5	.3	.3	<.05	<.05	<.05	9.6	10.7
6	.2	.2	<.05	.05	.05	9.8	10.1
7	<.13	.13	<.05	.05	.05	8.5	10.0
8	<.10	.10	<.05	.05	.05	9.7	10.0
9	<.14	.14	<.05	.05	.05	7.0	9.6
10	<.09	.09	<.05	.05	.05	9.4	10.0
DI Water				.71	.71	12.1	11.9
						Cd	
Analysis of Raw Waste Stream	140	5650	5990	95	75	<.5	

* Not pretreated for Cr^{+6}

All results in mg/L
< = less than
- = not analyzed
ND = not detected

The above data reflects the analyses of leachates prepared according to the USEPA Extraction Procedures as presented in the Federal Register, Vol. 47, No. 225, Monday, Nov. 22, 1982.

All analyses were completed according to USEPA methodologies. Values reported as "less than" indicate the working detection limit for the particular sample/parameter. Values reported as "less than or equal to" indicate that the particular sample may contain at least trace quantities of the particular parameter.

H-6

Environmental II
Session H

The Status Of Ultrafiltration And Microfiltration Applications For The Metal Finishing Industry

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THE STATUS OF ULTRAFILTRATION AND MICROFILTRATION APPLICATIONS FOR THE METAL FINISHING INDUSTRY

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INTRODUCTION

There are approximately 150,000 industrial plants in the United States, which, according to SIC code categorization comprise the metal finishing industry.

By definition, a "pollutant" generally refers to any plant discharge that regulatory bodies define as noxious. The metal finishing industry typically produces two distinct categories of pollutants in water discharges: oil-water emulsions and dissolved heavy metals.

This paper addresses two innovative technologies for treating these contaminants: ultrafiltration and microfiltration. These technologies are related in that they both utilize the engineering process of "cross-flow filtration". In this process, the flow of waste water is parallel to the surface of the filtering medium and the filtered water passes through the medium in a direction perpendicular to the waste water flow.

The fundamentals of each technology are described, and specific application detailed.

DESCRIPTION OF CONTAMINANTS

OILY WASTES- Oil may be defined as any substance that can be dissolved by hexane, chloroform or Freon TF. Oily waste water (oil-water emulsions) can contain as little as 50 ppm oil, or as much as 500,000 ppm. Because of the colloidal nature of the emulsion the oil cannot be separated by conventional gravity or dissolved air flotation processes.

A stable oil-water emulsion can be described as a colloidal system consisting of charged oil droplets surrounded by an ionic atmosphere. Surface-active agents such as natural organic materials or cleaners aid in maintaining a stable colloidal system. Emulsifiers are used to disperse the oil droplets throughout the water phase. An emulsifier typically contains an oil-soluble chemical which is non-polar with water-soluble branches which are polar. This combination of non-polar and polar constitutents within the same molecule gives the emulsifier an affinity for both water and oil, ensuring that the oil remains in a colloidal state by enabling it to overcome the natural forces of coalescence. Generally, an oil-water emulsion is milky-white, with micron-sized oil droplets evenly distributed throughout the water. These solutions are prepared by adding the concentrated oil product and emulsifier to water with simple mixing to provide even dispersal.

Typical emulsifiers have either anionic or non-ionic polar groups. Examples of anionic emulsifiers include petroleum sulfonates and sulfonated fatty acids. Non-ionic emulsifiers include ethoxylated alkyl phenols.

These emulsions combine the lubrication properties of oil with the heat transfer or cooling properties of water to provide a metal working fluid with the following characteristics:

Better heat transfer characteristics than oil

Lower fire hazard than oil

Less tool wear

Lower fluid surface tension to ensure better wetting and coating of metal surfaces

A used metal working fluid often contains "free" oil (unemulsified), metal fines, dirt and other suspended contaminants. In general, the pH is between 6 and 12, and temperature between sixty degrees and 140 degrees Fahrenheit.

HEAVY METALS - Toxic heavy metals introduced during metal finishing operations include silver, arsenic, cadmium, chromium, copper, lead, mercury, nickel, antimony and zinc. Generally, they are in a soluble form and come from the plating bath, either during rinsing operations or bath dumps.

CONTAMINANT SOURCES

OILY WASTES - The following metal working operations utilize oil-water emulsions:

Metal cutting operations such as machining use oil-water emulsions for both lubrication and cooling

Metal forming operations use oil-water emulsions for lubrication

Hot and cold rolling operations for steel and aluminum strip utilize oil-water emulsions for both lubrication and cooling

Heat treating/quenching processes use oil-water emulsions during the process of removing oily contaminants from metal parts

HEAVY METALS - The optimum rinse system design involves two or three tanks into which the parts are immersed and through which the rinse water flows in a counter-current direction,continuously removing traces of the plating bath from the parts.

Another source of heavy metals contamination is from plating bath dumps. Although relatively infrequent, the concentration of heavy metals directed to

the waste treatment system is easily ten to twenty times that found in normal rinse waters. Electroplating baths may last for months, if not years, before requiring dumping; electroless baths, on the other hand, are much less stable and often require replacing on a weekly basis.

WASTE TREATMENT PROCESSES

OILY WASTES -

Chemical Treatment

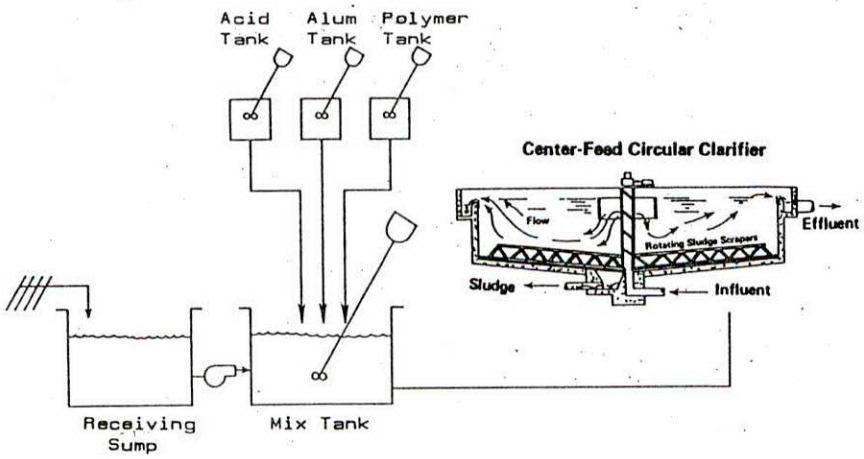
This typcially involves chemical demulsification followed by secondary clarification of the water phase. In other words, the emulsion is broken to yield an oil layer on top of the water. Chemicals utilized include sulfuric acid, waste pickle acid, alum (aluminum sulfate), iron sulfate and proprietary polymers.

Because the oil phase usually contains chemical floc, dirt, metal fines and some trapped water, the oil cannot be easily recycled.

Typically, acid is used to lower the pH which weakens the emulsion, and the aluminum ion from alum neutralizes the surface charge of the emulsion. Excess aluminum ion forms the floc which adsorbs the oil, and certain polymers can be added to aid in this coagulation process. If the waste contains clay or other heavy suspended solids, the floc will settle, but a minimum of a two hour retention time is required for good separation. In the absence of heavy suspended solids, the alum floc with the adsorbed oil will float and generally less than 20 minutes residence time is required to accomplish separation. Dissolved air flotation improves the rate of separation.

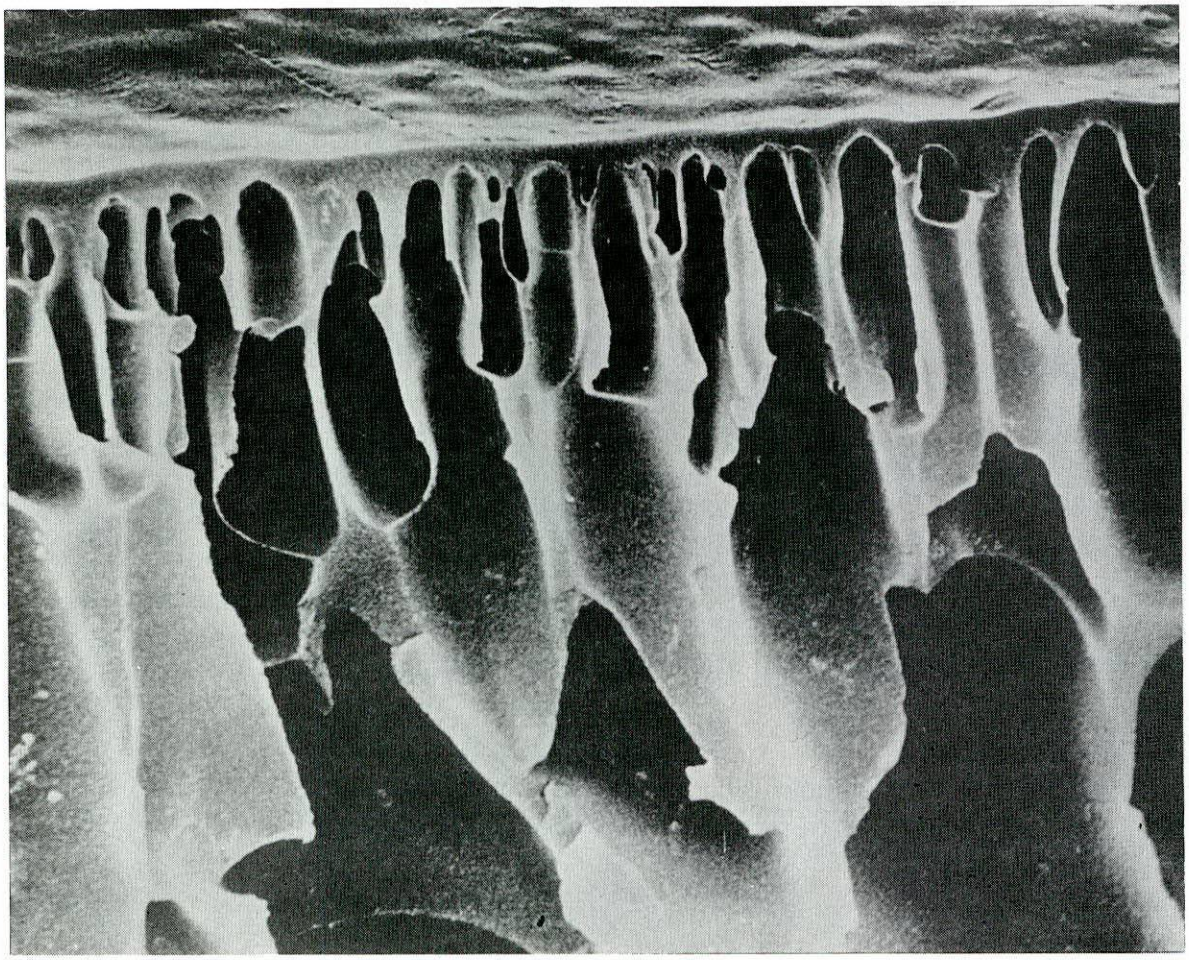
Figure 1 illustrates a typical chemical treatment systems.

FIGURE I
CONTINUOUS CHEMICAL TREATMENT PROCESS



Ultrafiltration Treatment

Ultrafiltration is a membrane separation process which utilizes a semi-permeable membrane which will reject relatively high molecular weight materials and allow water, salts and low molecular weight organic solute to pass through. Figure 2 is a photomicrograph of a typical ultrafiltration membrane cross-section.



Utilizing the crossflow filtration principle, ultrafiltration offers the following advantages over chemical treatment:

- Lower capital, installation and operation costs
- Insensitive to the chemical nature of feed solution
- High oil removal efficiency independent of oil concentration in the feed
- No chemical additions
- No oily sludge produced
- Minimal pre-treatment required

Concentrated oil can often be incinerated
Compact systems
Because the membrane provides a positive barrier to the oil, the chances of oil "break through" are minimized.

Typically, the oil can be concentrated up to 60-80% and depending on the specific application, can be recycled, hauled away, or incinerated for its fuel value.

The permeate may be pure enough to be sewered or reused in the process. In certain applications it may contain constituents which can be concentrated by another membrane process, reverse osmosis, and reused.

Ultrafiltration systems processing oily waste are currently operating on waste water flows as small as 300 gallons per day, and up to 100,000 gallons per day. Normally, the operating pressure is between 50 and 100 psi, and membrane elements last between one and one-half and three years before requiring replacement.

Typical alkaline cleaner baths contain hydroxides, carbonates, silicates, phosphates, titanium dioxide and both ionic and non-ionic surfactants. One application for ultrafiltration is to continuously recirculate the bath through a unit to remove the oil. Generally, the small portion of the surfactant which is rejected by the membrane must be added back to the bath to maintain chemical stability.

Ultrafiltration is also used effectively on the rinse following the alkaline bath to reclaim rinse water and concentrate the oil for disposal purposes.

Because the low molecular weight emulsifiers will often pass through the membrane leaving free oil behind, there is a danger that a film of oil will coat the membrane surface and affect its performance. Spiral wound and plate and frame configurations can be chemically cleaned by detergent based dispersants or solubilizing agents (acids, caustics, etc.), while tubular ultrafiltration devices can also use sponge balls or brushes to mechanically remove oil or other deposits.

Operating costs vary markedly with the application; however, a survey of over 200 units in operation revealed costs ranging from $2.00 to $7.60 per thousand gallons of waste treated.

HEAVY METALS -

Chemical Treatment

The traditional way to remove dissolved heavy metals from waste streams has been to add chemicals which cause the metals to form an insoluble sludge which is hauled to a toxic landfill.

The following factors need to be addressed in selection of the optimum chemical system for a particular waste stream:

- effectiveness of metals removal from solution
- ease of handling chemicals
- volume of sludge produced
- ease of dewatering sludge
- resistance of sludge to leaching in a landfill
- overall economics

1) Hydroxide Addition

The least expensive and most widely used precipitation chemistry is that of adding the hydroxide ion either as calcium hydroxide ($Ca(OH)_2$) or sodium hydroxide (NaOH). As the pH of the waste stream is raised, insoluble heavy metal oxides and hydroxides are formed and precipitate out with the aid of certain polymers that aid in flocculation and precipitation.

The advantages of this chemistry are that it is inexpensive and fairly effective with most of the heavy metals.

The disadvantages are that the solubilities of various metals vary with different pH values causing difficulty in trying to optimize the chemical system. Also, complexing agents such as EDTA (ethylenediaminetetraacetic acid), ammonia and phosphates can inhibit the formation of insoluble hydroxides.

2) Soluble Sulfide Precipitation

The addition of a soluble sulfide such as sodium sulfide (Na_2S) or sodium hydrosulfide (NaHS) results in the formation of heavy metal sulfide compounds that are quite insoluble, and precipitation is enhanced by the addition of flocculating agents.

The advantages of this chemistry are that it is effective over a broad pH range, and with most of the complexing agents. Sulfides also exhibit lower leachability in landfills than hydroxide compounds.

The disadvantages are that expensive chemicals are required (as compared to hydroxides) and hydrogen sulfide gas (H_2S) is readily released, particularly at lower pH values. This requires special air exhaust equipment.

3) Slightly Soluble Sulfide Precipitation

The reaction of sodium hydrosulfide (NaHS) with ferrous sulfate ($FeSO_4$) to form ferrous sulfide (FeS) results only in enough sulfide ion formation to react with the heavy metals in solution to form the insoluble sulfide.

The advantages of this system are that it is effective over broad pH range with complexing agents, it does not release hydrogen sulfide gas (H2S) and it will also reduce hexavalent chrome to the trivalent form.

The disadvantages are that it requires greater chemicals usage than the soluble sulfide system, that expensive chemicals are required (as compared to hydroxides) and that a greater sludge volume is produced.

4) Ferrous Sulfate Addition

This system involves lowering the pH to disassociate or weaken heavy metal complexes, the addition of ferrous sulfate (FeSO4) and elevation of the pH to a value above nine.

The advantages of this system are that it is very effective with complexing agents, produces a low sludge volume and does not release hydrogen sulfide (H2S) gas.

The disadvantages are that expensive chemicals are required along with close pH control.

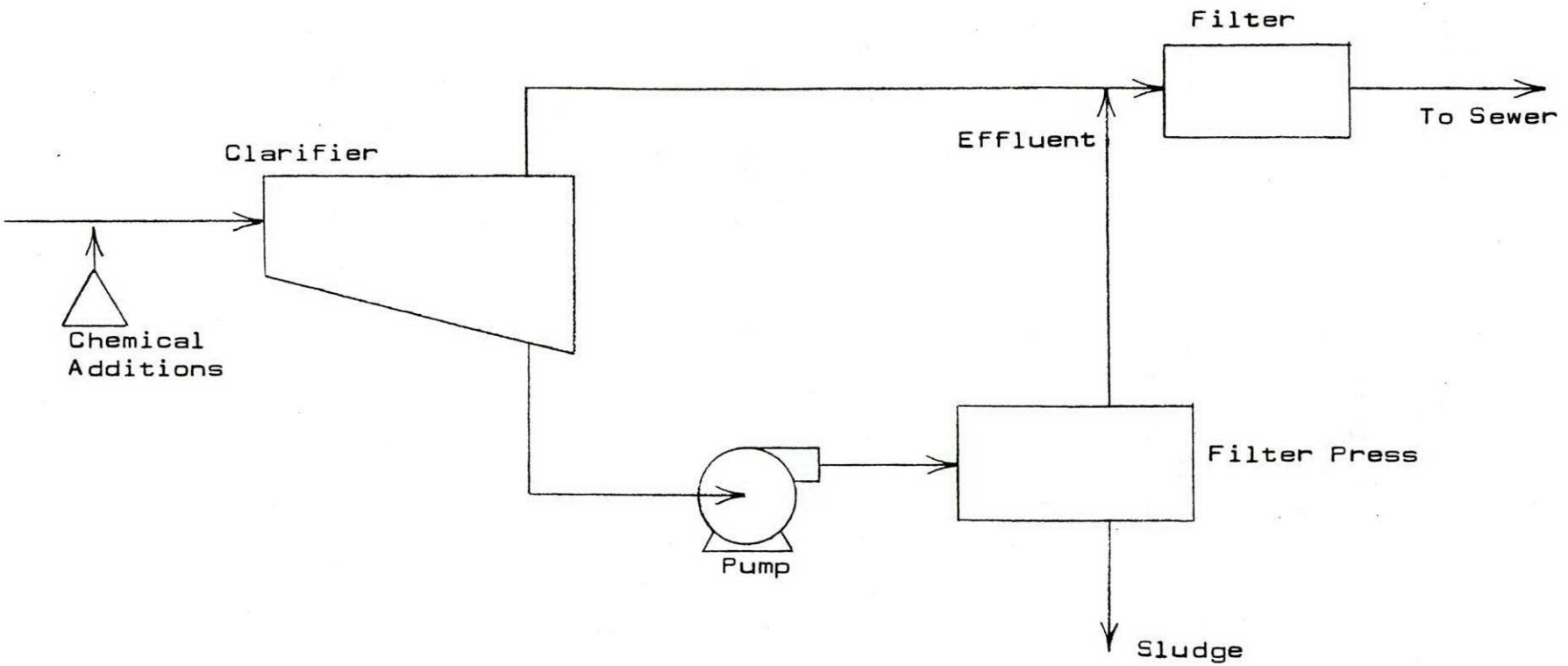
Although the increased use of such innovative clarification equipment as inclined plate or slant tube clarifiers has resulted in smaller, more efficient systems, tightened discharge restrictions and the inability of chemical systems to cope with even slight variations in the inffluent analysis have made the implementation of chemical treatment systems less than ideal.

Figure 3 represents a typical chemical treatment system. (Next page).

Microfiltration Treatment

Microfiltration can be defined as the removal of particulate material ranging in size from 0.1 to 10.0 microns (1000 to 100,000 angstroms).

Typically, devices used to accomplish this operate on a "through-flow" or "dead end" principle. This involves pumping the entire solution through the filter media with the particulate material left on or in the filter media. A recent development in filter technology known as "crossflow" or "tangential flow" filtration allows for continuous processing of liquid streams. The bulk solution flows over and parallel to the filter surface, and because this system is pressurized, water is forced through the filter media. The turbulent flow of the bulk solution over the surface minimizes the accumulation of particulate matter on the filter and facilitates continuous operation of the system.



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C3 INTERNATIONAL
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Phone: (612) 631-8082

Figure 3 - Chemical Treatment System
For Heavy Metals Removal

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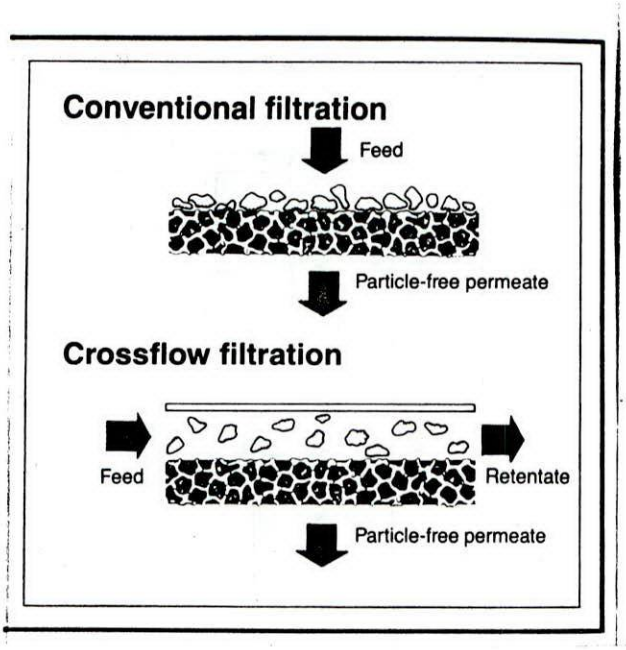
Figure 4 illustrates through-flow and crossflow filtration.



The application of cross-flow microfiltration technology to metal finishing waste treatment involves the addition of chemicals to the waste stream to effect precipitation and then continuous dewatering through the membrane filter which typically has a 0.1 micron pore size. The microfilter consists of a series of tubes measuring up to one inch in diameter. The polymeric membrane is designed to resist the pH range required to precipitate the heavy metals out of solution, as well as to withstand the abrasive affects of these suspended solids. The treated solution is pumped at turbulent velocities down the center of the tubes and a down stream valve creates the necessary back pressure to force clarified water through the microporous membrane.

Typically, the dewatered suspended solids (concentrate) are recylcled to the feed tank in order to increase the concentration of suspended solids up to 5-10%. A portion of this concentrate stream is continuously bled from the system, often to an inclined plate type clarifier for further dewatering up to approximately 20% solids. If increased dewatering is justified, this slurry can be directed to a filter press to bring the solids concentration up to 60%. Figure 5 illustrates a typical microfiltration system for heavy metals removal. (Next page).

The advantages of this approach over typical chemical treatment clarification are:

Compactness - the equipment requires relatively little area and can be engineered to fit available space.

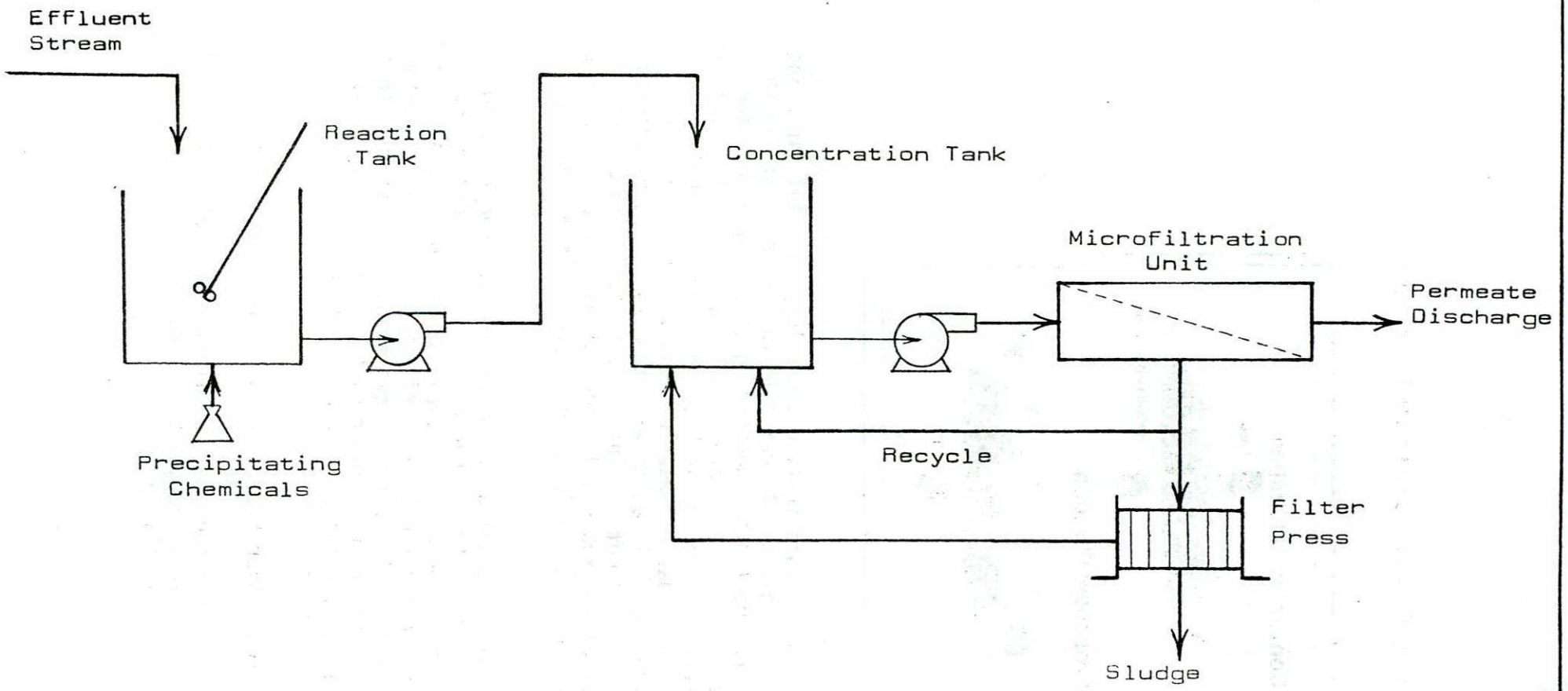


FIGURE 5 - HEAVY METALS REMOVAL UTILIZING MICROFILTRATION

Flexibility - because of the modular construction of the equipment, virtually any volume of effluent can be treated, and the equipment can be easily expanded to accommodate additional flows.

Versatility - the clarified water (permeate) can either be recycled or discharged directly to sewer, depending on use requirements.

Ruggedness - microfiltration devices are manufactured from tough, inert polymers which are resistant to mechanical and chemical degradation.

Ease of Maintenance - the modular construction and rugged design of the systems facilitates maintenance. If necessary, the tubes can be mechanically cleaned. The modular design simplifies replacement of the components, if necessary.

SUMMARY

Although new in their application to metal finishing waste treatment, the technologies of ultrafiltration and microfiltration offer significant promise in the quest to meet increasingly stringent discharge regulations in an efficient and economical manner.

I-1

Management Session I

The Evolution of the Finisher-Supplier Relationship

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THE EVOLUTION OF THE FINISHER-SUPPLIER RELATIONSHIP

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Let's begin by stating the obvious: Finishers and suppliers depend upon each other for their very existence. Without finishers there is no need for suppliers, and without suppliers there can be no finishers. This is nothing new; it's been that way ever since the 1830's, when a Russian named Jacobi tried to invent a motor-boat driven by DC power, and discovered electroplating instead.

It didn't take long for people to recognize there were a vast number of potential applications for this new invention. Technology developed at an amazingly rapid pace. By the early 1840's, electroplating had advanced beyond being a simple laboratory curosity to where it was practiced on a commercial basis in many of the major cities in the Western World. As far away as the United States, installations began plating parts on a (limited) production scale, and a new industry - electroplating - was born.

The separation of this new industry into two distinct areas, finishers (i.e., platers) and suppliers, occurred almost immediately. Thus finishers and suppliers have been interacting with each other for almost 150 years.

Any relationship that old has necessarily evolved from what it was initially. Tracing the total evolutionary process is too complex to cover here. Besides, it's of little more than accademic value. Therefore, we'll focus instead on some of the most significant changes which have occurred during the past five to ten years, along with the underlying factors that have contributed to the changes. And, finally we'll peer into the future, and try to predict further changes that seem likely to occur within the next ten to twenty years.

Before beginning, let me offer the following "disclaimer:" the opinions expressed are strictly personal. And, although I've tried to maintain an objective viewpoint throughout, it's hard not to have personal attitudes influence thinking. Where critical comments are offered, it's done on both sides of the relationship, and with the sole intent of improving communication and interaction between finishers and suppliers in the future.

The early 1970's were generally good years for both suppliers and finishers. And why not? Inflation and interest rates were relatively low, so price increases were infrequent. Credit problems, by and large, were minimal, and many finishers and suppliers were comfortable carrying receivables that would be totally unacceptable today. Product shortages due to trimmed inventories were almost unheard of. Only a very few geographical areas in the United States required effluent treatment, so <u>real</u> ecological pressures were modest, if not almost non-existent. All things considered, it's no wonder earnings were typically very good to excellent for both finishers and suppliers.

The good economic times were apparent in the ways finishers and suppliers interacted with each other; communication was as open as can ever be expected, and suppliers willingly provided plentiful, high caliber technical service and

sales assistance. In fact, it was not uncommon for finishers to complain they saw too much of their suppliers.

In the middle seventies, however, things changed dramatically, and with remarkable speed. The oil embargo of 1974 taught us in a matter of months the extent to which our lives and economic well being are dependent upon the cost and availability of petro-chemicals. These lessons are still very much apparent today, over 10 years after the fact.

The Law of Supply and Demand affected each of us almost immediately. Product shortages (some real, and some artifical) occurred quickly as the heretofore plentiful supply of raw crude was cut off as OPEC members flexed their collective muscle in the Middle East. Prices of all energy intensive goods and anything that contained petro-chemicals skyrocketed. Inflation increased rapidly, reaching double digit rates. The money supply dried up, and interest rates rose accordingly. In essence, the good times vanished for most of us.

For those of us in the metal finishing industry, the lessons of the mid '70's were especially tough. In our personal lives we had to learn to conserve energy, and to accept long lines when we went to buy fuel for our automobiles. In our business lives, finishers and suppliers both had to cope with an unusual rash of product substitutions which necessitiated a certain amount of shoot-from-the-hip product and/or process development.

Companies reacted to these circumstances over the next several years in very predictable fashion. Price increases became commonplace throughout the mid to later seventies as platers and suppliers both tried to pass on their increased cost of doing business to their respective customers. As you would expect, this only worked to a limited degree. Not all the additional cost could be passed on, and operating profits either suffered, or disappeared altogether during this period. As an alternative means of reducing operating costs, both finishers and supplers trimmed services, and critically reviewed the scope of their businesses. Marginally profitable departments and functions were either combined with others, or gradually phased out altogether. High priced (and in some cases, highly skilled) personnel were laid off or offered early retirement. Accountants preached the merits and necessity of zero-based budgeting. Fundamentally, almost all business relationships were severely strained as controlling operating costs became the only path to profitability and, in some cases, survival.

These changes have continued even the past few years. For example, on the supplier side, many organizations have significantly cut back their technical service and research staff personnel. Additionally, there has been a conscious effort put forth to wean customers from depending upon frequent visits by supplier personnel. The expensive regular preventative maintenance visits by field service technicans have been greatly curtailed or eliminated altogether for all but the largest and most important accounts. No longer are separate service and sales personnel available on a routine basis as they once were. Salesmen today are expected to act as both the sales and the service representative.

While all these changes sound logical, and perhaps even reasonable, they have created some problems. In particular, some of the replacement personnel that have been moved in to fill the vacancies created by layoffs or retirements are not as experienced as their predecessors. Thus the caliber of representation has, in some cases, sufferred.

Also, many suppliers have cut back on analytical services which historically have been available on a gratis basis to active customers. Policy changes such as this have left many platers in a bind when it comes to routine control of their plating solutions. This, at a time when more solution control is needed to learn the operating idiosyncrasies of the newer, less toxic processes. It's no wonder the in-plant performance has often been less than spectacular.

Finally, many suppliers have closed regional offices, warehouses, and labs in an attempt to minimize operating costs. This has furthered strained many old relationships, particularily with the smaller and medium sized finishers.

Not all of the changes that have taken place have been on the supplier side of the relationship, however. The typical plating shop also operates differently today compared to 5 to 10 years ago. On average, there are fewer support personnel involved in solution control, new process evaluation, etc., today than there were several years ago. What has happened in most cases is that the personnel that had these responsibilities in the past have had them changed. They are now devoting full time to waste treatment, and effluent control, two functions that have assumed greater importance in the overall scheme of things.

There has also been somewhat of a finisher "backlash" to many of the changes suppliers have implemented. Specifically, supplier loyality has, to a large degree, become a thing of the past during recent years. We can all cite many long standing relationships that have fallen by the wayside as finishers have reacted to what they describe as "supplier neglect."

Similarily, the distinction between price and value has been lost with many finishers. More and more, price has become the preeminent buying motivation.

It would be wrong to imply that all of the changes that have occurred during the past 5 to 10 years in the finisher-supplier relationship are due to the economic conditions that have existed. Likewise, it would be wrong to suggest that all these changes have been bad for finishers and good for suppliers, or vice versa. In many cases the changes have been beneficial for both parties. For instance, even though solutions are typically analyzed less often today than in the past, the analysis, itself, is much more complete. New instrumentation and analytical techniques provide an almost complete "fingerprint" of the total bath, often even including decomposition products.

There are also, unfortunately, changes that have taken place which benefit neither party, but are necessarily to comply with current government regulations. Examples of this are split shipments of certain hazardous chemicals to meet D.O.T. requirements. It adds significantly to freight costs, and benefits no one but the trucking companies.

So much for reviewing where we are today, and how we got there. Let's move forward and try to predict what further changes are likely in how finishers and suppliers will interact during the next ten to fifteen years.

It's unlikely that overall economic conditions will change dramatically in the near future. Therefore, to predict how the relationship will evolve, we need to examine the effect of continuing pressure to reduce operating costs (on both sides of the relationship). Also, we need to look at how further technological developments in processes, instrumentation, and communication will alter interaction. Finally, to complete the picture, we need to consider the long range impact of some of the more recently enacted government legislation. All of these are important considerations for both finishers and suppliers, if we are to continue moving forward in the '80's and '90's.

Having thus defined the factors which will influence the evolution of the finisher-supplier relationship during the next decade or so, let's begin crystal balling.

* In-plant analytical techniques and equipment will change dramatically. Sending samples to a supplier for analysis will become a thing of the past in all but the most serious trouble-shooting situations. Computer controlled "black boxes" will handle this chore on-site routinely and with a high degree of efficiency. This could occur in the relatively near future since the analytical technology for this already exists; it's simply a matter of economics, which should improve as more and more finishers integrate the sophisticated equipment that is currently available into their plating operations.

* There will be greater and more efficient utilization of telecommunications equipment and technology by both finishers and suppliers. More communication (on both sides) will be by phone, rather than in person. This will include conventional phone conversations, as well as modem-to-modem communication. This computer-to-computer communication will likely include the transfer of analytical results and recommendations, trouble-shooting information, and order processing. Also, it's probable that many of the more progressive suppliers will offer technical training assistance to their customers via computers and/or closed circuit satelite television broadcasts.

* Considerably more time and money will be spent developing the skills of finishing shop employees. Many of the larger shops now go to great lengths to train their key personnel. What will change in the future is that more shops will implement similar programs that will include both in-depth technical training and exposure to basic management concepts. The technical training will be done in concert with suppliers, who have an important economic stake in developing customers that are as self-sufficient as possible. The management training will likely be done by the finishing companies themselves, or by outside organizations specializing in this type of training.

* The role of the typical service technician will change noticeably. Less of his time will be spent on routine problem solving in customers' plants. Improved training and greater in-depth communication between finishers and suppliers will allow platers to do more of this themselves. Instead, service technicans will spend a greater percentage of their time in cooperative en-

gineering efforts with platers. Complete finishing systems that will provide coatings with specific properties will be jointly engineered by finishers and suppliers.

* Both suppliers and finishers will focus their efforts on developing close relationships with larger accounts. Furthermore, as long as interest rates remain in the double digit range, payment habits will play a significant part in determining the degree of interaction that takes place with customers.

* Finishers will become increasingly objective in their choice of suppliers. They will place more emphasis on high caliber technical cooperation and expertice in a specific area of finishing, than on the price per pound or gallon of a given material. The net result will be fewer instances of plant-wide single source responsibility, but more instances of single supplier responsibility on a given processing line.

* Both suppliers and finishers will continue to become more specialized in their businesses. On the supplier side, it's likely many organizations will reduce the scope of their product lines to concentrate on fewer areas of activity in finishing. Whereas in the past it was common for a single supplier to sell everything from gloves to automatic plating machines, there will be more specialization in the future. The "jack-of-all-trades" supplier will, for the most part, exist only in those geographical areas where there are relatively few platers, and hence few suppliers locally.

To effectively develop and market this more specialized technology, it's likely that suppliers will further departmentalize, and internally create separate groups responsible for specific areas of high technology finishing. Certain to have their own departmental status are those groups working in technology relating to areas such as: finishing for the electronics applications, electroless plating, including plating on non-conductors; and highly sophisticated, microprocessor controlled plating and waste treatment equipment.

On the finisher side, we'll typically see fewer shops (both captive and job) attempting to provide as many different finishes to their customers as was the case in the past. This trend toward specialization is already evident in many of the shops that have been built within the past 10 years.

* More specialization by suppliers and finishers will probably also mean even tighter product liability controls in the future. As this occurs, we'll see a significantly greater reliance by both finishers and suppliers on electronic devices for automated process control. Ultimately, these control devices will become as commonplace in the finishing industry as calculators are now.

* Bilingual communication will become much more common than it is now. Several suppliers have already taken the first step, and now offer product literature, service information, and training information in Spanish, as well as English. In the future it's possible this will be expanded to include the so-called universal language, Esperanto.

* There will be significantly more international pooling of finishing information and standards. We have already seen this in the automotive and electronics industries. Standards that will apply on a world wide basis in many more industries are likely just a few years away.

In summary, then, the finisher-supplier relationship will evolve in a manner which continues to reflect the innerdependence that exists between the two parties. What has generally been viewed as a "partnership, with each side having a vested interest in the success of the other," will develop into more of a marriage, with an even greater committment to joint success.

A quotation from the popular book, IN SEARCH OF EXCELLENCE, might help to illustrate an attitude which must tipify the finisher-supplier relationship in the future. It comes from the chapter, "Close to the Customer."

> "Probably the most important management fundamental that is being ignored today is staying close to the customer to satisfy his needs and anticipate his wants. In too many companies, the customer has become a bloody nuisance, whose unpredictable behavior damages carefully made strategic plans, whose activities mess up computer operations, and who stubbornly insists that what he purchases should be one of the highest quality at the lowest possible cost."

The finishers and suppliers of the 21st Century must remain entrepreneurial. This cannot change, for without profits there can be no progress. What must develop in the future, which is not part of the relationship now, is a greater understanding of the needs of the other "partner." In other words, what the one side needs from the other that will make things better, more efficient, and ultimately more profitable for both parties.

There are many factors which have not been considered here that could also affect the finisher-supplier relationship in the future. Examples are: additional government legislation; the international economy, and the strength of the US dollar versus other currencies; etc.. A sensible discussion of these topics, quite honestly, is left to others with more expertice in these areas.

I-2

Management Session I

Computers In Day-To-Day Management

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COMPUTERS IN DAY-TO-DAY MANAGEMENT

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I-3

Management Session I

Evolution Of Quality Control In A Job Shop Environment

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EVOLUTION OF QUALITY CONTROL IN A JOB SHOP ENVIRONMENT

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I-4

Management Session I

Working With Your People

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WORKING WITH YOUR PEOPLE

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J-1

Light Metals I
Session J

Electrolytic Coloring of Anodized Aluminum for Decorative Finishes

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ELECTROLYTIC COLORING OF ANODIZED ALUMINUM FOR DECORATIVE FINISHES

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Atlanta, Georgia

ABSTRACT

While the primary development and introduction of electrolytically colored finishes into the U.S. market had its impetus in architectural applications as an alternative to integral color anodizing, further work with the process has lead to applications pertaining to other decorative finishes, such as, automotive trim. Many of the electrolytic colors are more stable than the organic dyes, which has resulted in an accelerated interest for a variety of applications. This paper will present a comparison of electrolytic coloring methodology with the existing methods of dyeing and integral coloring and will elaborate on the advantages and disadvantages of these three coloring processes.

INTRODUCTION

Electrolytic coloring of anodized aluminum surfaces has been commercially dominant in Europe and available, but not widely used, in the U.S. for almost 15 years. Its principal use has been for architectural Class I (A44) finishes with a minimum film thickness of 18 microns (0.7 mil) [1]. Prior to 1980 the primary method of achieving such finishes in the U.S. had been with the integral color anodizing process (A42). However, since 1978, when Reynolds International, Inc. introduced electrolytic coloring of anodized films to form an equivalent product with greatly reduced energy requirements, the electrolytic coloring process has taken over very quickly in the architectural market in the preparation of decorative finishes that are highly durable and fade-resistant for exterior applications [2]. These products have found wide acceptance in such building applications as store fronts, railings, curtain walls, doors, and windows. The finish is also being used in automotive applications, primarily for car bumpers and trim [3]. Other applications include builder's hardware, such as, shower enclosures, light standards, shelving brackets, and a variety of products, such as, boat masts, signs, belt buckles, picture frames, cookware, and camera housings.

There has been a need for more-durable colors to complement the present system of organic dyeing, which results in colors having only a moderate resistance to fading in Class I (A43) and Class II (A33) exterior applications [4]. Dyed finishes are more commonly found in the decorative class (A23) with films of 8-10 microns (0.3-0.4 mil), which are used for non-architectural aluminum products [5]. Electrolytic coloring has the capability of fulfilling many of these applications.

Since there are advantages and disadvantages to any of the systems, it is necessary to understand these processes, to be able to compare them to the applications anticipated, and to decide which would be best for those applications.

ANODIZING [6],[7]

An understanding of color anodized finishes, of necessity, requires an understanding of the anodizing process. Anodizing utilizes an aqueous conductive solution (electrolyte) and a direct current which passes through an aluminum work piece (immersed in the electrolyte) called the anode (because of it's positive quality in the circuit) to the cathode (which is the return to the power supply). The electrochemical reaction which takes place on the surface of the work piece is simply the oxidation of aluminum which forms a cellular oxide film. The film is strongly adherent to and provides corrosion protection for the underlying metal surface. Since the resultant anodized film is essentially transparent and highlights the metal surface beneath, the first decorative films were simply based on the "natural" appearance of the aluminum after being cleaned up and etched or chemically brightened.

The cellular structure of the anodic oxide has microscopic cavities, called pores (Figure 1.), which penetrate the cells, stopping at a barrier layer of oxide which completely covers the metal surface [8]. As evidence of the presence of these voids, pure, crystallized aluminum oxide has a density of 3.5-3.9g/cm^3, while a typical value for an anodic oxide film is 2.32g/cm^3 [9]. Other more direct evidence is available from electron microscopy of anodized films using ion backscattering of the cross-section of the pore structure [10] or using scanning electron microscopy (SEM) of an enlarged pore structure (Figure 2.) on the surface of an anodized film, such as occurs with phosphoric acid [11].

These pores result from one principal factor--dissolution of the aluminum oxide by the electrolyte. This dissolution occurs in competition with the oxide formation reaction, which is a function of the concentration of electrical energy (current density) at the metal surface [12],[13]. Several parameters in the anodizing step control these competing reactions and affect the size of the pores and the density of the aluminum oxide. In order of importance, they are:

1. Temperature.
2. Acid Content.
3. Sloping or Ramping.
4. Current Density.
5. Voltage.
6. Air Agitation.
7. Aluminum Content.
8. Electrolyte Additives.
9. Alloy.
10. Alloying Constituents.
11. Electrolyte Impurities.
12. Metal Impurities.

Control of only some of these parameters will not be beneficial, as others, individually or together, if ignored, can negate the desired qualities. It is important to know and understand the effects of all of them.

The electrolyte solubility properties are principally controlled by the temperature and the acid concentration of the

electrolyte, while the electrical properties are controlled by sloping, current density, and voltage. Variations of these parameters can produce a variety of oxide films having different qualities, which can be designed to produce a variety of commercially desirable anodized aluminum products.

Conventional Anodizing [14]

Anodizing electrolytes can be composed of chromic acid, phosphoric acid, or sulfuric acid, as well as lesser known conductive chemicals. The electrical supply may consist of DC power only, AC power only, AC imposed on DC, or pulsed DC power. However, the most versatile, least expensive, and most easily operated method of anodizing is with a sulfuric acid electrolyte and a low-voltage direct current. Common conditions include temperatures of 18-30°C (65-85°F), 150-190g/L (14-17%wt) of sulfuric acid, 14-18 volts DC, and current densities of 0.9-1.6amps/dm^2 (8-15amps/ft^2). Within these ranges the process is referred to as "conventional anodizing". The film quality requirements are voluntarily controlled by specifications which act as guidelines for product consistency [1]. These conditions will produce an anodic film which is corrosion-resistant, attractive, and functional for non-aggressive applications, such as, interior, commercial, and personal-use items, and exterior residential finishes.

Industrial Hard-Coat [14]

Having provided a means of protection against corrosion by "intentionally oxidizing" the surface of the aluminum under controlled conditions, the next most important quality of the film is abrasion resistance. The principal concerns related to this quality are handling the product without marring the surface, lengthening the time of service in exterior applications, and increasing surface to surface wear resistance, where contact is either stationary or moving. However, because of the presence of the pores, the hardness and abrasion resistance of the anodic film may be significantly reduced. Knowledge of the effects of altering the anodizing parameters has resulted in methods which diminish pore size, increase oxide density, and increase the hardness of the film, resulting in improvement in ease of handling and versatility of use.

The principal parameters controlled are temperature, acid concentration, and power, but the other parameters will also affect ultimate hardness, and they must be considered in determining the end use of the product and the hardness desired. The temperature of the electrolyte will be colder, -10°C to +10°C (14-50°F), and the acid concentration (sulfuric acid being the most commonly used) will range from 180-215g/L (16-19%wt). Voltages may vary from 20-80 volts DC as current densities are controlled from 2.9amps/dm^2 (24amps/ft^2) to 5.0 amps/dm^2 (45amps/ft^2). There are several processes which utilize some or all of these factors to create an extremely abrasion resistant aluminum oxide film.

However, because of the reduction of the pore size which occurs in these processes, the industrial hard-coat films do not lend themselves to subsequent coloring techniques, and they are generally not used for decorative applications.

Organic Additive (15)

Because of the high energy requirements for producing hard-coat films at low temperatures (high refrigeration costs) and at high current densities and voltages (high power costs), studies were carried out to determine if there were chemical means of controlling electrolyte solubility, which creates the greatest problem in achieving a hard film. The work resulted in greatest problem in achieving a hard film. The work resulted in the use of a variety of possible organic chemicals, which, when added to the electrolyte, reduced the dissolution effects within the oxide pore. The additives enter into the oxidation process and reduce the reaction temperatures at the base of the pore. In varying quantities ranging from 1-2%vol each, hard finishes can be produced at room temperatures of 15-21°C (60-70°F), moderate current densities of 2.6-3.9amps/dm^2 (24-36amps/ft^2), and moderate voltages of 18-30volts. It was also determined that film growth would continue up to five mils at room temperature, while under conventional power conditions film growth was limited to about two mils with dissolution offsetting film growth. With this process, films can be devloped with a significant reduction in the energy costs associated with other hard-coat practices. Also, these films can be colored and thus be used in the production of decorative finishes.

Superimposed AC [16] and Pulsed DC [17],[18]

For the same cost-reduction reasons used for the multipurpose anodizing electrolyte work, methods have been developed which alter the power supply rather than the chemistry of the anodizing step. With superimposed AC, a constant direct current is generated on the load to a certain voltage level, over which is added an AC voltage which fluctuates between a desired higher level and the minimum, constant DC. With pulsed DC, a direct current is applied to a certain voltage level, either a minimum or a maximum, and then, using special electronic controls, the DC voltage is moved up or down within those limits in a pulsing manner. Both the amplitudes and the freqencies of the superimposed AC and the pulsed DC processes can be varied as desired. Varying the power supply to the load provides energy relief to the electrochemical reaction taking place within the pores, allowing a cool-down to occur. This results in a cooler running reaction, a reduced dissolution factor, smaller pores, increased oxide density, and thus, an increased hardness. While these processes have been introduced to industry as hard-coating techniques, their compatibility with electrolytically-colored, anodized films has not been established.

COLORED ARCHITECTURAL FINISHES [6],[7]

Early in the history of anodizing, the quality of porosity was found to lend itself to a tremendous variety of decorative options. These microscopic cavities were able to receive and retain materials within the pore, which would impart colors to the final finish. Thus began a series of investigations (which continue to this day) relating the conditions under which the film is generated to the resulting cellular structure's ability to take on color, and determining how this might be utilized to produce a variety of decorative anodized aluminum products.

Organic Dyeing

The first technique utilizing porosity for coloring was based on intensely colored organic chemicals, dissolved in an aqueous solution, into which the anodized load of parts was immersed. The colored solution penetrates the pores of the film, and the organic material is adsorbed from the solution onto the inner surface of the aluminum oxide cell. When the load is removed and rinsed the adsorbed material, remaining within the film pore, imparts a color to it. Because the process is so simple, a large variety of colors have been developed. However, not all dyes were found to be suitable for all applications. Studies showed that the dye is generally adsorbed in the pores very near to the surface of the film, which makes the color more susceptible to loss over time from natural abrasion (which occurs to all anodized films), and from the bleaching rays of sunlight, since the chemicals are organic and are in a transparent film.

Over the years much research has been done on the multitude of organic dyes available and most have been categorized into classes of usage. There are many dyes which can be expected to give good exterior service, while many other dyes are suited only to interior service--protected from sunlight and weathering conditions.

Inorganic Dyeing [19]

Recognizing the color stability limitations of organic dyes as early as the 1930's, alternate compounds were sought which might provide more stable colors. It was believed that inorganic colored compounds would provide this answer. In order to generate many of these compounds, chemical reactions had to take place between two different species which would lead to a colored complex or precipitate. Since it was necessary that this reaction take place within the pore of the anodized film, two separate chemical solutions were prepared. The anodized load was immersed into the first solution for a specified time, removed, rinsed, and then placed in the second solution. The chemicals in the second solution would carry out a chemical oxidation/reduction reaction, which caused the colored complex or precipitate to form within the pore. Upon rinsing and sealing, if the material was stable enough, the anodized film would then have a decorative color. Over the years various studies have been done on many of the inorganic reactions which can occur under these circumstances and their colored products evaluated

for stability. Most of these compounds were found to generate only weak to moderately intense colors of which only a few were stable enough to be useful. In the U.S. the only commercially successful process has been dyeing with ferric ammonium oxalate to produce a gold color. The success of this process is due to its single tank operation with the color precipitation reaction occurring in one immersion step instead of two separate immersion steps. The only other process that has had any commercial use is the reaction between cobalt acetate and potassium permanganate solutions, which produces a light to medium gold-bronze color. Other reaction products include sulfides, chromates of heavy metals, ferrocyanides (Prussian Blues), and other metal-organic complexes. However, because of the two or more multiple dips required after anodizing to generate color and the use of specialized or expensive chemicals, these processes have been considered too difficult and expensive to operate and therefore have never become commercially popular.

Integral color

Utilizing the basic principals of hard-coat anodizing, but changing the acid used from sulfuric to a sulfo-organic acid and keeping the aluminum concentration under strict control, a method was developed which imparts an earth-tone color at the same time the part is being anodized. Depending upon the amount of anodizing (film thickness), the color of the finish can be varied from a very light bronze to black. The main criteria which set this method apart from other anodizing techniques were the organic acid used, the low aluminum concentration in the electrolyte, room-temperature operation, high voltages, and moderately high current densities. Also, the quality of porosity was no longer a factor in producing color since the color became an integral part of the lattice structure of the oxide film during anodizing [20]. The result of the process was not only a colored finish, but also one with extremely good abrasion-resistance or hardness (similar to those of the hard-coat processes) and color-fastness. The singular disadvantage was that the finish appearance was sensitive to variations of alloying constituents. From this there developed a series of specially-produced alloys which were compatible with the process. At the same time a group of alloys were developed which could be used to vary the bronze effect and produce a gray tone. The integral color anodizing technique has been and continues to be the standard of the architectural industry, but because of its present-day, prohibitive production cost, it is rapidly being replaced with electrolytic coloring methods.

Electrolytic Coloring [21]

This process returns to the system in which anodizing is first carried out to desired specifications in sulfuric acid and then followed by coloring in a subsequent step. The basis of the second step is electrochemical with an alternating current being passed through the load and the electrolyte, in which the load is immersed, in such a way as to reduce a dissolved metallic ion to

metal within the pores near to the base of the anodized film (Figure 3.). This deposits an elemental coloring agent, which is not as susceptible to the oxidation and bleaching energy of sunlight and is in a location away from the film surface where weathering takes place.

Because the anodic film is generated independently of the coloring step, the process is more flexible in producing a variety of film qualities with respect to hardness and finish appearance followed by addition of the desired color. It is also less sensitive to variations in alloy composition, because particulate is not trapped within the film structure. Special alloy controls are not necessary, however, it must be remembered that the film is transparent, and alloy variations that affect the appearance of the clear anodized film or the base metal surface will be noticeable in the final colored finish.

Multipurpose Anodizing Electrolyte & Electrolytic Coloring

As mentioned before, one of the important factors involved in providing an acceptable, exterior, architectural-quality finish is the resistance to abrasion. The integral color process has served this requirement well for many years, but, because of rising power costs in recent years, the electrolytic coloring methods, which require less energy, have become more attractive. However, in order to compete with the finish quality of integral color, it was necessary to combine the electrolytic coloring technology with hard anodizing technology [22],[23]. Since the two steps are independent of each other, this was readily possible, and a process exists which combines the two methods to produce an abrasion-resistant, champagne to black, color-fast, architectural finish which is comparable to the integral color finish. Used in this manner the clear anodizing tank can be used for conventional anodizing, hard-coat anodizing, or preanodizing for electrolytic coloring.

Interference Colors [24],[25]

Although not new technology, interest in the commercial potential of this technique has only recently developed because of increased interest in the electrolytic coloring methods. The basis of this operation is in an additional anodizing step using phosphoric acid as the electrolyte, which is used after a sulfuric acid anodic film is generated. The load is passed to the phosphoric acid anodizing electrolyte, where because of the increased solubility properties of the phosphoric acid in conjunction with the passage of a direct current, the pores are enlarged at their base. When this film is passed to the electrolytic coloring tank, the deposited metal takes on a different quality of light interference and diffraction, and the colors produced are different than the expected bronze tones. Colors that have shown some degree of promise include blues, maroons, and greens. However, as yet there has not been a commercial demand for this technology, possibly because of the additional step needed to produce the color effect.

Overdyeing of Electrolytic Coloring [26],[27]

This is another process which has also seen accelerated interest because of the recent activity of electrolytic coloring. In this process the aluminum is anodized, electrolytically colored, and then immersed in an organic dye solution just as would be done for regular dyeing. The result is the overdyeing of different bronze tones to create an expanded group of colors which could not be generated by either process individually. There are several interesting colors which have been created in this manner, some of which are now in commercial production in Europe and to a lesser extent here in the U.S. As explained before, there are limitations of use because of stability, but several dyes are available which are sufficiently stable for exterior application, which could result in some interesting looking buildings in this country. Overdyeing also requires an additional step in the total coloring process.

PROCESS COMPARISONS [28]

In describing the various processes, several points have been made about the advantages and disadvantages of each of them. It is now time to take a look at them in a directly comparative manner. There are several factors which would influence a decision as to which process might be best for a given application. Since there are many differences between plant operations and their finished product requirements, none of these factors will apply to all plants. Each plant must choose a process carefully in order to satisfy its own specific needs.

There is a great deal of information on any of these items of comparison so it is not practical to present all of the details pertaining to any particular one. Again, the goal will be to present an understanding of what is involved in the selection process, rather than making a recommendation of one process over another in any specific application.

Alloy Response

The most common anodizing-quality alloy is 6063. This probably accounts for 80+% of all architectural anodizing work, whether residential, commercial, store front, or curtain wall. However, there are many other alloys which can be anodized, plus there is a large variety of 6063 alloys which have been developed with significantly-varying alloying constituents. For many years this was a serious problem for the integral color process, because of the way the color tended to form. Particulate from the surface of the base metal is trapped in the oxide layer imparting the color. This particulate is mostly aluminum with the result being that the film develops a bronze tone. However, it was soon learned that variations in silicon or iron content in the alloy interfered with this color in the form of adding gray particulate and/or reducing specularity. This required a specific alloy for all anodized products, which could not be substituted. Other alloys were eventually developed which were capable of producing different finish appearances such as gray.

However, this required an expensive alloy preparation and has not been used for many years. Because of the wide spread variety of anodizers, from those who do their own extruded or rolled products to those who do anybody's, it has become impossible to control the variety of alloys and alloying ingredients used and most anodizers have to be able to do just about anything.

This problem has enhanced the attractiveness of using the electrolytic processes because they are not as sensitive to alloy variations. Most any alloy is suitable for anodizing, although there are some that will not produce an anodized film of a quality worth coloring. Usually these are the high silicon and copper alloys, which are limited to either heavy-film, hard-coat uses or to thin film, dyed decorative uses. The electrolytic processes, which are independent of the film produced, lend themselves readily to thin or thick films and to conventional or hard-coat finishes. This is not to say that there is no variation, but to say that the variation that occurs results in a less-noticeable difference and also, that, because the two steps are independent, the process can be run to compensate for the anticipated result. This can be very cost effective, especially if there is no control over the supply of metal. Dyeing will respond in a similar manner to electrolytic coloring, since it also is a two-step system [5].

Color Possibilities

Integral color is a single bath operation which was designed to produce colors from light bronze to black. In some cases it could produce other colors, if special alloys could be obtained. However, this has not been practical nor cost-effective, and the integral color process today has available only the light to dark bronze range. The gray finish is no longer available because of the high cost of special alloying, and the black finish is no longer produced because of its high power cost.

Dyeing is much more versatile with respect to the variety of colors that can be produced. However, this process requires a variety of solutions which may or may not be interchangeable. In the past this has required several tanks--one for each color. New technology has been developed which allows for spraying the dye solution onto the previously anodized parts. This requires one special spray tank and several smaller solution storage tanks, which supply the solutions to the spraying mechanism [29]. A large variety of colors are available, but, as stated before, they are not all compatible with all applications.

With the electrolytic coloring processes there is also a variety of colors available. Like the dyes, the metal salt baths produce one color each. However, that color can vary in intensity to produce a large variety of shades. The bronze bath will produce shades from champagne to black going through a number of bronzes. Other baths can produce gold (comparable to FAO gold), red, blue, yellow, and green, with each one requiring a different electrolyte. It is possible to interchange the solutions within the same tank with rinsing between changes, but it is more desirable to have individual tanks available.

Capital Investment

The capital investment involved in the various choices can be summarized in the following table. (Since this information can not allow for all the possible combinations of plant operations, the table summarizes what would be required for a specific change to a particular process.)

TABLE 1

Anodizing Process	Tanks	Rectifiers	Rinses	
Clear/Convent.	1	1	2	
Hard-Coat	1	1	2	
MAE*	1	1	2	
Color Process				**Preanodize**
Dye	1/Color	0	2	Yes
(or two tanks for all colors [29])				
Integral Color	1	1	2	No
Electrolytic	1/Bronzes	1	2	Yes
(Other Colors)	1	0	0	Yes

(*Multipurpose Anodizing Electrolyte)

Besides the anodizing tank, rectifier, and rinses, integral coloring requires an acid purification unit for control of the aluminum content. Although no rectifier is needed, dyeing usually requires that the coloring solutions be heated [5]. With electrolytic coloring, one tank is needed for the bronzes and another tank for the other colors, but one rectifier serves all colors, and the rinses can be shared.

Energy Consumption

Energy consumption can be summarized as follows:

TABLE 2

Process	Rectifier Power*	Process Time	Coating Thickness	KWH per ft^2/mil
Clear/Convent.	12ASF@18V	25min	0.4mil	0.225
Hard-Coat	24ASF@40V	63.5min	2.0mil	0.508
MAE**	24ASF@23V	22.5min	0.7mil	0.296
Dyeing	(Heating)	15min	0.4mil	0.048***
Integral Color	24ASF@70V	28min	0.7mil	1.120
Electrolytic	6ASF@15V	3min	0.7mil	0.0045

(*ASF=Amps per Square Foot)
(**Multipurpose Anodizing Electrolyte)
(***This value is KWH/ft^2 and is based on an open 5000gal tank heated up each day from 70°F prior to use and operated at 150°F for 8 hours/day to dye four 800ft^2 loads/hour of conventionally anodized aluminum having a film thickness of 0.4mil [30]. Two anodize tanks would be required to keep this tank full.)

and as follows:

TABLE 3 [31],[32]

Process	Heating Needs	Cooling Needs	Refrigeration Tons/10,000Amps
Clear/Convent.	No	Yes	34
Hard-Coat	No	Yes	81
MAE*	No	Yes	58
Dyeing	Yes	No	(See TABLE 2.)
Integral Color	No	Yes	180
Electrolytic Color	No	--	--
Bronze to Black	No	Yes	15 (3,000Amps)
Others	No	No	--

(*Multipurpose Anodizing Electrolyte)

Sample Energy Cost Comparison Calculations

While the previous tables summarize the relationships of one process to another, the following sample calculations show the manner in which the energy values in Table 2 were achieved and use those values to make a cost comparison. (The values used in these calculations are "typical" values for a given process, but do not necessarily represent the values experienced by any "particular" plant's operation, which may be higher or lower. Each individual plant would have to "plug in" its own values.)

$$\frac{\text{ASF* x Volts}}{\text{1000Watts/KW}} \times \frac{\text{Time(min)}}{\text{60min/Hr}} \times \frac{\text{Cost(¢)}}{\text{KWH}} = \text{Cost/Ft}^2$$

Calculation Formula

(*ASF=Amps per Square Foot.)

Electrolytic Color VS Integral Color

1. Electrolytic Color

a. Anodize Step (Clear, Sulfuric at 24ASF)

$$\frac{\text{24ASF x 23Volts}}{\text{1000W/KW}} \times \frac{\text{22.5min}}{\text{60min/Hr}} \times \frac{\text{8¢}}{\text{KWH}} = \text{1.656¢/Ft}^2$$

b. Electrolytic Color Step

$$\frac{\text{6ASF x 15Volts}}{\text{1000W/KW}} \times \frac{\text{3min}}{\text{60min/Hr}} \times \frac{\text{8¢}}{\text{KWH}} = \text{0.036¢/Ft}^2$$

c. Total Cost = 1.692¢/Ft²

2. Integral Color

a. Anodize and Color Simultaneously

$$\frac{\text{24ASF x 70Volts}}{\text{1000W/KW}} \times \frac{\text{28min}}{\text{60min/Hr}} \times \frac{\text{8¢}}{\text{KWH}} = \text{6.272¢/Ft}^2$$

3. Energy Savings

$$100\% - \left[\frac{1.692¢}{6.272¢} \times 100\%\right] = 73.0\%$$

The energy savings achieved on architectural finishes with electrolytic coloring over the integral coloring is quite significant and explains why the change is occurring so rapidly to the two-step anodizing process. However, since interest is also moving in the direction of non-architectural decorative finishes, it is useful to make a comparison of electrolytic coloring with organic dyeing.

Electrolytic Coloring VS Organic Dyeing

1. Electrolytic Coloring

   a. Anodize Step (Clear, Sulfuric at 24ASF to 0.4mil)

$$\frac{24\text{ASF} \times 23\text{Volts}}{1000\text{W/KW}} \times \frac{13\text{min}}{60\text{min/Hr}} \times \frac{8¢}{\text{KWH}} = 0.957¢/\text{Ft}^2$$

   b. Electrolytic Color Step

$$\frac{6\text{ASF} \times 15\text{Volts}}{1000\text{W/KW}} \times \frac{3\text{min}}{60\text{min/Hr}} \times \frac{8¢}{\text{KWH}} = 0.036¢/\text{Ft}^2$$

   c. Total Cost $= 0.993¢/\text{Ft}^2$

2. Organic Dyeing

   a. Anodize Step (Clear, Sulfuric at 12ASF to 0.4mil)

$$\frac{12\text{ASF} \times 18\text{Volts}}{1000\text{W/KW}} \times \frac{25\text{min}}{60\text{min/Hr}} \times \frac{8¢}{\text{KWH}} = 0.720¢/\text{Ft}^2$$

   b. Dyeing (15min @ 150°F, see Table 2)

$$0.048\text{KWH/Ft}^2 \times \frac{8¢}{\text{KWH}} = 0.384¢/\text{Ft}^2$$

   c. Total Cost $= 1.104¢/\text{Ft}^2$

3. Energy Savings

$$100\% - \left[\frac{0.993¢}{1.104¢} \times 100\%\right] = 10.0\%$$

The significance of this calculation is not the apparent 10% cost savings of electrolytic coloring, since this could be altered by operational practices and productivity on the part of either process, but the closeness of the two processes; that is, electrolytic coloring is not necessarily more costly to operate than dyeing.

CHOOSING A PROCESS [6],[28]

The choice of a process to produce decorative anodized products is not easy. It is likely to be even more difficult if certain steps are not followed and criteria adhered to. The most common mistake is to put investment cost considerations ahead of process considerations. These should come last in the list and be the factor which determines if you can afford to do what you need to do. The following list of guidelines, in order of importance, may help in making such decisions.

1. Product Line--What products will be produced for what purpose? Will there be a single product or a variety of products?
2. Film Quality--What film qualities will be needed for these products? Remember that the anodized film is the functional part of the finished product, not the color. If the film does not perform well, then the value added by color will be zero. Therefore, it is necessary to determine the quality specifications required for the product line [1]. These qualities include corrosion resistance, coating thickness, coating weight, coating density, and abrasion resistance [9].
3. Anodizing Method--Which anodizing method will provide the needed film qualities for a variety of products or a single product? What is the compatibility with desired color products?
4. Color--What color or colors are desired? Is the coloring method compatible with the anodizing method?
5. Color Qualities--Are they durable for the intended product line (color-fastness)? What color variety is available?
6. Line Availability--How will the anodizing and color steps fit into present line operation (retrofit)? Is there space available? If the plant is to be new, greater flexibility of choice exists.
7. Productivity--With the product line(s) established, it is necessary to forecast productivity, in order to size equipment.
8. Pollution/Effluent Guidelines--This is becoming an extremely important criteria in a process selection for any given location. Chemical compatibility of the waste stream is essential to an approved process.
9. Operational Cost Comparison--At this point it becomes important to evaluate the individual processes and determine their operation costs and evaluate profitability, based on the previous items.
10. Capital Cost--Having established the previous values, the investment costs can be determined along with the potential profitability and eventual payback of any improvements. It is at this point that cost factors can be shifted around or compromises made. However, the original parameters of film quality should not be altered to achieve a cheaper system, because, in the long run, product quality will determine product acceptability.

CONCLUSION

The following table presents a summary of the advantages and disadvantages of the various processes which have been discussed:

TABLE 4

Anodizing Process			Abrasion Resistance	Energy Cost	Capital Investment
Natural			Low	Moderate	Moderate
Hard-Coat			High	High	High
MAE			High	Moderate	Moderate
Coloring	Color				
Process	Variety	Fastness			
Dyeing	High	Low	Low	Moderate	Moderate
Integral	Low	High	High	Very High	High
Electrolytic	Moderate	High	High	Low	Moderate

While it is necessary to weigh all the advantages and disadvantages of these processes and to decide which one(s) would serve a particular product line, electrolytic coloring has developed into an excellent choice between the cost and color variety limitations of integral coloring and the large variety of dyes with durability limitations. Electrolytic coloring has the potential to provide whatever quality of anodized film is desired followed by a selection of durable colors.

****

References

[1] "Designation System For Aluminum Finishes", Publication No.45, The Aluminum Association, Inc., Washington, D.C., 1980.

[2] "Coloring Advances Sharpen Anodizing's Competitive Edge", Modern Metals, May 1983, pp 20-28.

[3] R. W. Mahn, "Electrolytic Coloring For The Automotive Industry", Plating and Surface Finishing, The American Electroplaters' Society, February 1984, pp 40-42.

[4] D. C. Montgomery, "The Coloration Of Anodic Coatings For Architectural Applications By Using Organic Dyes", Plating and Surface Finishing, The American Electroplaters' Society, December 1978, pp 48-50.

[5] F. P. Stiller, "Coloring Anodized Aluminum", Metal Finishing Guidebook Directory, 1984, Vol 82-1A, pp 469-474.

[6] A. W. Brace. and P. G. Sheasby., "The Technology of Anodizing Aluminium", Technicopy Ltd., England, 1979.

[7] S. Wernick and R. Pinner, "The Surface Treatment and Finishing of Aluminium And Its Alloys", Robert Draper Ltd., England, 1972, Volumes I and II.

[8] H. L. Craig, Jr. and E. F. Barkman, "Current Status of Anodizing Theory", Aluminum Finishing Seminar, The Aluminum Association, Chicago, March 19-21, 1973, A4.

[9] "Standards For Anodized Architectural Aluminum", Publication No.46, The Aluminum Association, Inc., Washington, D.C., 1978.

[10] P. G. Sheasby, "Electrolytic Colouring--Processes and Properties", Aluminum Finishing Seminar, The Aluminum Association, St. Louis, March 1982.

[11] D. J. Schardein, "Plating On Anodized Aluminum", Plating and Surface Finishing, The American Electroplaters' Society, February 1984, pp 64-67.

[12] G. H. Kissin, "Mechanism of Anodic Coating Formation On Aluminum", Anodized Aluminum, STP 388, ASTM, 1965, pp 34-61.

[13] R. C. Furneaux, "Recent Anodizing Theory and Its Implications", Aluminum Finishing Seminar, St. Louis, March 1982.

[14] D. Thomas, "Anodizing Aluminum", Metal Finishing Guidebook Directory, 1984, Vol 82-1A, pp 458-468.

[15] K. H. Dale, U. S. Patent No. 3,524,799

[16] M. Lerner, "Energy For Cooling Low-Voltage Hard Anodizing Baths For Aluminum", Plating and Surface Finishing, The American Electroplaters' Society, August 1983, pp 60-63.

[17] J. L. Woods, U.S. Patent No. 3,857,766.

[18] J. L. Woods, "A New Hard Anodizing Process For Aluminum", 63rd Annual Technical Conference, The American Electroplaters' Society, Denver, Spring 1976.

[19] J. M. Kape and E. C. Mills, "The Production Of Coloured Anodic Films Without The Use Of Dyestuffs", Transactions of the Institute of Metal Finishing, 1958, Vol 35.

[20] E. Szontagh, A. B. Kiss, and E. Kocsardy, "Porous Anodic Aluminium Oxide Layers With Oxygen Deficiency", Aluminium English, Aluminium-Verlag GmbH, Germany, 1983, Vol 59-9, pp E307-E309.

[21] R. W. Mahn, "The Relationship Of Electrolytic Coloring To Clear Anodizing Techniques", 70th Annual Technical Conference, The American Electroplaters' Society, Indianapolis, June 1983.

[22] A. J. Walsh, U. S. Patent No. 4,179,342.

[23] G. R. Darrow., U. S. Patent No. 4,180,443.

[24] J. Sato, "Some Improvements In The Electric Colouring of Anodized Aluminium", Plating and Surface Finishing, The American Electroplaters' Society, March 1978, pp 53-55.

[25] P. G. Sheasby, J. Patrie, M. Badia, and G. Cheetham, "The Colouring Of Anodized Aluminium By Means Of Optical Interference Effects", Transactions of the Institute of Metal Finishing, 1980, Vol 58, pp 41-47.

[26] C. Th. Speiser, "New Dyeing Systems On Adsorption Basis For Anodized Aluminium", Transactions of the Institute of Metal Finishing, 1980, Vol 58, pp 121-127.

[27] D. C. Montgomery, "The Coloration Of Anodized Aluminium Architectural Compoments By The Overdyeing Of Integral or Two-Stage Electrolytically Colored Oxide Films", 67th Annual Technical Conference, The American Electroplaters' Society, June 1980.

[28] J. Schrantz, "Anodizing Aluminum", Industrial Finishing", February 1981, pp 16-22.

[29] C. Th. Speiser and E. Gruninger, "Why Spray Dye Anodized Aluminum", Products Finishing, June 1984, pp 60-66.

[30] T. Richards, "Heating Plating Solutions", Metal Finishing Guidebook Directory, 1984, Vol 82-1A, pp 783-786.

[31] "Aluminum Finishes Process Manual", Reynolds Metals Company, 1973, pp 73 and 74.

[32] J. Gesumaria, "Cooling Of Plating Solutions", Metal Finishing Guidebook Directory, 1984, Vol 82-1A, pp 788-794.

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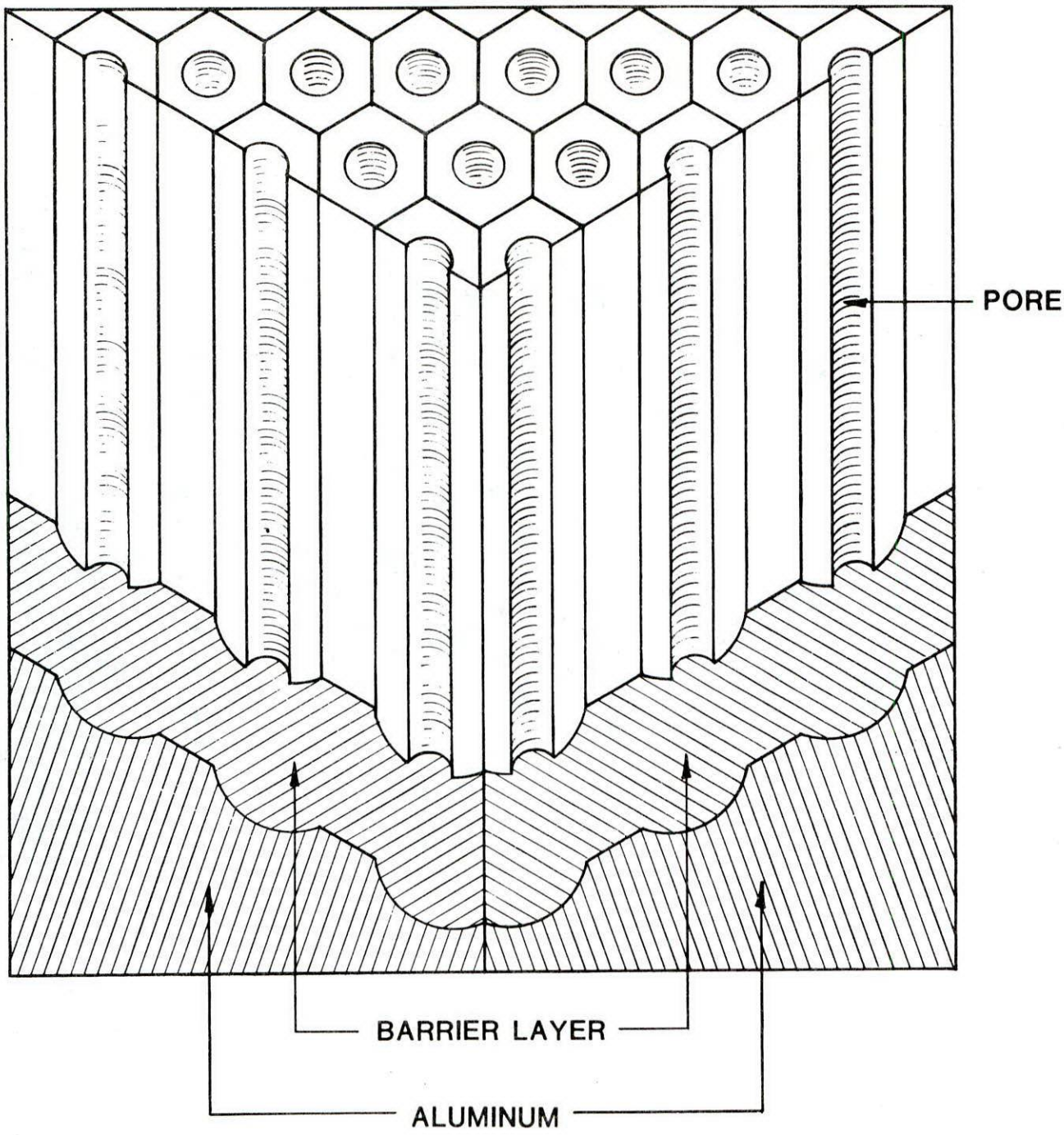
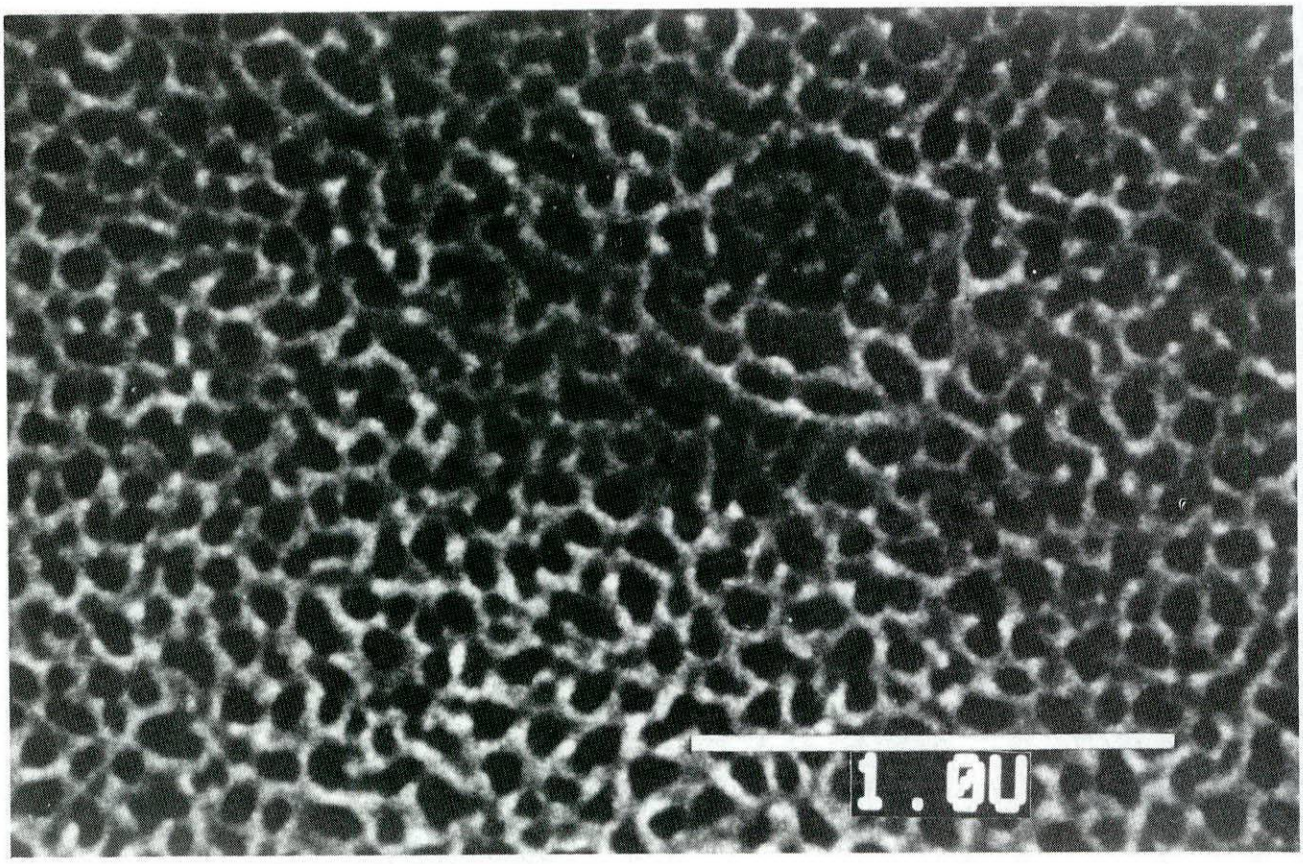


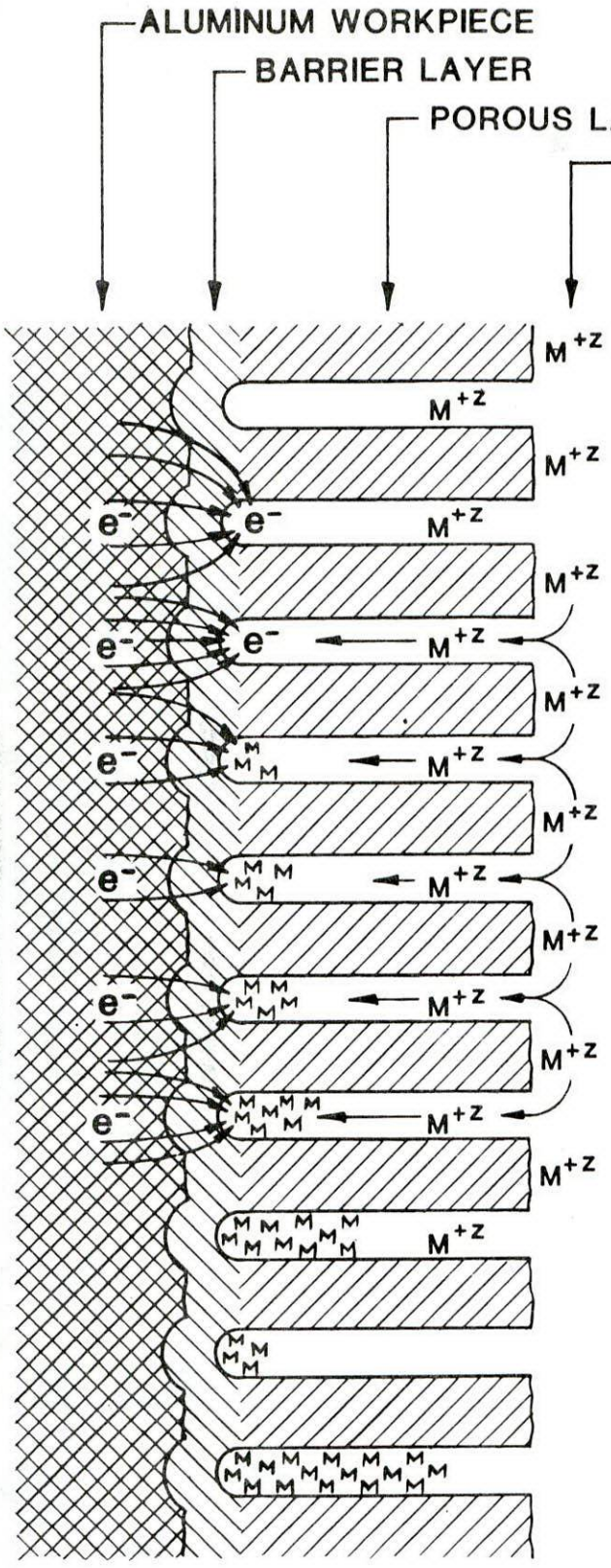
THREE - DIMENSIONAL SCHEMATIC OF ALUMINUM OXIDE FILM

FIGURE 1.



SURFACE VIEW BY SEM OF ANODIC OXIDE PORE STRUCTURE AFTER 10-MINUTE PHOSPHORIC ACID ANODIZING CYCLE (X36000)

FIGURE 2.



1. FILM PORE - ELECTROLYTE AND METAL IONS DIFFUSE INTO PORE.
2. POWER ON - ELECTRONS (e^-) FLOW INTO PORE AT BASE.
3. METAL IONS MIGRATE TO ELECTRON SOURCE.
4. METAL IONS PICK UP ELECTRONS AND DEPOSIT AS METAL (M).
5. RESISTANCE INCREASES TO ELECTRON FLOW. (INCREASE NEGATIVE VOLTAGE OVER POSITIVE VOLTAGE.)
6. POWER ADJUSTED - MIGRATION OF METAL IONS INCREASES.
7. AS METAL DEPOSITION CONTINUES COLOR INCREASES.
8. POWER OFF - FINAL COLOR IS ACHIEVED.
9. EXAMPLE - CHAMPAGNE
10. EXAMPLE - BLACK

THE ELECTROLYTIC COLORING STEP

FIGURE 3.

J-2

Light Metals I
Session J

Improved Electrolytic Coloring Of Anodized Aluminium Using Tin Electrolytes

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Paper not received in time for printing

IMPROVED ELECTROLYTIC COLORING OF ANODIZED ALUMINIUM USING TIN ELECTROLYTES

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Paper not received in time for printing.

J-3

Light Metals I
Session J

Electrolytic Coloring of Anodized Aluminum Using Nickel-Based Electrolytes

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ELECTROLYTIC COLORING OF ANODIZED ALUMINUM USING NICKEL-BASED ELECTROLYTES

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INTRODUCTION

The application of electrolytic two-step anodizing processes have become so commonplace that it is scarcely necessary to review the fundamentals of the process in an introduction to a paper on the topic. Nevertheless, a brief review must state that aluminum can be anodized by a conventional process such as sulfuric acid anodizing to produce a colorless film. Then, in the second step, a metal salt solution, buffered to some more or less acid state, is used to deposit the metal into the pores of the oxide to produce a colored film in the gold-bronze-black range. This film can then be sealed in any one of a number of sealing baths to yield a decorative and protective surface whose color is lightfast, and which has the protective qualities at least as good as a clear anodized surface.

Anodized finishes produced in this manner now almost completely dominate the market once held by integral color anodic finishes. Since the introduction of the first commercially viable process based on the Asada patent(1) and marketed under the Anolok trademark, the generic process has proliferated into a bewildering array of proprietary processes, almost all of which are based on salts of cobalt, nickel and tin as the coloring elements. In the United Kingdom, Europe and North America, the dominant processes use cobalt or tin whereas in Japan several nickel based processes are commercial (2). Each process claims certain advantages, but each also suffer certain problems. For example, tin processes appear to be the easiest to use, once the stability problem of the divalent tin is overcome, but the tin processes also are faced with a smut problem if the pores are over-filled (3). Also, the tin deposition appears to be not as uniform on a microscopic level as that produced in cobalt or nickel. The average thickness of the tin in the pores is higher, but some microscopic areas contain little tin (4). For this reason, tin processes requrie thicker films to produce black colors, ie 0.5 mil compared to 0.3 mil for cobalt. It has been claimed that tin stringers, reaching almost to the surface of the oxide could provide pathways for corrosion although this has not been borne out by testing (3,4).

Comparing cobalt and nickel, one finds that cobalt electrolytes are easier to operate and have higher tolerances for bath contamination than nickel electrolytes, however, cobalt is more expensive and cobalt prices are subject to greater fluctuations than nickel. Black colors can not be obtained with cobalt on film thicknesses of less than 0.3 mil.

The principle questions raised in selecting a system should be the following:

Bath Stability

Cobalt and nickel baths are quite stable. The stability of tin baths depends on the additive stabilizers and even the best additives cannot completely prevent tin (II) oxidation.

Contaminant Sensitivity

Tin baths appear to be the least sensitive to contamination with cobalt next and nickel last. It has been claimed that contamination is a problem with nickel baths. This problem has been greatly reduced.

Electrolyte cost

The price per pound of metal is lowest for nickel, but this is not the only consideration. The chemical formulation of the metal, the bath concentration and the quantity of metal necessary to produce a given color must also be considered.

Drag-out losses

Two factors need consideration here. The economic factor requires a decision to dispose of dragout or to recycle. The environmental factor determines whether the drag-out can be dumped or must be recycled or otherwise treated. Most tin losses appear as stannic oxide, which has resale value and does not generally present an environmental hazard. Economics would appear to dictate a cobalt recovery program whereas nickel recovery is dictated by both environmental and economic considerations.

Throwing power

Cobalt and tin baths appear to be satisfactory in this regard with properly formulated baths. Nickel was thought to be not as good but new technology has proven nickel to be as effective.

Power supply for coloring

Most commercial power supplies are simple 60 hz AC units which are interchangeable from one process to another although some of the tin and mixed tin-nickel processes use a more sophisticated and expensive supply.

Anodizing and film thickness requirments

All of the color processes require careful control of the anodizing process to achieve uniformity and reproducibility. The tin process require a sligthly greater film thickness, generally, to produce darker colors than cobalt and it has been claimed that black colors are impossible with nickel. New technology has overcome this. The purpose of this paper is to describe a color anodizing process using nickel electrolytes which has most of the advantages of the presently available commercial processes and few of the disadvantages (5,6).

GENERAL DESCRIPTION OF THE PROCESS

The color bath is a nickel salt solution which may be made up from one of several simple nickel salts. The distingushing feature of this process is that it uses a higher concentration of nickel in combination with a higher operating temperature in the color bath. This combination is synergistic. A higher temperature at ordinary nickel concentration offers no benefit and, conversely, a higher nickel content at ordinary temperature offers no benefit. The combination, however, results in higher rate of nickel deposition.

The higher bath temperature offers an additional important advantage. Evaportion losses of water from the color bath provide head space in the color tank so that drag-out from a series of counter-flowing rinses is put back into the color tank.

The ultimate drag-out from the rinse decreases roughly by a factor of 5 for each additional rinse, so that with three successive counter flowing rinses the drag-out from the last rinse is reduced to a very manageable level.

A third distinct advantage of this system is that with three counter flowing rinse tanks, the drag-out from the third rinse has been reduced to a point at which the work may go directly into a nickel based seal at a concentratin such that it serves as nickel make-up for the seal. Ultimately, then, the only nickel drag-out losses are those that the anodizer would experience from a nickel seal bath alone. Since the color bath components are completely compatible with the seal, this minimizes the contamination of the seal bath.

TECHNICAL DESCRIPTION OF THE PROCESS

Relation of the Color Generation Rate to the Color Voltage The depth of the color generated is related to the color voltage and also to the operating time. Either one of these parameters may be used for process control. Figure 1 shows the weight of nickel deposited per unit area as a function of the coloring voltage for a fixed time of 10 minutes. Figure 2 shows the weight of nickel deposited for a given voltage as a function of the coloring time. In both series the nickel in the film was detemined by an x-ray spectroscopic method.

Relation of the Color Generation Rate to the Nickel Content and Bath Temperature

These data, obtained from a small,carefully controlled bench scale experiment, are shown in Table I. Usually, a nickel content in the coating of 0.1 mg/cm^2 or greater will produce a black color and this was observed here also. All of the panels were black with the exception of the first one at the lowest temperature and nickel bath content. In a production facility, the color generation rate is generally decreased by as much as a factor of 2 by several scale-up conditions. Examination of Table 1 suggests, therefore, that a black color would be difficult to obtain except at the highest temperature and nickel bath content shown under these conditions. The results also show the synergistic effect of nickel content and temperature. At 25°C an increase in temperature from 25 to 50°C increases the color rate by about 50%, but at about 90 g/l Ni the same increase in temperature increases the color rate by 100%.

Control of Drag-out Losses

The rinse system is shown schematically in Figure 3. An equilibrium will be established in the rinse tanks that depends principally on two factors: the drag-out rate, D, and the bath evaporation rate, V. The equations relating the rinse concentrations to these factors are

$$\text{3rd Rinse} \quad C_3 = \frac{C_0 D^3}{VD^2 + D^3 + V^3 + V^2 D}$$

$$\text{2nd Rinse} \quad C_2 = \frac{C_0 D^2 + C3V\,(V + D)}{V^2 + VD + D^2}$$

$$\text{1st Rinse} \quad C_3 = \frac{C_0 D + C2V}{V + D}$$

where C_0 is the concentration of Ni in the bath and C_n (n=1,2,or 3) is the concentration in each rinse. Curves calculated for the three rinses as a function of drag-out rate for a reasonable evaporation rate are shown in Figure 4. By making sure that the parts drain well above each tank before going into the next tank, it is entirely possible to reduce the value of C_3 to about 1 or 2 g/l of nickel. Air agitation in the color tank, while not necessary for the coloring operation, is useful to increase the evaporation rate.

The Problem of Spalling and Bath Contamination

One of the major problems encountered by all two-step color processes is the phenomenon oxide spalling, in which small, pinhead size areas of oxide pop from the substrate, exposing bare metal. In the extreme, large sheets of oxide may detach.

This occurs if the AC color voltage is too high and aggravated by the presence of sodium or potassium ion contamination in the bath. It is more of a problem with alloys containing about 1.5% or greater magnesium. We have also shown that, even if the oxide does not spall on coloring, it may be susceptible to spalling voltage. We have established a limit of about 200 ppm sodium for the common automotive alloys, 5252 and 7029, but have operated as high as 2g/l sodium for the architectural alloys with no problem. We also have two highly promising proprietary procedures which should push these limits even higher.

The discussion of spalling in the literature usually suggests that it is the result of hydrogen evolution at the metal-oxide interface which cannot escape fast enough and physically blasts the oxide from the surface. We speculate,instead, that it is the result of a hydrogen embrittlement phenomenon since it appears to occur most frequently with those alloys that are susceptible to this. One of the effects of hydrogen embrittlement is that hydrogen atoms enter the metal crystal lattice, causing it to expand. If this expansion occurs relative to a rigid oxide lattice to which it is attached, the adhesion of the oxide to the metal will be destroyed. This mechanism is currently under investigation in our laboratory and forms the basis for one of the methods of limiting its effect. In any case, in a practical sense, spalling is not considered to be a problem with this process, except marginally in the case of the automotive alloys.

Throwing Power

The effect of the increase in nickel content on throwing power is shown in table 2, for a series of metal strips colored at 50^0C. In this series, the strips were positioned perpendicular to a single counter electrode and the nickel content of the

oxide after coloring was measured as a function of the distance from the end of the strip. This shows that the throw of nickel into the oxide farthest from the counter exlectrode is about doubled by an increase in the bath nickel content from about 25 g/l to 90 g/l. Qualitative observations on pilot and production scale suggest to us that the throwing power of the coloring bath is almost as good as that of the sulfuric acid anodizing bath itself. This may, in fact, be due to a fortuitous circumstance. We have found it easier to produce darker colors on thin oxide films than on thicker ones. With recessed areas, for example, on complicated extrusions, the sulfuric acid anodized films will be thinner in the recesses than on more open areas, closer to the cathodes. When the part is colored, these recessed areas, having a lower film thickness will then preferentially receive color because of the film thickness effect and this will tend to balance out the color on the part.

Coating Performance

Coatings prepared by this process have been tested in the laboratory for acid dissolution, fading on UV exposure, abrasion resistance, for acid dissolution, CASS and salt fog performance. They have been placed on outdoor exposure at two marine sites and one industrial site. Controls were equivalent panels anodized in sulfric acid, but not colored, and intergral color coatings. Coatings were prepared on 5005 and 6063 alloys and were sealed in a proprietary nickel acetate seal.

Two series were placed outdoors. The results are not yet complete, however, the first series showed no pitting after 18 months at the industrial site. The test was terminated at 18 months at one marine site. All panels showed some pitting, but the pit count for the nickel colored panels was the same as that of the controls of equivalent thickness.

The accelerated test results shown in Table 3, 4 and 5, show the nickel colored panels to be equivalent to clear sulfuric acid panels in all respects and equivalent to intergral color panels in all respects and abrasion resistance.

Alloy Effect

The alloys 1199, 3003, 5657, 5005, 6061, and 6063 all behave very similarly with regard to the coloring rate and the relation between coloring rate and voltage. Also, spalling is a minimal problem with these alloys. The alloys 5252, 5182 and 7029 behave like the others at lower coloring voltages, but they spall just beyond the peak coloring voltage.

The only peculiar alloy problem, aside from spalling, that we have encountered was with one particular lot of 5005 alloy. Black colors could not be obtained on this metal. Examination by Scanning Electron Microscopy and Energy Dispersive X-ray (EDAX) revealed the cause of the problem. The problem lot of metal had about twice the density of large Al(Fe, Mn) Si and Mg_2Si second phase constituents as an alloy which colored normally. Some of these particles were occluded in the oxide film and wherever this occured, the particle "shadowed" the oxide to nickel deposition, leaving an excessive area of the oxide uncolored and resulted in a lighter color than normal.

REFERENCES

1. T. Asada, US Patent #3,382,160, May 1978.
2. J. M. Kape, Trans. Inst. Met. Fin., 1984, 62, 41
3. H. T. Gohausen and H. Puderbach, ALUMINUM, 1983, 59, No. 10, E379.
4. P. G. Sheasby, Aluminum Finishing Seminar Technical Papers. The Aluminum Association, March 30-April 1, 1982. p. 145.
5. P. W. Bolmer, Golden West Regional Conference of American Electroplaters' Society, Colorado Springs, Co., April 1, 1984.
6. B. R. Baker, R. L. Smith and P. W. Bolmer, US Patent #4,431,409, February 14, 1984

TABLE 2. NICKEL CONTENT OF OXIDE VERSUS DISTANCE FROM COUNTER ELECTRODE AS A FUNCTION OF BATH NICKEL CONCENTRATION

14 volt AC (RMS)
3 minutes
5205 Alloy

Distance from end of strip nearest counter electrode (cm)	1.5	7.5	14.0	20.0	% Decrease at 200 cm
Bath nickel concentration (g/l)					
23.8	0.081 mg/cm^2	0.037	0.025	0.022	73
32.6	0.084	0.039	0.029	0.025	70
44.2	0.078	0.042	0.032	0.030	62
64.2	0.087	0.050	0.039	0.037	57
88.6	0.087	0.051	0.041	0.039	55

Table 1. NICKEL CONTENT IN OXIDE AS A FUNCTION OF BATH NICKEL CONCENTRATION AND TEMPERATURE

14 VOLT AC (RMS)
10 minutes
5205 Alloy

Concentration of Ni in Bath (g/l)		23.8	32.6	44.2	64.2	88.6	% Increase Over Entire Conc. Range
Bath Temp (°C)	F						
25.0	77°F	0.094 mg/cm^2	0.100	0.118	O.114	0.102	9
30.0	86°F	0.106	0.127	0.130	0.131	0.156	47
35.0	95°F	0.117	0.138	0.155	0.170	0.172	47
40.0	104°F	0.129	0.146	0.162	0.177	0.192	49
45.0	113°F	0.141	0.151	0.158	0.173	0.194	38
50.0	122°F	0.131	0.138	0.153	0.171	0.198	51
% Increase over entire temp. range		39	38	30	50	94	

FIGURE 1

NICKEL CONTENT OF THE FILM AS A FUNCTION OF COLOR VOLTAGE 5205 ALLOY 10 MINUTES

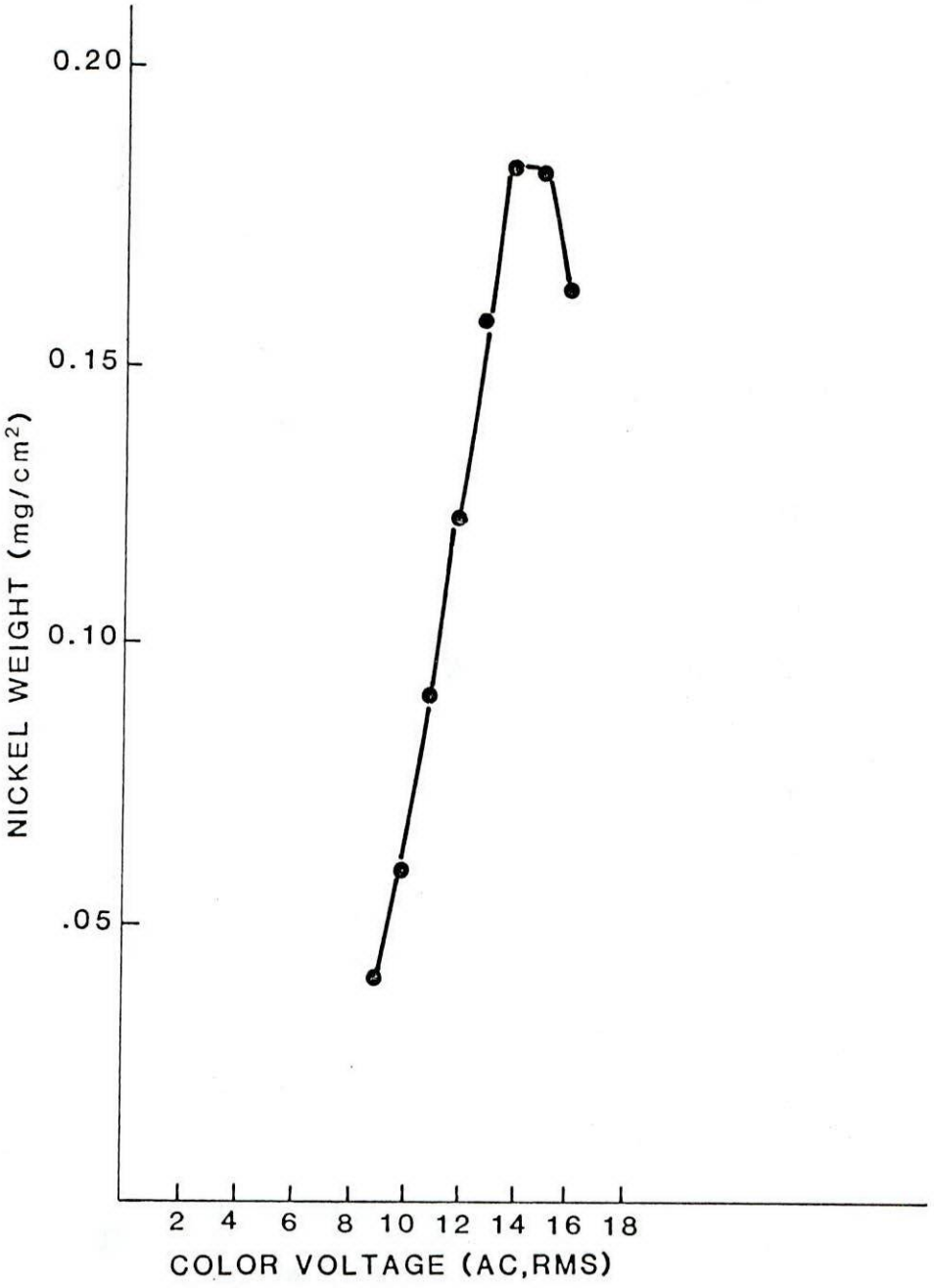


FIGURE 2

NICKEL CONTENT OF THE FILM AT
14 VOLTS AC AS A FUNCTION OF TIME

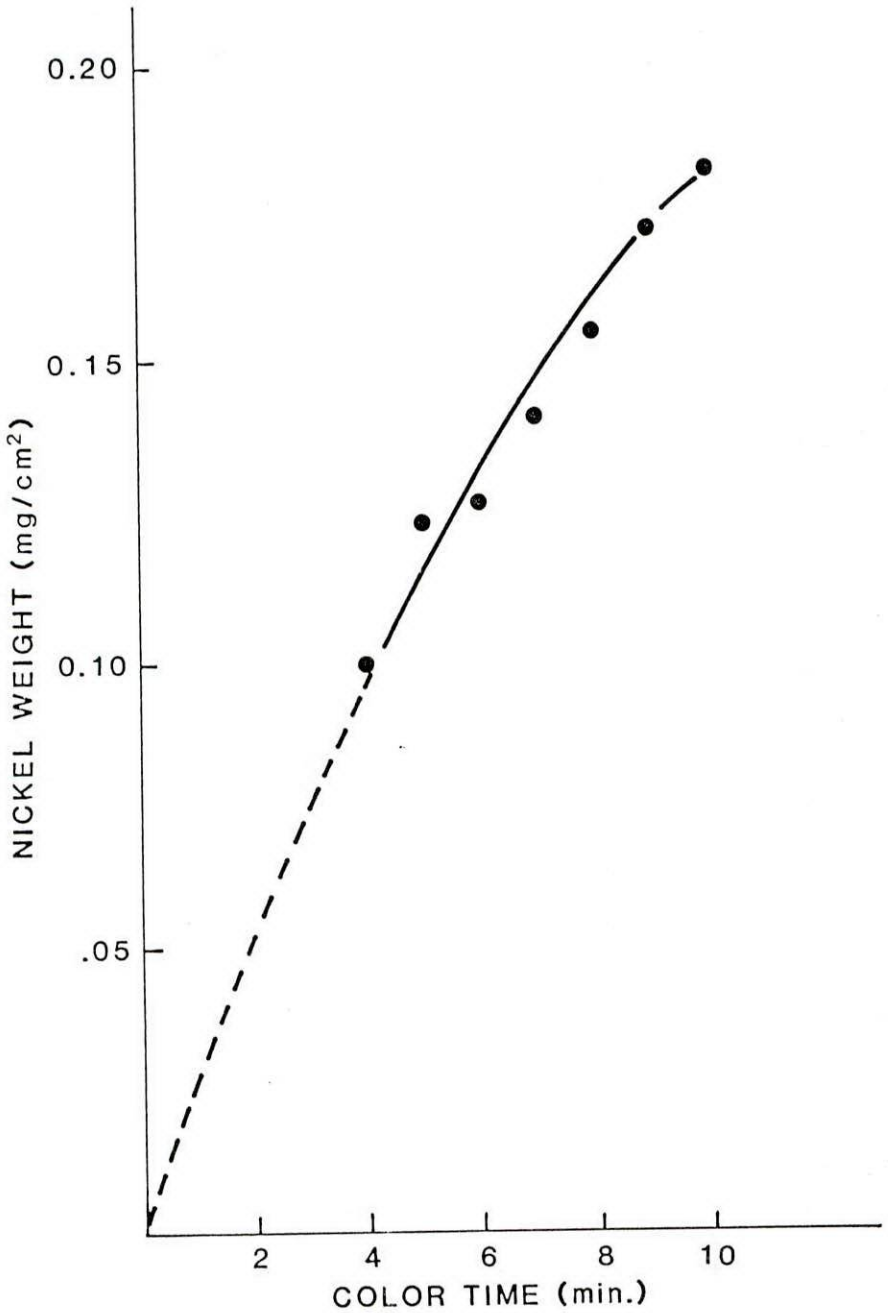


FIGURE 3

COUNTER-FLOWING RINSE SYSTEM FOR BATH RECOVERY

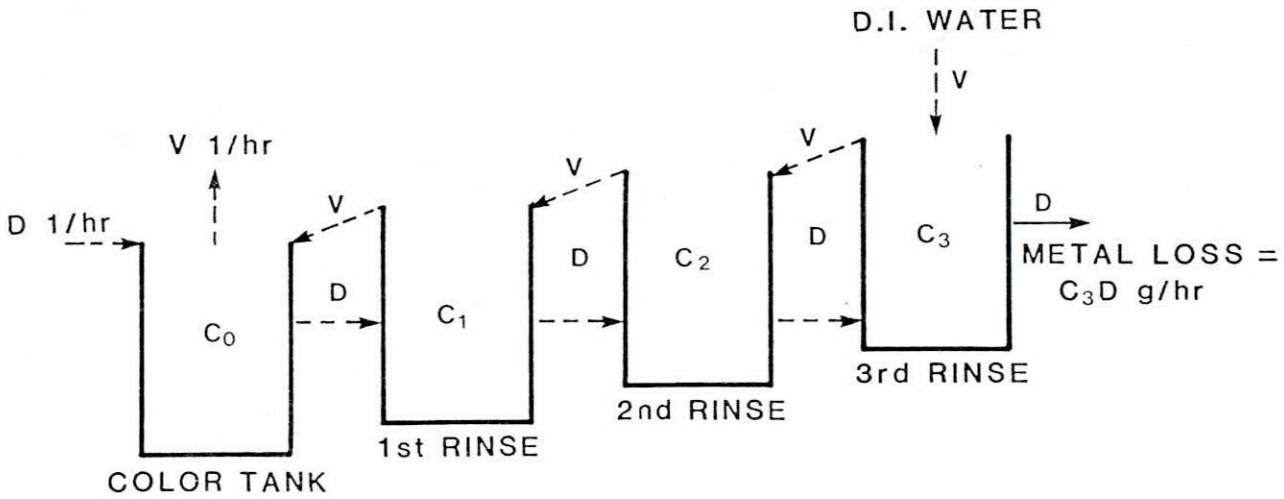
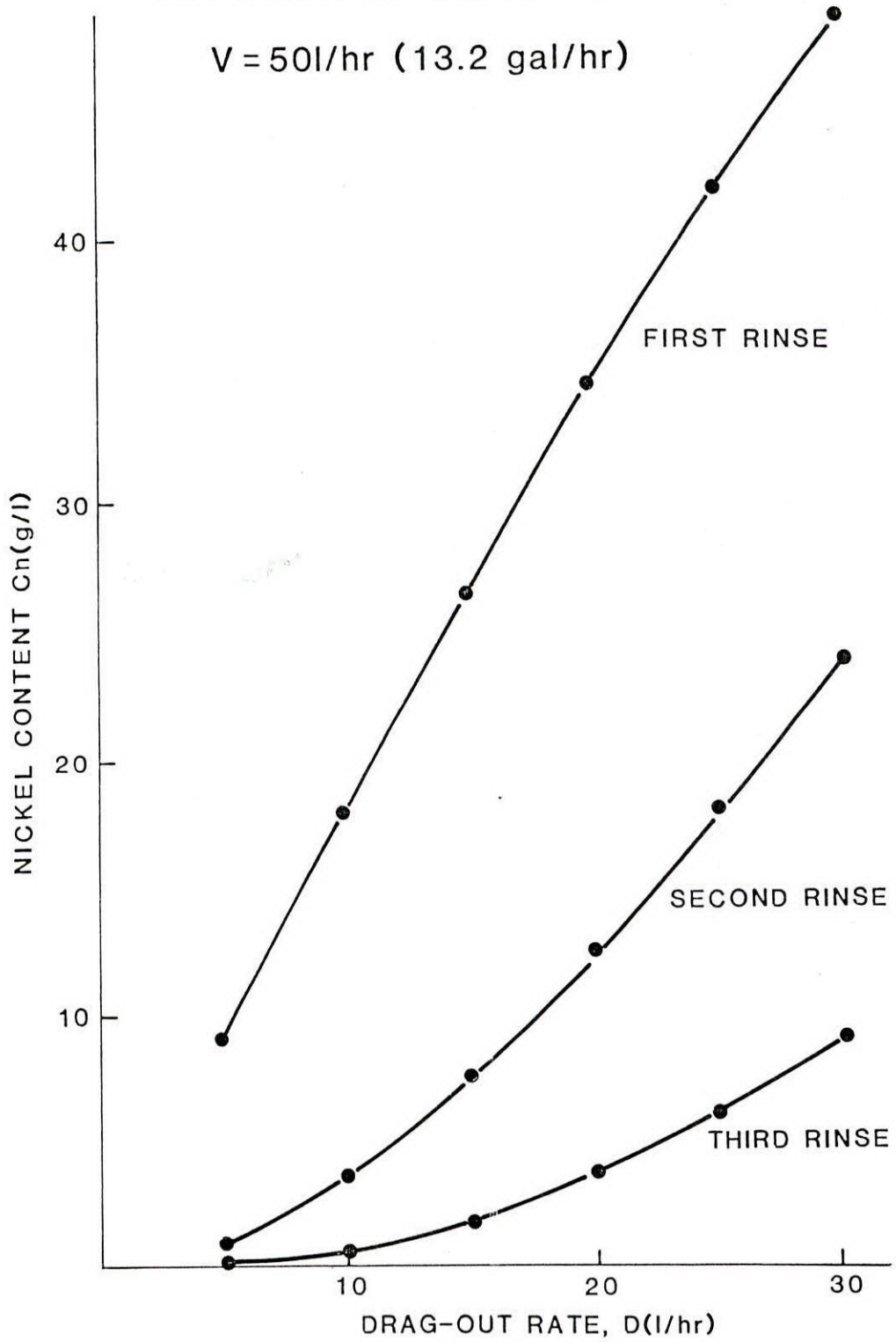


FIGURE 4

RINSE CONCENTRATION OF NICKEL AS A FUNCTION OF DRAG-OUT RATE



J-4

Light Metals I
Session J

Two-Step Electrolytic Color Specifications

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Paper not received in time for printing.

TWO-STEP ELECTROLYTIC COLOR SPECIFICATIONS

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J-5

Light Metals I
Session J

Analytical Control For The Decorative Anodizer

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Analytical Control for the Decorative Anodizer

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The need for process control is mandated by the depletion and contamination of the various baths each time a part is immersed for cleaning, brightening, etching, etc... The purpose of analysis is to keep the concentration of bath constituents or contaminants within acceptable limits. The range of conditions which produce quality finishes is determined by a combination of practical and technical factors as well as customer requirements. Reproducibility is not achievable if basic process parameters such as time and temperature are not maintained. Therefore, it is assumed that equipment and personnel operate consistently and that adjustments can be made as soon as a substantial deviation is noted. Also, the lack of simple procedures or workable equipment for chemical additions and bath decantations may negate any benefits derived from routine analysis. Since chemical makeup is discussed later, and adequate control equipment and supervision is assumed, we will first consider the basic lab equipment.

The initial equipment cost is within the reach of most finishing shops, especially if one considers the cost involved in using an outside laboratory, and possible savings in chemical consumption. However, the greatest benefit is the faster response time which results in fewer rejects and a smoother functioning operation.

For pH checks and titrations, a reliable pH meter is a must and is, of course, far more accurate and much easier to use than papers or indicators. The glassware required includes beakers, pipettes, burettes, flasks, graduated cylinders, etc... A magnetic stirrer and stir bars are very convenient, although not essential. One instrument which has proven to be quite useful in analyzing low concentration components and dye baths is the spectrophotometer. This is particularly important in detecting and eliminating interfering contaminants, although the $1,000 cost may be prohibitive at the onset of establishing a laboratory. A listing of equipment required is included in Appendix 1 and it should be noted that some items, although not essential, have proven to be real timesavers. Our experience is that most of the equipment lasts five years or more, so it is less expensive on a long term basis, to buy equipment which makes the analysis run quicker and easier.

In addition to hardware, chemicals are required to perform the various tests, and are available from either material suppliers selling bright-dip, etchants, cleaners, etc... or from lab and chemical equipment retailers. If one must make the solutions in house, then a good balance or scale, accurate to at least 0.1 gram, is necessary. The actual solutions required are listed with the titration procedures, Appendix 2.

Finally, a suitable location must be found for the laboratory. It is very important that its location be convenient to those that need it. We have found that some things are best close to the place of sampling even if the equipment gets more wear and abuse. The finest instrument is of little value if it is too difficult or time consuming to use, such that the `cure' of analysis is worse than the `ailment' of poor control. A pH meter, especially, is most useful if it is within 50 feet of the majority of the tanks which are to be checked. Therefore, it is conceivable that some items could be duplicated with the less expensive piece in the plant at ready access for quick control and the more expensive instruments in the laboratory for critical checks and final adjustments. Once the equipment is set-up, we can consider the actual types of tests which are routinely required.

The majority of the analytical procedures can be represented by a small group of method types of which the pH check is the simplest and the titration is the most common and useful. It is important to remember that although a method is simple and practical, the technician must always be careful with details or the value of the test may be seriously undermined. A good example is the pH test, which involves placing a probe in the sample and reading the pH directly from a digital readout or scale. The integrity of the reading may be in doubt if the slightest contamination is left on the probe from the previous sample or if the beaker is not properly rinsed. This is especially important when checking the sealing bath which is usually very pure water with little or no buffering agent to stabilize the pH. Therefore, it is advisable to pay close attention to the minute details and if the reading obtained is suspect it should be carefully rechecked.

Titrations are the most useful and most common of the analytical methods available to the aluminum finisher. Even the simple "dropwise" kits supplied with some proprietary cleaners are a crude, but useful titration. The basic concept involves consuming the active ingredient in the sample with a reagent which reacts with the active agent. A known volume of reagent is added until a pH or color end point is reached. The measured volume of reagent or titrant, is multiplied by an appropriate factor and the concentration of the sought after component is calculated. This method is usually used for routine control of cleaners, anodizing baths and etches, as well as for determining the amount of acid or alkali needed to neutralize a bath before dumping it. In the same category, although a bit more complex, is the titration involving the addition of intermediate reagents to convert or consume the active agent. This is often done because the reaction times are slow or the endpoint is too difficult to see without first converting the sample into a different form. This is demonstrated in the Aluminum in Bright-Dip Procedure where the aluminum is completely chelated and the excess chelant is titrated for, with a copper solution. By subtracting the amount of copper required from the amount of chelant added, one can calculate the amount of aluminum initially present.

For checking chemical bath composition the final class of tests are color comparative or spectrometric. As the name implies the test result is interpreted by the depth of color in a sample either originally or after the addition of one or more reagents. Here there is a determination or

comparison of colors. The more of a chemical species that exists in the sample, the deeper the color will be. The spectrophotometer is quite useful in that it reads out directly in known units, rather than requiring a visual comparison of the color. One obvious problem with the subjective visual color comparison is that colors are perceived differently by individuals and results can vary significantly. Therefore, the purchase of a spectrophotometer is highly recommended as it is useful for testing very low concentrations of contaminants in such baths as the seal, anodize and deionized (DI) rinses, as well as make up water and the boiler condensate. Dye bath concentration can also be measured either directly (after dilution) or after reacting or stripping the dyed parts. All in all, the instrument is worth its cost and is a marvel of simplicity to use.

The final group of tests discussed are not analytical, but rather performance oriented methods to evaluate the quality and integrity of the anodized surface. Such parameters including anodic thickness, weight, hardness, density, etc., are evaluated as well as the quality of the seal on the coating. Destructive and non-destructive tests are used with the former being the most common and most reliable. The actual details of these tests and the analytical methods previously mentioned will be briefly discussed later.

Once the basic lab concepts are understood the most important element in the control program to be considered is the personnel required. The procedures are clear enough that almost anyone can accurately perform the analysis, however, there must be a clear set of instructions available as well as a schedule of the tests required. We have had good success with having the anodizing line operators perform the tests at specified intervals. They have followed the procedures accurately and when checked, the results have been very reliable. The weak point in such a system is in the continual supervision required, to assure that the tests are performed on schedule and that appropriate adjustments to the process baths are always made.

A sample test schedule appears in Appendix 3 and the time required to perform these is less than two hours per day. The actual tests specified will differ for every plant and it is suggested that the production supervisor, plant engineer, foreman and chemical suppliers be consulted to better determine what particular tests are necessary. As with all plant procedures, schedules should be periodically reviewed and updated as needs change.

It is imperative that records be kept of all additions and dumps. A supervisor or foreman, who is convinced of the need for good process control, should review the sheets to assure compliance with the schedule and make recommendations and observations on the corrective procedures used. These records will also be quite helpful, in the case of a major failure, in determining the cause or causes. Addition records have also provided us with data required to institute a program of chemical conservation which has saved considerable material costs as well as reduced the effluent load.

Once the equipment has been procured, an area has been made available and people have been selected, we can look at a generalized anodizing facility

to discuss the specific tests and methods required. A typical flow chart is in Appendix 4 and the test procedures will be discussed in the order of work flow. All analytical procedures and instructions for making of standard solutions are listed in Appendix 2 so only general details and special precautions will be included in this text.

The first tanks in the anodizing line are likely to be cleaners. These are usually either mild alkaline or mild to strong acid based materials and are often proprietary in nature. Therefore, the supplier should be consulted and his recommended procedure for control followed. An acid cleaner for instance, which is phosphoric acid based, is controlled by titrating with 1 normal strength base (NaOH) to a pH of 4.0. The milliliters of titrant used is multiplied by a factor of .94 to get percent acid by weight and in the interest of simplicity, we have rounded the factor to 1, so that the acid strength can be read directly from the burette. The optimum range for this acid cleaner is 4-7%, so a daily check in the morning is more than adequate to assure consistancy. An addition of acid, which is reclaim from the aluminum bright dip, is made whenever the concentration drops below 4% or if the cleaner is not working well. Inadequate strength can be detected by grease, compound or water breaks on the parts. A pool of oil floating on the bright dip is a good indication that the cleaner is not doing it's job. For simplicity, the surfactant additive package is added to the cleaner on a ratio of volume basis along with the 35% phosphoric acid added to strengthen the bath. Here again observation of the bath is helpful in that the foam blanket height can indicate an excess or need of the surfactant additive.

The etch bath unlike the cleaner, must be held within a fairly narrow range to achieve good results. The procedure is a titration with two endpoints. The first giving the free caustic in the bath and the second indicating the dissolved aluminum. It is very important that if the aluminum level is above 20g/l that the free alkalinity (caustic) is at least half of the dissolved aluminum concentration. If there is inadequate free alkali the aluminum (rock hydrate) will deposit on the side walls of the tank never to be removed. It is rare for an anodizer to make this mistake more than once.

Since the strength of the etch affects the final appearance of the work and rock hydrate is so undesirable, it is recommended to analyze the bath at least once daily. If large amounts of work are etched per shift, additions to the bath can be made more frequently such as at the beginning and middle of the shift. Small dumps made more often rather than one large one, would also help keep the bath in balance. We use a spray which wets the parts down on removal from the etch bath to reduce the chance of parts staining due to drying in transfer. This has the added benefit of making our baths function similar to a 'never dump' etch in that a small amount is lost to overflow each workload which keeps the aluminum level from climbing too high. It is important when dumping the bath to retain a small portion to make up with the new bath. An etch with a very low aluminum concentration produces glossy, not matte finishes. It should also be noted that the etch bath is not a cleaner. It may remove oils and grease from aluminum but there is often a telltale stain left on the part and oils in the bath may cause excessive foaming, which increases the possibility of drying and

staining during transfer. The etch is possibly one of the most neglected baths in the anodizing line. The small effort required to properly control the operating conditions will be rewarded with consistent matte white finishes.

The most difficult bath in the line to control is the bright dip. The bath operates near or above the boiling points of nitric acid and water, which are the two major constituents, besides phosphoric acid. Therefore, if left alone enough water and nitric would be lost to evaporation such that the quality would be unacceptable and if allowed to continue, the bath could solidify into a hard mass of aluminum phosphate. Before discussing the analyses required for the bright dip, it is important to consider the need for precise control on the additions and immersion times used. This requires writing down the quantity of water and nitric added and when. Without a workable addition system, the most rigorous lab work will be of no avail as the bath reaches equilibrium very slowly.

Phosphoric acid is the major constituent in the bath and is added to raise the working level to make up dragout losses. Since the makeup acid has a lower specific gravity than the working bath, small additions are made to avoid adding too much water. If possible, no more than 5% of the total bath volume should be added at one time. Since the phosphoric makes up the main component in the bright dip, there is no apparent reason to analyze for it.

Water is lost to dragout and evaporation and some is dragged into the bath as well. The water concentration can be controlled by checking the specific gravity of the working bath at a constant temperature. Usually 75 F is used, however, that can be changed by 10 degrees or so as long as the same temperature is used each time. In taking the sample it is important to allow sufficient time for the small air bubbles in the solution to rise to the top of the sample before filling the cylinder and inserting the hydrometer. The specific gravity can range from 1.70 to 1.76 depending on operating conditions such as dissolved aluminum, nitric acid concentration and bath operating temperature. The optimum can only be found with experience using ones own particular alloys, but the bright dip suppliers are very helpful in choosing good operating conditions. Here again, small additions are better than large ones. Since little effort is required to check the specific gravity, it is a wise precaution to take a sample every few hours and note the time and check it after it has had a chance to cool. A small bench placed near the bright dip to hold some lab equipment, would serve well for this and other tests.

Nitric Acid is lost to the reaction, evaporation and dragout and is checked by titration using a reducing agent to consume the nitric. In performing this test, the technician must be careful to follow the procedure as results can vary. Here is where carefully, well documented additions really pay off. If the foreman is sure that the nitric has been added according to schedule and that no radical bath upset has occurred then he is not likely to be fooled by a deviant analytical result. The color of the bath gives an approximate indication of the nitric level but usually it is out of range before it is noticable. Since the nitric concentration affects the quality sharply it should be checked at least twice per shift and maybe more often

if there is poor control on additions.

The least critical check on the bath is the analysis for dissolved aluminum. If the bath is operated at equilibrium and dumps are small or nonexistent, then this check need only be performed once weekly. The aluminum concentration has a direct effect on cost of operation and if the aluminum level is consistently low, as much reclaim rinse as possible should be returned to the bath for economy.

Contamination due to dragin is a serious problem in a bright dip bath. Chlorides in the make up water which adhere to the parts will lower the specularity of the bath and in sufficiently, high concentrations will convert the bright dip to an acid etch. Therefore, if local water has Cl- levels greater than 2 PPM, only DI water should be used for additions and for higher Cl concentrations the work may even have to be rinsed in DI water before bright dipping. Prerinsing the parts in the reclaim rinse to which a few PPM of silver nitrate has been added helps reduce Cl- dragin and improves the economy of the bright dip bath by reusing some phosphoric acid. In severe cases silver nitrate can be added to the bright dip directly but only in concentrations of less than 10 PPM. (1)

Some heavy metals can poison the bright dip and are difficult to check for often causing the same defects as water and nitric imbalances. It is therefore important to be very careful not to immerse any parts in the bath which have plated surfaces or foreign metal of any type, i.e., rivets, screws, etc. Dragin of metals is also possible if a dirty pump is used or if buckets and sample containers are not well rinsed. It is recommended to designate equipment that is used only for bright dip samples and additions and then to rinse it well anyway. The only cure for heavy metals contamination is dumping all or some of the bath which is very costly. In the case of organic dragin, from the cleaner, etc., a dump may not be required but a few hours may be wasted waiting for the organic to break down. The time and money which is lost, when a dragin problem occurs, justifies taking every precaution against metallic and organic contamination.

Desmuts and deoxidizers are used in most lines but the supplier must be consulted for a control method as the active ingredients vary and are proprietary. Good results can often be achieved by observing the appearance of the work and simply adding when necessary. The only analytical procedures we find necessary for a nitric acid desmust is to determine the amount of caustic required to neutralize before dumping the bath.

The anodizing baths are simple to control but the frequency of dumps and additions is determined by the kinds of performance specifications to be complied with. The normal range of operating parameters is 160-200 g/1 sulfuric acid and 5-12 g/1 dissolved aluminum. For work requiring a minimum anodic thickness, or for dyeing, the sulfuric concentration should not vary more than +/- 10 g/1 from the optimum and specific applications or experience may dictate tighter control (+/- 5 g/1). Aluminum is dissolved from the anodic coating as it is formed and increases in concentration as the bath is used. Decantation or ion exchange is used to lower the aluminum

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1. Stauffer Chemical Company. Patent No. 3,410,803.

concentration but with decantation sulfuric acid must be immediately replaced as it is also lost.

The time required to calculate the concentrations in the anodizing bath and determine the correct dump and addition can be greater than to perform the actual analysis. If tight control is necessary it is helpful to provide a master sheet which shows the factors and equations used in the calculations. This eliminates the need to remember numbers, improves accuracy, saves time and is a permanent record. For those adept with computers or programmable calculators it is simple to put the calculation sheet computer program and the operator need only input the titration values to find the correct concentrations (see Appendix 5). Our simple program gives the sulfuric and AL concentration as well as suggests a possible dump and addition. It will allow the operator to specify either the quantity of acid to be added or the inches of level to be dumped and responds with the other parameter. This is especially helpful as we purchase sulfuric acid in 13 gallon units and it is much easier to add a full carboy than measure some fraction. With the anodizing analysis being performed at least 500 times yearly (4 baths X 125/yr) the few minutes saved are significant and the easier the procedure is the greater the likelihood that the analysis will be performed in the first place.

Phosphate contamination in the anodizing bath is a problem as P04 is easily dragged-in from the bright dip. Levels of 1000-2000 ppm P04 significantly degrade the quality of the anodic coating by rendering it unsealable, unreceptive to dyes, softer, and in some cases gray. The procedure for P04 analysis is listed and should be performed as often as practical experience dictates. Since P04 is only removed by dumping the bath it is best to eliminate the problem at the bright dip. Extra rinsing, warm water rinsing, and/or desmutting can all help lower the amount of P04 which migrates into the anodize. Do not use a rinse which is used just prior to sealing as the seal bath is much more sensitive to P04 contamination, than the anodize. Rinses should be carefully considered and their order of use rearranged if necessary to facilitate the best rinsing of parts after bright dip and to minimize the migration of P04 in to either the anodize or seal. In our case the addition of a spray booth rinse after bright dip reduced the P04 in anodize by 60-70% eliminating the need for special dumps just to lower the P04 concentration.

The most common sealing bath for decorative applications is the DI water seal. It is run at 210 F and at a controlled pH of 5.5-6.5 and various additives are available to help reduce smut formation on the surface if the seal is working well enough for smut to be a problem. It is best to control the pH at as high a level within the range as possible as higher values promote faster sealing. In most facilities the influx of small amounts of sulfuric acid from the anodize, causes the pH value of the seal to drop. If uncontrolled, the pH and rate of sealing will be unacceptably low. Initially the pH should be monitored at least twice an hour until experience shows this unnecessary. If the pH is low, additions of ammonia are made to raise it, and conversly acetic acid is used to lower it. The additives for smut prevention sometimes contain a buffering agent which helps to stabilize the pH. Sodium or ammonium acetate can be added in concentrations of

0.1-0.3 g/l to further stabilize the bath. This will cause the pH value to drop more slowly and reduce the frequency of monitoring necessary but it also increases the amount of ammonia required to raise the pH. It is helpful to determine the approximate amount of ammonia used and to make complimentary additions throughout the day. This will keep pH fluctuations to a minimum and simplify the control function.

Many chemicals are detrimental to the sealing bath with PO4 and silicate being the worst and most common. Concentrations as low as 5 ppm of either significantly degrades seal performance and 20 ppm poisons the bath completely.

Since the source of the PO4 migration has already been discussed we will concentrate on silicate which is present (5-10 ppm) in the raw water. SiO2 is dragged into the seal bath through the rinses but the most significant source is the DI plant itself. Unfortunately SiO2 is only loosely held in the resin bed, if at all. Therefore when the anion bed of the DI system is almost exhausted any introduction of a strong anion such as C1-, SiO2 etc. will cause the SiO2 to be preferentially released. This is not detected by the conductivity meter on the DI unit but immediat]y ruins the seal if this water is used for bath make up. It is not unusual to see concentrations of 100-200 ppm SiO2 in the DI water when this condition, known as silicate breakthrough occurs. The only way to eliminate this is to regenerate the DI plant frequently and to monitor the Di water or seal bath for SiO2. If significant SiO2 is still detected the DI plant should be checked and if necessary the regenerations performed more frequently. In some cases the resin should be replaced or the system upgraded. If seal specifications must be met it is especially important to aggressively reduce PO4 and SiO2 contamination and continually monitor levels in the seal. Daily checks for PO4 and SiO2 are necessary in many cases with a fraction of the bath being dumped if levels greater than 5 ppm are indicated.

Chloride contamination in the seal is less common but can cause a complete shut down of the line. In the acidic seal solution, Cl promotes the attack of the anodic coating and small white corrosion pits appear on the surface of the part. Even if the white deposits could be wiped off the imperfection in the surface is susceptible to further attack and corrosion. If Cl is suspected, detection is simple, as the addition of silver nitrate solution to a Cl contaminated sealing bath produces a white cloud. Temporary relief is sometimes possible by making the work cathodic using sacrificial magnesium anodes or a small rectifier. Caution is advised as spalling of the anodic coating is possible and if too much voltage (>2) is applied stainless steel will pit severely. The only permanent solution is to eliminate the problem at the source which is usually the DI plant. A malfunction during regeneration can cause insufficient rinsing of the cation bed leaving Cl to leach back out into the DI water. Once pure, high quality, (free of PO4, SiO2, Cl) water is again available the bath should be completely dumped, rinsed out and refilled with DI water.

Many chemicals found in the anodizing facility could contaminate the seal bath but their effect is usually less severe than those previously mentioned. To minimize the likelihood of a problem it is important to

dedicate certain equipment such as beakers, pitchers and pumps for use only in the seal bath. No sample should ever be dumped back into the seal and the bath should never be used as a rinse tank! Since only 15 ml of bright dip solution is needed to significantly contaminate a 1000 gallon bath it is essential that all operators are properly trained. Good operating practices, effective supervision and careful analytical control will improve the quality of the seal bath and thereby improve the quality and integrity of the anodized work.

Dye baths and nickel acetate seals are often found in the anodizing shop and, although less sensitive precautions about contamination apply. Nickel acetate concentration can be determined using an EDTA titration and pH control is also very important. Dye bath concentration can be approximated by diluting a sample and comparing it to known standards. If a series of standards is prepared for each dye the spectrophotometer can match the sample to a standard and the approximate concentration is implied. To save time and reduce error the bottles containing the solutions can be marked with the quantity of dye required to bring the bath back up to the optimum concentration. The pH is important with all dyes and, depending on use, a check each shift is recommended. For advice on the use of buffers to stabilize dye baths, the manufacturers should be consulted. They can also supply a more accurate procedure for dye analysis but these may require too much time and effort to be real practical.

The final group of tests to be discussed involve the performance characteristics of the finished part. These tests, either destructive or nondestructive, help determine if the procedures for control are operating as designed and if adequate control is being realized.

Nondestructive instruments can measure (by implication) the quality of seal, anodic thickness, reflectivity of the surface, specularity, etc.). Unfortunately, these instruments share a common limitation of working best on a flat surface which is not always available. Since the inherent accuracy of many instruments is also a problem with thin coatings, i.e., less than .2 MIL. the "destructive" methods are preferred. Two tests which share a common stripping solution are quite useful in demonstrating compliance with customer specifications or when evaluating sealing bath additives or procedures. A solution of phosphoric and chromic acid is used to strip the anodic coating from a sample and, by weighing the sample before and after an actual weight of anodic coating can be calculated (ASTM B 137-45). The same solution operating at a lower temperature can be used to attack the anodic coating for a specified time and the loss of coating is then determined. The quality of sealing is implied by this method since the better the seal performance the less dissolution of coating should occur. This test (the acid dissolution test) is described in many specifications, ISO # 3210 and ASTM-B680 being a few.These are very useful evaluating the seal quality as quantitative results are obtained.

The modified dye stain test is perhaps the best known seal performance test. It involves precleaning a sealed surface with 50% Nitric acid and placing a drop of dye on the surface for 5 minutes. If a stain results it is assumed that the surface was not well sealed. This test has the obvious

limitation of not working on dyed work and results are either pass or fail. This does not permit any comparison from batch to batch and the results have often been misleading. It is however a simple quick method which if used with discretion can indicate a gross problem with the sealing bath.

The most common reason for using a performance based test in house is the requirements of customers. Decorative applications do not require excessive resistance to corrosion so this type of testing is seldom required. Suffice it to say that there are numerous specifications which involve subjecting the parts to various solutions and evaluating the integrity of the parts after a specified exposure. We have at times been required to measure photometricly the actual light output of the reflectors which we manufacture. Usually the customer provides a fixture and procedure for comparing the output to a known standard. Minimum and maximum values are set and any parts out of specification must be reprocessed. To use any of these tests effectively, the equipment must be set up and the effort to perform them must be minimal. In all cases the decision to test the performance of the parts is based on the requirements for the pieces and on customer demands. Since these tests are somewhat self-incriminating, an outside group such as quality control should also monitor compliance with any standards set by customers.

To accomplish a reasonable degree of consistency the need for complete process control should be evident. Rigorous monitoring of the concentrations and conditions of the baths, and carefully made additions will significantly increase efficiency by better utilizing raw materials and reducing rejects and reruns. Record keeping helps management evaluate and amend the ongoing control system and is useful in investigating major upsets and defects. Good analytical, process, and material control all combine to help the decorative anodizer produce superior work, at a reduced cost, and with a high level of consistency.

APPENDIX 1

Equipment List

Pipettes - 2 each of 1ml, 2ml, 5ml, 10ml & 20ml

Pipette Stand

Beakers - 6 each of 150ml, 250ml, 400ml

Drying Rack for Glassware

Burettes - 4 Self zeroing 25ml
2 Standard 25ml

Burette Rack for Std. Burettes

Magnetic Stirrer and stir bars

Graduated Cylinders - 10 ml, 25ml, 100ml

Hot Plate

Volumetric Flasks - 100ml, 200ml, 1000ml

Polypro bottles for solution storage

pH meter and probes

Balance beam scale or Digital scale

Timer

Spectrophotometer

Hydrometers - 1.60 - 1.80 Scale
1-1.450 Scale
1.0 - 2.0 Scale

Calculator

APPENDIX #2 - TITRATION PROCEDURES

PHOSPHORIC ACID CLEANER ANALYSIS

Pipet a 10 ml sample into a 150 ml beaker
Add approx. 50 ml of DI water and a stir bar
Titrate with 1N base to a pH of 4
ml's of base = a = % acid

ETCH ANALYSIS

Pipet 10 ml of Etch solution into a 150 ml beaker
Add approx. 50 ml of water and a stir bar
Titrate to a cloudy endpoint
Record ml's of 1n Acid used = a

Titrate to a pH of 9.0
Record ml's on 1N acid used = b
g/l `free NaOH' = a X 4.4
g/l dissolved Al = (b-a) x 2.7

ANODIZING SOL. ANALYSIS

aluminum and Sulfuric Acid

Pipet a 5ml sample into a marked 250 ml beaker
Add 100 ml water and a stir bar
Titrate with 1N Base to a pH of 3.6
Record ml's of 1N Base used = a
Titrate to pH of 10.0
Record ml's of Base used = b
Acid conc = a X 9.8 g/l
Alum. conc. = (b-a) X 1.35
Use program in TI59 to do calcs.

Phosphate

Dilute 2 ml's of Anodizing solution to 200 ml
Check for PO4 as below
Card Reading X 100 = PO4 conc. in ppm.

SEAL BATH

Phosphate Determination

Fill 2 Spec. Cells with 25mls of Seal Sol.
Put 1 ml of Molybdate Reagent for Phosphate and
1 ml of Amino Acid Reagent into 1 cell and swirl
Set timer for 10 mins. and Zero spectrophotometer using Blank
Read Phosphate concentration after 10 minutes on card

SEAL BATH CONT'D

pH Determination

Make sure pH probe is well rinsed in DI water and Seal Solution is cool. Immerse probe in sample and wait for meter to settle on a reading 15-30 secs. If in doubt check meter using a known buffer.

BRIGHT DIP ANALYSIS

Nitric

Put 1 ml of bright-dip solution into a 150 ml beaker
Add30 ml of 85% Phosphoric acid @ 150 F
Titrate with Ferrous Ammonium Sulfate to the first permanent brown endpoint.
% Nitric by wt = ml of FAS/Specific Gravity X Factor (See Reagent List)

Specific Gravity

Measure Specific Gravity by filling cyclinder with Bright Dip solution at 75 F and immersing Hydrometer in Solution.

aluminum

Pipet 1 ml of sample into a 200 ml volumetric flask.
Fill with DI water and mix well.
Pipet 10 ml of this diluted solution into a 150ml beaker
Add 20 ml of .01M EDTA solution and a stir bar.
Add 6-7 drops of Pyrocatechol indicator and raise pH to 6.5-6.6 using dilute ammonia. Be very careful not to contaminate sample with any aluminum from beakers or probes as it is very sensitive.
Add approx. 10 ml of Pyridine and titrate with .01 CuSO4.
ml's = b a = ml's of EDTA or blank value*

Al g/l = (a-b) X 5.4 g/l

*Blank value is determined by performing aluminum in B.D. Analysis (above) with a drop of 85% H3 P04 instead of the diluted solution, add EDTA and proceed as above. mlS of .01 CuSO4 = Blank = a. Al g/l = (a-b) X 5.4 g/l

NICKEL ACETATE SEAL:

Pipet 10 ml seal to 150 ml beaker.
Add 2-5 drops glacial acetic acid.
Heat until clear.
Add 10 ml of buffer.
Add 1 murexide indicator tablet and dissolve.
Titrate with 0.01m EDTA to purple end point.
g/l nickel acetate = ml's of 0.01m EDTA X 0.249.

PREPARATION OF REAGENTS

1N BASE

Add 100 mls of 10N base and dilute to 1 liter with DI water.(1)

10N BASE

Can either be purchased or made up by dissolving 400 g of NaOH in 1 liter of DI water.

1N ACID

Add 51.1 gms. 96% H_2SO_4 or 27.8 ml and dilute to 1 liter.(2)

PYROCATECHOL VIOLET

Dissolve 0.1 g reagent grade pyrocatechol violet in 100 ml of distilled water.

PYRIDINE SOLUTION

Dilute 100 ml of reagent grade pyridine to 1 liter with distilled water.

AMMONIUM HYDROXIDE

Mix one part reagent grade ammonium hydroxide with four parts distilled water.

0.01 M COPPER SULFATE SOLUTION

Dissolve 24.97g copper sulfate pentahydrate in distilled water and dilute to 1 liter. Dilute 100 ml of this solution to 1 liter to make .01 M copper sulfate.

BUFFER SOLUTION

Dissolve 53.5g ammonium chloride in 600ml distilled water. Add 350ml concentrated ammonium hydroxide and dilute to 1 liter with distilled water.

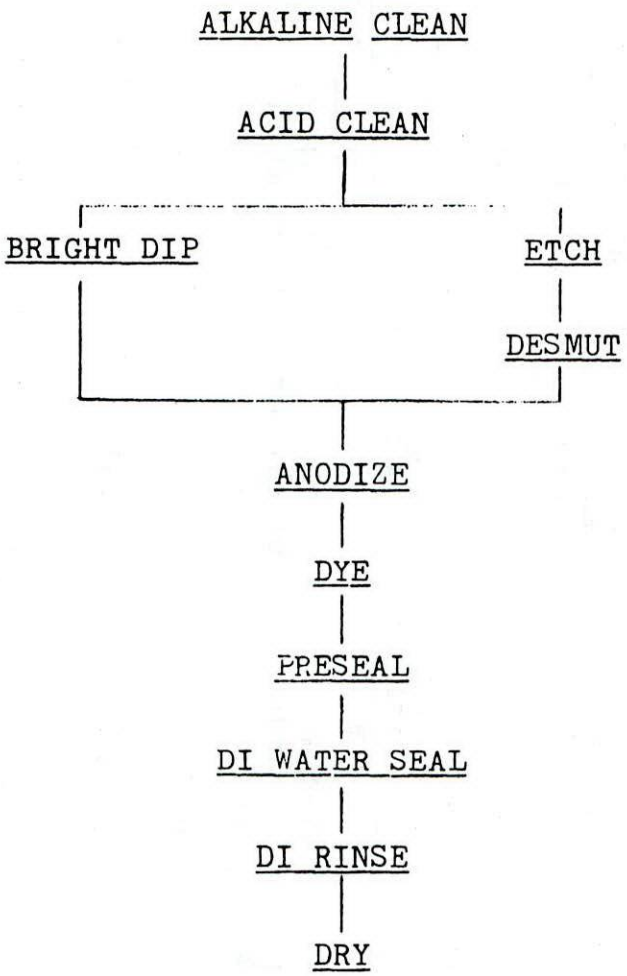
FERROUS AMMONIUM SULFATE SOLUTION

Dissolve 186g Ferrous Ammonium sulfate in 400 ml. DI water. Add 50 ml's Conc. Sulfuric acid and dilute to 1 liter. Determine Factor by performing Nitric Analysis using .3g of KNO_3 instead of a bright dip sample. Factor = 18.71/mls of FAS.

APPENDIX 3: DAILY TEST SCHEDULE

MONDAY	TUESDAY	WEDNESDAY	THURSDAY	FRIDAY
Seal Ad. & pH Bright Dip Nitric & SG	Seal Ad. & pH Bright Dip Nitric & SG	Seal Ad. & pH Bright Dip Nitric & SG	Seal Ad. & pH Bright Dip Nitric & SG	Seal Ad. & pH Bright Dip Nitric & SG
	Alum in BD		Alum in BD	
Etch & Cleaner	Etch & Cleaner	Etch & Cleaner	Etch & Cleaner	Etch & Cleaner
Ni Acetate pH Gold dye pH Black dye pH	Ni Acetate pH Gold dye pH Black dye pH	Ni Acetate pH Gold dye pH Black dye pH	Ni Acetate pH Gold dye pH Black dye pH	Ni Acetate pH Gold dye pH Black dye pH
Seal pH	Seal pH	Seal pH	Seal pH	Seal pH
Bright Dip- SG Temp sheet Neutralizer	Bright Dip- SG Temp sheet Neutralizer	Bright Dip- SG Temp sheet Neutralizer	Bright Dip- SG Temp sheet Neutralizer	Bright Dip- SG Temp sheet Neutralizer
PM	PM	PM	PM	PM
Seal pH Bright Dip Nitric & SG	Seal pH BrightDip Nitric & SG	Seal pH Bright Dip Nitric & SG	Seal pH Bright Dip Nitric & SG	Seal pH Bright Dip Nitric & SG
	Anodizing Sol.	Boiler	Anodizing Sol.	Inventory
Seal PO_4 Dump DI water	Seal PO_4Dump DI water	Seal PO_4 Dump DI water	Seal PO_4 Dump DI water	Seal PO_4 Dump DI water Guage BD tank Anod. dump
Bright Dip- SG	Bright Dip- SG	Bright Dip- SG	Bright Dip- SG	Bright Dip- SG
Seal pH	Seal pH	Seal pH Inventory	Seal pH	Seal pH Inventory

APPENDIX# 4


ALKALINE CLEAN
ACID CLEAN
BRIGHT DIP
ETCH
DESMUT
ANODIZE
DYE
PRESEAL
DI WATER SEAL
DI RINSE
DRY

APPENDIX 5

ANODIZING SOLUTION CALC SHEET

Date: _____ Tank _____

Titration Endpoint #1 (pH 3.5) _____= a

Titration Endpoint #2 _____ = b

Sulfuric Conc. (a1) _____ = a X 9.8 g/l

Alum Conc. (b1) _____ = (b-a)X1.8 g/l

Fraction dumped (f1) _____ = (1-b1)/6.5*(or desired A1 conc)

Inches dumped _____ = Fraction X depth of tank in inches

Sulf. Acid make up _____ = 175 - (a1 X f1 X Factor 1)

Factor 1 = Anod. Tank Size in Gals/1781.

```
ANOD ANALYSIS PRGM


TANK NUMBER ?
          14.
TITRA VALUE 1 PH3.5?
          16.5
TITRA VALUE 2 PH 10?
          22.

 CONC G/L
        161.7     SULF
        7.425     ALUM

DUMP INCH , GALS SULF
          0.      DUMP
          4.      SULF

          7.      DUMP
         13.      SULF
```

```
TANK NUMBER ?
          15.
TITRA VALUE 1 PH3.5?
          17.5
TITRA VALUE 2 PH 10?
          24.2

 CONC G/L
        171.5     SULF
        9.045     ALUM

DUMP INCH , GALS SULF
         12.      DUMP
         17.      SULF

          9.      DUMP
         13.      SULF

         18.      DUMP
         26.      SULF
```

J-6

Light Metals I
Session J

Treatment and Toxicity of Aluminum Anodizing Effluents

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TREATMENT AND TOXICITY OF ALUMINUM ANODIZING EFFLUENTS

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Abstract

Effluent toxicity is a growing concern of regulatory agencies and the regulated industry alike. Because of the complex nature of many effluents, little or no toxicity data may be available to serve as a guide when developing permit limits. This paper describes toxicity testing conducted at two integrated aluminum finishing facilities either to facilitate obtaining discharge permits or as a condition of the discharge permits. A brief description of wastewater treatment facilities is included.

Introduction

Biomonitoring of industrial discharges to waterways has become increasingly common in the past few years. Many new discharge permits issued since 1980 have some type of biomonitoring requirement. The increasingly stringent regulations governing direct discharges of industrial wastewater coupled with a paucity of pertinent toxicity data can sometimes leave the permit writer and prospective permitee at an impasse. The permit writer and permittee must work together to see that the limits which are established are sufficiently restrictive to protect the environment, while at the same time not so overly restrictive as to be impractical or impossible to achieve.

In the Fall of 1980, Ethyl Corporation submitted an NPDES discharge permit application seeking permission to discharge approximately 200 gallons per minute of treated wastewater from an aluminum anodizing facility located in the Midwest. The basis for the requested discharge limits was operating experience at two other company facilities which utilize similar processes and where the wastewater would be expected to have characteristics similar to that from the new anodizing facility. Historically, pH, suspended solids, BOD, chromium and aluminum have been the regulated parameters of chief concern for this type of manufacturing facility. The State found most of the proposed limits acceptable but expressed concern over the possible toxicity of aluminum at the proposed concentration limits of 5 mg/l average, 10 mg/l maximum. This led to extensive efforts to gather data sufficient to satisfy the State that the proposed discharge would not cause environmental damage.

Wastewater Treatment System

It became obvious from the start that a state-of-the-art wastewater treatment system would be needed to insure minimal adverse impacts on the small receiving stream. The key component to such a treatment system is proper pH control.

Best available treatment (BAT) technology was utilized to treat the wastewater from the new anodizing facility. The BAT system is comprised of the following equipment: (1) a two stage neutralization step with separate tanks to handle concentrated liquor dumps, (2) a Lamella clarifier with inlet flash mix and floculation chambers, (3) a continuously backwashed sand filter for final effluent polishing, (4) a sludge thickener and (5) a plate-and-frame hydraulic filter press. A schematic diagram is shown in Figure 1. This system should normally reduce aluminum concentrations in the treated effluent to very near the solubility limit and deliver a filter cake which can easily be disposed.

Toxicity of Aluminum

Aluminum is the most abundant metal and the third most abundant element in the earth's crust. It exists naturally only combined with other elements, usually including oxygen. These aluminum compounds comprise some 15 percent of the earth's crust, with all soils and many rocks containing aluminum compounds.

There are no demonstrated adverse effects on man from low concentrations of aluminum in drinking water. Exposure of humans to low levels of aluminum has become commonplace through the widespread use of aluminum salts in water treatment without any apparent ill-effects. Research into the effects of aluminum in aquatic environments has been less conclusive, however. A rather comprehensive review of the subject of toxicological properties of aluminum was conducted by Burrows in 1974 with subsequent publication of the data in 1977[1]. This work included a discussion of several studies involving numerous species exposed to varying concentrations of aluminum. Unfortunately, the question of possible toxicity of the effluent could not be resolved from a review of the available literature.

Resolution of the question of the toxic effects of the proposed discharge was an absolute necessity before any discharge limits could be established. Because of the sometimes conflicting data available in the literature, it was necessary to conduct bioassays on actual effluent from a similar aluminum finishing operation.

Toxicity Testing

Because of the need for toxicity data to obtain the discharge permit for the new plant and subsequent permit

requirements at an existing plant, Ethyl has now completed effluent toxicity testing at two of its Aluminum Division sites. Toxicity testing requirements have now become a part of the NPDES discharge permit at one site and may be included for the second site in the future. It is important that particular attention be given to the design of the toxicity test. Specifically, consideration must be given to the test species, duration of the test, and test conditions.

The test species should be representative of the native fauna indigenous to the receiving stream. Test organisms should be evaluated for compatability with stream salinity and sensitivity to physical changes. For example, many aquatic organisms are highly susceptible to abrupt temperture changes and our experience has been that Daphnia will die rapidly when the water contains even minute amounts of surface wetting agents (surfactants, detergents).

For cost control purposes, the shortest practical time period to obtain the desired information should be used unless otherwise directed by the regulatory agency. Generally, the minimum time period is 24 hours for a simple static bio-assay to determine acute toxicity. The standard length for a continuous flow bio-assay is 96 hours. The test procedures to study reproductive effects can last up to several weeks.

Test conditions should be set to simulate actual field conditions if possible. Water temperatures must be held relatively constant throughout the test and care taken to see that dissolved oxygen levels are not depleted. The test organisms should be in good condition and free of any disease or parasites.

Results of Toxicity Tests

Plant 1

Working with the State regulatory agency, a bioassay test was developed to determine the toxicity of the treated aluminum anodizing plant effluent. This test was designed and conducted in accordance with established USEPA procedures[2]. The fathead minnow (Pimephales promelas) was chosen as the test organism.

A static 24-hour screening test was conducted to determine the dilutions to be used in a 96-hour continuous flow bio-assay to follow. Dilution water in each case was taken from the receiving stream at a convenient access point five miles upstream of the discharge. No lethal toxicity was indicated by the static test and none of the fish exhibited any physiological signs of stress. Test results are shown in Table 1 below.

TABLE 1

24-Hour Static Test

				Test Organism		
% Effluent	Tank*	pH	Temp. °C	Mean Length (MM)	Mean Weight (g)	Mortality/ No. Tested
100	A	8.3-7.7	22	44	0.67	0/4
100	B	8.3-7.7	22	41	0.60	0/4
75	A	8.2-7.8	22	37	0.53	0/4
75	B	8.2-7.8	22	45	0.87	0/4
50	A	8.1-7.7	22	44	0.65	0/4
50	B	8.1-7.8	22	37	0.57	0/4
25	A	8.0-7.7	22	38	0.53	0/4
25	B	8.0-7.7	22	44	0.63	0/4
0	A	7.8-7.6	22	39	0.63	0/4
0	B	7.8-7.6	22	43	0.75	0/4

*Each dilution was duplicated as a precautionary measure.

Following completion of the static test, a 96-hour continuous-flow bioassay was conducted. Because there were no mortalities in the 24-hour static screening test, replicate test chambers at 100, 36, 21.5 and 7.8 percent effluent were used in the 96-hour test. The control chambers consisted of 100% dilution water taken from the receiving stream. The automatic dilution system used is illustrated in Figure 2. Twenty fish (ten per replicate chamber) were placed in each concentration. At 24-hour intervals during the test the temperature, dissolved oxygen, pH, conductivity, alkalinity and hardness of the water in each chamber were checked. Water samples were taken at 24 and 72 hours from each chamber and tested for aluminum concentration. Frequent observations of the physiological status of the fish (loss of

equilibrium, paralysis, mortality) were made. Table 2 shows the test results. Effluent aluminum concentrations at 24 and 72 hours were 5.0 and 4.3 mg/l, respectively.

Four percent of the fish were lost during the test as a result of natural random mortalities. No mortalities occurred in replicate chambers with one dead fish in each of the 100, 36, 21.5 and 7.8 percent effluent chambers. Two mortalities occurred in one of the control chambers. All mortalities occurred between the 72-hour and 96-hour time intervals.

Plant 2

As a condition of the discharge permit, a 24-hour static bioassay was conducted on the effluent from a second Ethyl aluminum anodizing facility in 1983. Dual test chambers of 100 percent effluent as the test solution were used. Two chambers containing carbon filtered tap water were used as controls. Parameters monitored during the test were temperature, dissolved oxygen, pH and conductivity.

Ten fathead minnows (Pimephales promelas) were randomly loaded into each of the test chambers. The fish were observed for signs of physiologic stress (loss of equilibrium, paralysis, etc.) during the test. No mortalities occurred in either the test chambers or in the control chambers during the 24-hour test period. The data are presented in Table 3.

Summary

No effluent toxicity was observed at either of the two facilities where toxicity tests were conducted. Activities at both of the two facilities included secondary aluminum smelting, casting, anodizing, painting and other surface finishing operations.

The test results indicate that well treated effluent from a typical aluminum finishing operation is non-toxic to fish.

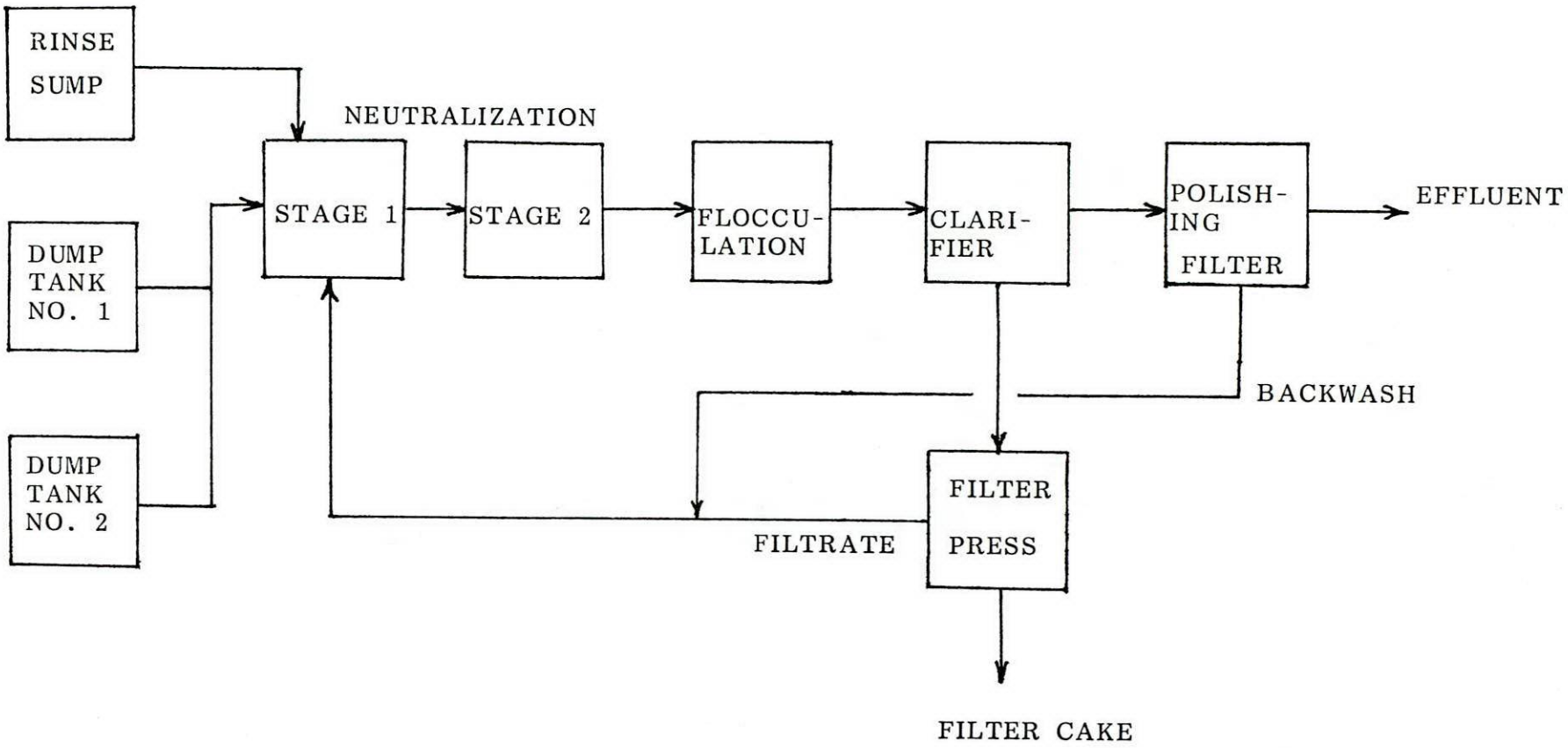

FIGURE 1

Schematic Flow Diagram
BAT Wastewater System

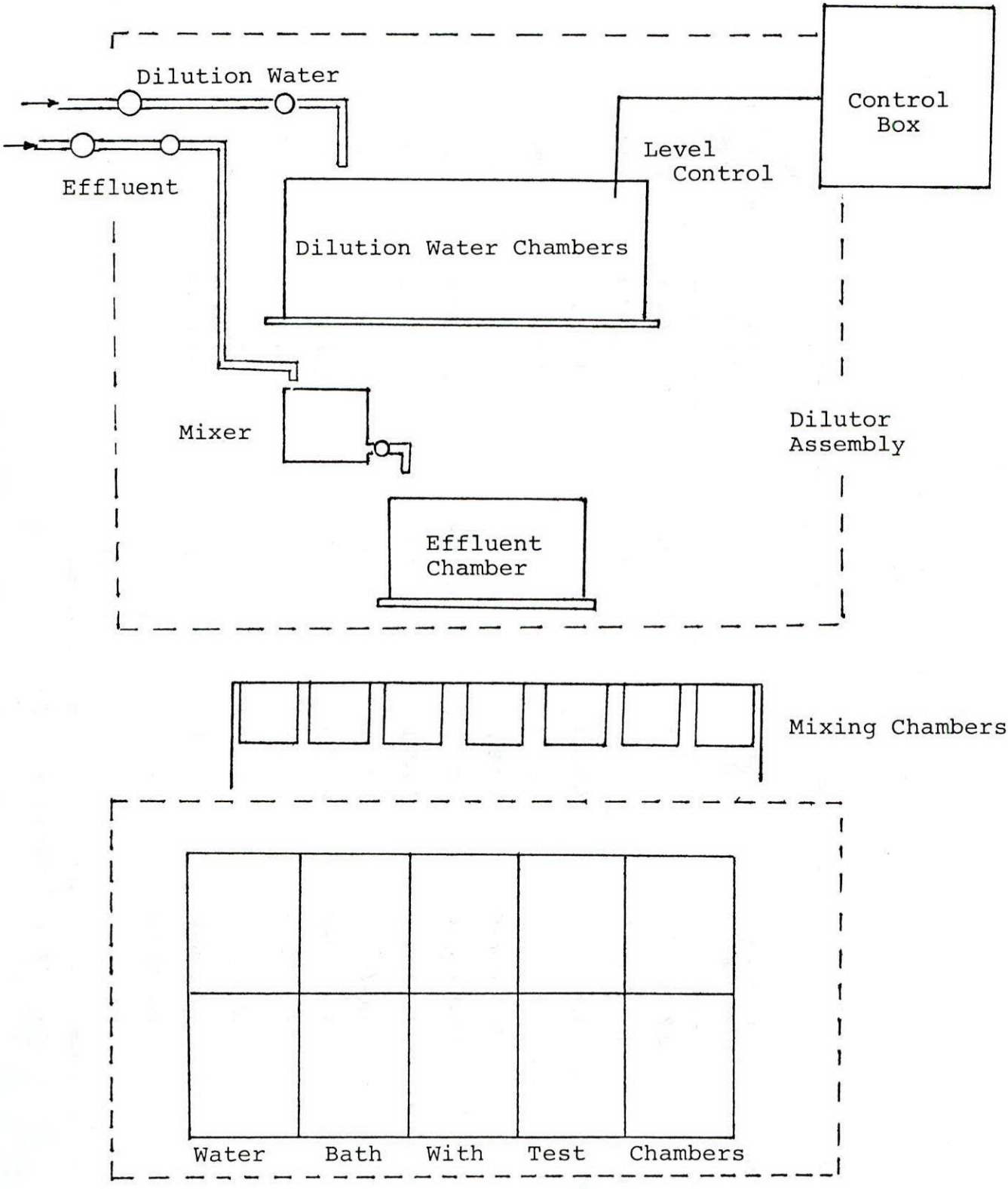

FIGURE 2

Continuous-Flow Bioassay Diluter System

TABLE 2

TEST PARAMETERS FOR ETHYL CORPORATION
96-HR CONTINUOUS-FLOW BIOASSAY

Test Concentration (%)	Conductivity (µmhos/cm)	pH (units)	Temp. (°C)	D.O. (mg/l)	96-hr Survival Mortality/ No. Tested
100A	1,790-2,800/2,256	8.1-8.4	22-23/22.3	6.7-7.5/7.1	1/10
100B	1,710-2,850/2,244	8.1-8.5	22-23/22.3	6.9-8.0/7.4	0/10
60A	1,110-1,800/1,437	7.9-8.3	22-22/22	7.4-8.2/7.7	0/10
60B	1,110-1,820/1,450	7.9-8.3	22-22/22	7.4-7.8/7.6	0/10
36A	790-1,160/980	7.7-8.2	22-22/22	6.1-7.8/7.3	0/10
36B	780-1,220/972	7.8-8.2	22-22/22	7.4-8.3/7.8	1/10
21.5A	480-810/660	7.7-8.1	22-22/22	7.3-8.2/7.8	0/10
21.5B	490-790/658	7.7-8.1	22-22/22	7.4-8.5/7.9	1/10
13A	380-600/489	7.6-8.0	22-22/22	6.2-7.9/7.5	0/10
13B	370-570/469	7.8-8.1	22-22/22	7.5-8.5/8.0	0/10
7.8A	305-430/365	7.6-8.2	22-22/22	7.5-8.6/8.1	1/10
7.8B	310-440/371	7.6-8.1	22-22/22	7.3-8.6/8.0	0/10
0A	150-160/154	7.7-8.0	21-22.5/21.8	6.6-8.6/7.6	0/10
0B	148-155/151	7.7-8.1	21-22/21.7	7.7-8.7/8.3	2/10

All data reported as range/average; pH reported as range.

TABLE 3

WATER QUALITY AND FISH DATA COLLECTED FOR THE 24-HOUR
STATIC BIOASSAY OF THE WILLIAM L. BONNELL WASTEWATER
FEBRUARY 2-3, 1983

Test Solution (Percent Effluent)	Water Quality Parameters*				Fish** Length (cm)	Fish** Weight (g)	24-Hour Percent Survival
	D.O. (mg/l)	Temperature (^{o}C)	pH	Conductivity (μmhos/cm)			
100 A	7.2 / 5.8	15.0 / 16.0	6.9 / 6.8	1,700 / 1,680	5.4 / 4.5-6.3	1.1 / 0.6-1.6	100
100 B	7.4 / 5.9	15.0 / 16.0	6.9 / 6.8	1,700 / 1,700	5.5 / 4.4-6.6	1.2 / 0.6-2.2	100
Control A	8.2 / 6.1	16.0 / 16.0	7.2 / 7.3	345 / 355	5.6 / 4.9-6.6	1.2 / 0.8-1.9	100
Control B	8.7 / 6.3	16.0 / 16.0	7.3 / 7.3	360 / 360	5.5 / 4.6-5.9	1.3 / 0.7-1.7	100

*Reported as initial/final.
**Reported as mean/range.

K-1

Electroless
Session K

Direct Plating Of Zinc Die Casts With Electroless Nickel

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DIRECT PLATING OF ZINC DIE CASTS WITH ELECTROLESS NICKEL

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Abstract

This paper will describe a new and unique plating process for the plating of zinc die cast materials directly with electroless nickel. This novel process replaces the need for a copper cyanide strike conventionally used in today's plating industry. In addition to eliminating the need for cyanide in the plating process, significant improvements are seen in coverage capability and corrosion protection of the zinc substrate. As a result, not only are reject rates lowered due to a more complete coverage, but also parts with complex geometries are now able to be plated successfully.

Discussion

Die casting is the most versatile method of fabricating complex metal shapes with close dimensional tolerances at low cost. Recently in the electronics industry, the move from aluminum die cast materials to zinc die cast materials has been prompted by the longevity of dies used for zinc die casting versus comparable dies used for aluminum die casting. As a result, new plating processes had to be developed for the protective coating needed for reliable corrosion protection of zinc die cast alloys.

The most popular zinc alloy used in die casting today is Zamak 3. Its composition is 95.96% zinc, 4.0% aluminum, and 0.04% magnesium.[1] It can be shown thermodynamically that zinc is a fairly reactive metal which has an appreciable tendency to corrode. Roetheli, Cox, and Littoreal have indicated aggressive corrosion rates of zinc in strongly alkaline, acid and oxygenated solutions.[2] Under natural atmospheres and relatively neutral aqueous solutions, minimal corrosion rates occur due to zinc's dense and tightly adherent layers of oxide, oxyhydrates, and basic carbonates.[3] Therefore, to offset all possible negative conditions, protective metallic or non-metallic coatings are necessary for zinc die cast parts.

Until recently, cyanide copper had been the state-of-the-art technique in providing the barrier coating for subsequent plating of zinc die cast parts. A typical composition of a cyanide copper bath is as follows:[4]

Copper	1.8 - 3.5 oz/gal
Free CN	.75 - 1.5 oz/gal
Rochelle Salt	2 - 5 oz/gal
Soda Ash	2 - 8 oz/gal
pH	11.5 - 12.5
C. D.	15 - 75 amp/ft^2
Temperature	120 - 140°F

Time 1 - 3 min.

Due to the fact that the cyanide copper bath is mildly alkaline, its chemistry allows it to be a natural strike bath for zinc die cast materials. The danger of blisters and/or adhesion failure is minimized by its compatibility with zinc.

However, due to the inherent inadequacies of electrolytic plating, complex parts with recessed areas and blind holes are difficult to plate by this method. Several differences can be seen with cyanide copper strikes versus total electroless nickel plating. A chart below depicts some of these:

Feature	Cyanide Copper	Electroless Nickel
Over-all coverage	Fair, poor LCD	Good
Complex part plating	Difficult to plate	No problem
Type of racking	Contact, barrel or rack	Barrel or rack
Corrosion protection	Fair, poor in LCD	Fair
Waste treatment required	Treat for cyanide and heavy metal	Treat for heavy metal only

Due to the environmental and improved performance advantages of alkaline electroless nickel plating, much work has been done recently to develop and improve a process to plate zinc die cast parts consistently blister-free with good adhesion. The following is a brief outline of a new process that has performed well in both experimental and production modes.

Plating Cycle for Zinc Die Casts

1.	Abrasive tumbling		
2.	Non etch soak cleaner	150°F, 5 min.	
3.	CWR		
* 4.	Electroclean	R. T., anodic 60 sec.	
5.	CWR		
6.	Neutralizer/Activator	R. T., 60 sec.	
7.	CWR		
8.	HWR		
9.	Alkaline Electroless Nickel	180°F, pH 9.5, 15-20 min.	
10.	CWR		
11.	Activator	R. T. - 120°F, 30 sec.	
12.	Acid Electroless Nickel	190°F, pH 5.0, 10-30 min.	
13.	CWR		
14.	HWR		
15.	Dry		

*OPTIONAL

Each step in the process works in concert with the others and a complete understanding of each step is necessary to plate consistently and successfully.

A thorough cleaning of the zinc die cast parts is vitally important to the success of this process. Before proceeding to the actual cleaning cycle, visual inspection of the parts is very important. Faulty casting techniques result in surface layer defects such as crevices, skin blisters, hemispherical pores, and/or cracks. Blistering can occur during plating or soon after as the result of hydrogen gas generated by the reaction between zinc and corrosive solutions entrapped within pits and crevices.[5] Post-heat treatments can accelerate blister formation traceable to the same corrosive chemicals or any entrapped oil or gasses.

To lower the incidence of surface defects, abrasive tumbling or wheel abrading of the zinc die cast parts is recommended as the first step in the process. Fissures, skin blisters and other defects with a depth of 25-50 micrometers can usually be erased with abrasive tumbling.[6] This will retard the probability of blister formation. Mechanical adhesion and deoxidation of the zinc surface can also be achieved as a result.

The second step of the process involves a non-etch soak cleaner. The purpose of this cleaner is to remove the bulk oils and buffing compounds that may be present. Properly developed formulations are necessary here to avoid the preferential attack of the aluminum phase of the zinc alloy. Aluminum phase corrosion coinciding with subsurface porosity induces cavities that tend to entrap corrosive solutions once again. Subsequently this causes blisters due to the evolution of hydrogen gas.[7] Loosely adherent gelantinous aluminum compounds formed here can also be a source of blistering.

After the soak clean, anodic cleaning can be used to complete the removal of oil, grease and soil. Improper wheel abrading can actually lodge impurities within the zinc alloy interface which can only be removed electrolytically. Time cycles vary from 30 - 60 seconds.

The next step is the neutralizer/activator step. This step is utilized to neutralize any soak or electrocleaner which precedes this step. In addition, this step should remove all traces of black films or semi-adherent smut.

Following this neutralizer step, a hot water rinse is highly recommended to remove any residual alkaline or acid solutions entrapped within surface crevices or pores. These sites can easily become process blisters if the corrosive contaminants are not diluted or removed.

After the pretreatment is concluded, the parts are then introduced into an alkaline electroless nickel bath. A properly designed alkaline nickel with a high tolerance to zinc contamination should be used. Typical alkaline nickels used for ceramics and/or plating on plastics are not suitable for zinc die cast parts. The purpose of this bath is to replace the copper cyanide strike mentioned earlier. Given the properties

of an electroless bath, good uniform coverage of parts should be achieved. Typical thickness of the alkaline nickel deposit should be in the range of .05 - .2 mils to eliminate any porosity of the alkaline nickel deposit. This step is as vital to the success of this process as the pretreatment. A properly designed alkaline nickel should have the following characteristics:

1.) Must be buffered in the 9-10 pH range to minimize zinc dissolution.
2.) Should have excellent stability toward zinc contamination to avoid spontaneous decomposition.
3.) Should yield a dense, amorphous coating at low thicknesses to minimize porosity for the subsequent acid nickel overcoat.
4.) Should have quick coverage of the zinc substrate to minimize the zinc dissolution into the bath.
5.) Should be as low stressed as possible to retard stress cracking and adhesion failure at thicker deposits.

After the alkaline nickel barrier coat is deposited, the plated parts are then rinsed and activated for the subsequent acid electroless nickel overcoat. The activating solution serves two purposes. First, the activating solution will improve the adhesion between the two nickel layers by rendering active the alkaline nickel deposit towards the acid nickel. Secondly, the activating solution is a qualitative way to determine if uniform coverage and proper nickel thickness have been achieved in the alkaline nickel bath. Any porosity or poor coverage will be evident by the gassing of parts in the activating solution. Assuming no gassing is evident, the parts then proceed to the acid electroless nickel. If gassing does occur in the activating solution, the parts should be placed back into the alkaline EN for further plating.

The acid electroless nickel serves as the corrosion resistant layer which provides the protection necessary to minimize the attack of the zinc alloy. The acid nickel is the typical type of electroless nickel run at a pH of 4.8 at 190°F. It, too, must be very tolerant to zinc contamination. If bright deposits are required, a bright acid electroless nickel should be used here. A typical corrosion test that must be satisfied is a 96-hour humidity test at 40°C. Final nickel thickness is usually in the area of .3 - .6 mils depending on the part specification.

Typical drying techniques are used in the final step. Methanol, hot D. I. water, or water displacement liquids can be used successfully minimizing water stains.

Summary

In conclusion, zinc die cast parts can be plated successfully with electroless nickel directly. It is somewhat complex due to the fact that care should be used in every step of the plating process. Poor cleaning or poor alkaline nickel performance can lead to many rejects.

Understanding the mechanism of proper cleaning and nickel reduction as well as evaluating the plating cycle on a piece by piece basis will allow continuous success of the plating of zinc die cast parts direct with electroless nickel.

Acknowledgements

The author acknowledges the contribution of Kashmira Parikh for carrying out the experimental work.

References

1. Metals Handbook, Selection and Application of Zinc Alloys, 1961, p. 1161.

2. Roetheli B., Cox G., Littreal, Metals and Alloys 3, pp. 73-76, 1932.

3. G. G. Gawrilov, Chemical Nickel Plating, Portcullis Press Ltd., Surrey, England, 1979, p. 120.

4. Metal Finishing Guidebook, 1984, p. 173.

5. J. V. Petrocelli, A. Phillips, "Trans Electro Chem. Society" 85, 257 (1944).

6. R. W. Mowery and A. E. Leatherman, Tech. Paper No. 64, Society Die Casting Engineers (Nov. 1968).

7. J. V. Petrocelli and A. Phillips, "Trans Electro Chem. Society" 85, 257, (1944).

K-2

Electroless Session K

Electroless Deposition Of Nickel And Gold On Metallized Ceramics

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Paper not received in time for printing

ELECTROLESS DEPOSITION OF NICKEL AND GOLD ON METALLIZED CERAMICS

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K-3

Electroless
Session K

Corrosion Characteristics Of Electroless Nickel Coatings In Chemical Process Environments

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CORROSION CHARACTERISTICS OF ELECTROLESS NICKEL COATINGS IN CHEMICAL PROCESS ENVIRONMENTS

Report No. 1

by R. P. Tracy
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Abstract

The corrosion resistance of Electroless Nickel (EN) coatings on steel substrates exposed to industrial chemicals were studied as a function of phosphorous content and also compared to laboratory data available on nickel 200 and mild steel.

EN coatings were found to offer excellent chemical resistance to a variety of corrodents but failed in commerical 75% phosphoric acid which is also normally not compatible with nickel and nickel alloys.

Test results and preliminary economic appraisals indicate EN coatings on process equipment could offer considerable capital savings over solid nickel, teflon lined or glass lined construction.

Field trials with EN coatings applied to various process equipment used in the production of these chemicals are in progress as a result of these studies. Longer term, higher temperature testing with these and other chemicals will be conducted in the future.

Introduction

The Chemical Process Industry has witnessed a considerable increase in activity in the development of EN coatings over the past few years. The reason for this interest and excitement is the potential savings and new applications for EN coatings.

Development of standards and improved quality techniques are adding to the reliability of the product resulting in increased demand and competitive pricing. With each new application for EN coatings, process capabilities are being increased and new capital is created to fund basic research into the product.

Materials Engineers are looking at EN coatings as a potential cure for many previous unresolved corrosion problems. The possibility also exists that use of these coatings may signal a reversal in the large amount of capital required for some chemical plant construction resulting in more favorable conditions for producing certain chemicals previously too expensive to produce. Potential exists for gains in product purity, environmental safeguards, safety, and reliability in manufacturing and transporting of chemical products.

The capability to line large process size vessels was developed and patented(1) in the early 1950's. Process controls were not developed sufficiently to produce a consistant good quality product and adhesion and porosity problems became apparent. Very little activity can be documented on the use of EN coatings for corrosion resistant applications since that time. Recent activities (2, 3, 4) have convinced materials engineers that the industry is ready to work with them in testing, design and development. Pricing of EN coatings have become more competitive and the material appears to have a bright future in the CPI.

Recent examples of potential cost effective applications at OCC include the coating of a grinder screen for wear resistance in the manufacture of phenolic resins. The cost of EN coating, screens that measure approximately x 14" x 30" x 3/16" containing 3/8" diameter holes (40% open area) with 1.0 mil of wear resistant coating, is $25 each. The coating is expected to extend the screen life, by a factor of four, realize a savings of about $500/screen and save additional maintenance and downtime.

Coating of a thermowell-sample tube assembly for use in a sulfur dichloride tank car costs about $700 for 3.0 mils of a corrosion resistant EN coating. The original cost of the assembly was about $1200. The EN coating is expected to extend the service life of the assembly from two years to five years.

Occidental Chemical Corporation has began field trials in energy from waste applications, bolting for use in chloride and other atmospheric environments and in several areas of the manufacture and handling of the chemical products employed in this testing program.

The biggest obstacle left to be overcome by the EN coating industry is the size limitation that presently exists for coating process equipment.

Experimental Procedure

Environments

Eight chemicals, manufactured or used in the manufacture of chemicals at Occidental Chemical Corporations (OCC), Niagara Falls, New York, plant were selected for Testing. The chemicals and their sources are listed in Table No. II.

Caustic Soda (Sodium Hydroxide) is used in the manufacture (5) of cellophane, rayon, wood pulp, soap, chemical intermediates, dyes, drugs, cosmetics, water softening compounds; in bleaching, dying, and printing textiles and mercerizing cotton; in food processing and petroleum refining. Errosion/corrosion problems of large and expensive vapor bodies, steam chests and pump impellers have plagued the industry, especially since the implementation of quadruple effect evaporation systems. Nickel 200 is used almost exclusively in the manufacture and handling of caustic soda under a variety of conditions and temperatures.

®E-Brite 26-1 has been used for evaporator tubing and austenitic stainless steels have been used for 3rd and 4th effect (weak caustic) vapor bodies. The combined properties of lubricity, hardness, abrasion, wear, and corrosion resistance that EN coatings offer suggest that their use in the manufacture of caustic soda may have considerable promise. The corrodent selected was a liquor sample obtained from the first effect (final evaporation step) of a quadruple effect caustic evaporation system containing approximately 45% sodium hydroxide, 5% Sodium Chloride and the remainder water.

Occidental Chemical Corporations final product thionyl chloride was included in the testing program because a large portion of the process equipment used in its manufacture and shipment is fabricated from Nickel 200, lead, glass, or teflon lined. The product is readily hydrolyzed by moisture in air liberating hydrogen chloride and sulfur dioxide, which is corrosive to most metals and permeates most plastics. The product which is a clear, pale yellow to red liquid, is used in organic synthesis to replace various groups with chlorine (5) especially in the preparation of organic acid chlorides. It may be used to introduce sulfur alone or in combination with oxygen.

Phosphoric acid (75%) is produced as a by product of Occidental Chemical Corporations Sodium Hypophosphite process. The material is produced by burning of phosphine gas and absorbing phosphorous pentoxide in water to form 75% phosphoric acid for direct sale to local industry. Phosphoric acid is used in food processing, (5) pharmaceuticals, gelatines, glues, adhesives, metal processing, rust proofing, boiler treatments, chemical polishing, flame-retardents, fabrics, and plastics as a

®E-Brite 26-1 is a registered trademark of Alleghany Ludlum Industries, Inc.

strong acid catalyst. The product is an odorless, water white, sparkling clear liquid with no turbidity.(5) Nickel 200 has limited usefulness in commerical phosphoric acid solutions and published literature by Huntington Alloys (6) indicate a corrosion rate of 0.3 -0.5 mils/year can be expected in 50-82% Phosphoric Acid at ambient temperatures. Testing of EN coatings in Phosphoric Acid was selected to determine if the nickel-phosphorous coating would display improved chemical resistance over Nickel 200 to commerical Phosphoric Acid.

Orthochlorobenzyl chloride (OCBC) both final product and crude product is handled by Nickel 200 and glass lined equipment because the product is polymerized with the liberation of hydorgen chloride when contacted with steel or metal halides. The product is an intermediate used in the production of agriculture chemicals, pharmaceuticals, and plastics. (5)

Final product Phosphorous Oxychloride is a water-white fuming liquid (5) used in the manufacture of organic phosphates, plasticizers, gasoline additives, chlorinating agents, catalysts in the production of dyestuffs, medicines, and intermediates. The material is handled by glass lined steel (acid resistant), nickel, teflon, and kynar, but permeates most other plastics. Phosphorous Oxychloride will slowly hydrolize into phosphoric acid and hydrochloric acid in the presence of moisture.

Occidental Chemical Company's final product Benzotrichloride (toluene trichloride) (5) is a clear colorless liquid with a sharp characteristic odor used in organic synthesis, preparation of dyestuffs and as a source of Benzonyl group. The chemical reacts with water and alcohol to produce HCl. The corrosion rate of mild steel is relatively low (0.2 mpy) when exposed to BTC but discolors and contaminates the product resulting in the need for producing and handling the product with nickel, nickel alloys, and organic linings.

Benzoyl chloride final product is a clear, colorless liquid with a sharp characteric odor (5) used in the manufacture of organic peroxides, synthetic perfumes, pharmaceuticals, dyes, resins, pesticide intermediates and may be used

to introduce the Benzoyl group into organic compounds, especially through friedel-crafts reactions. The corrosion rate of mild steel exposed to dry BOC is about 0.2 mpy but is produced and handled with nickel, nickel alloys, and organic linings because of product purity considerations.

Test Samples

Three different electroless nickel coatings were tested with the characteristics listed in Table No. I. Phosphorous contents of 1-2%, 6-8%, and 10-11% were selected at 2.0-2.5 mils of thickness to determine the effect of phosphorous content on corrosion rates. Testing was conducted to ASTM G-31 "Laboratory Immersion Corrosion Tesing of Metals" under the test conditions as listed in Table No. II and as prescribed by ASTM B733 "Autocatalytic Nickel Phosphorous Coatings on Metals." The Electroless Nickel Coatings selected were all commerically available. The coatings were applied to cold rolled AISI 1010 mild steel panels, (4' x 6' x 0.020" thick), 1/4 hard mill finished by mill rolling with ground rolls. The panels were cleaned by vapor degreasing, packaged in rust inhibiting paper to control rust and oil stains, and sent to be EN coated following the procedure listed in Table No. I. Prior to testing, the panels were subjected to ferroxyl testing as listed in ASTM B733 9.61. Only specimens exhibiting a negative result were used in the testing program.

Specimens were measured with a digital caliper accurate to 0.001" and surface areas were calculated and recorded. Each specimen was cleaned by scrubbing with alconox dissolved in warm water followed by thorough rinsing in water and in a suitable solvent (methanol) and air dried. The dried coupons were weighed on an analytical balance to an accuracy of $\pm$ 0.1 mg and weights were recorded. The samples were stored in a desiccator for 24 hours and reweighed to insure that a constant weight was obtained and then returned to the dessicator until used.

Exposure Conditions

Specimens were partially immersed in 3000 ml glass resin flasks except for Sodium Hydroxide tests which were

conducted in a nickel pot with the same dimensions. Blank samples of each corrodent were run along-side the tests to use as a comparison. Each test container was fitted with a reflux condensor and a thermometer or thermowell. The solution volume-to-speciman area was 125 ml/sq. inch. Testing was conducted at ambient temperatures under static conditions, with no aeration.

Cleaning Specimens After Test

After 15 days of exposure, the samples were removed from test and rinsed with a suitable non-reactive solvent. Methylene Chloride was used for OCBC, Benzotrichloride and Benzoyl Chloride, acetone for thionyl chloride and phosphorous oxychloride, and water for Sodium Hydroxide and phosphoric acid. Each specimen was cleaned by scrubbing with alconox dissolved in warm water followed by a thorough rinsing in water and methanol, and air dried.

Interpretation of Results

Weighing was performed on the same analytical balance that was used for the original weights and samples were stored in a desiccator for 24 hours, then reweighed to insure that a constant weight was obtained. All specimens were stored in a desiccator until they were returned to testing. Correction was made for weight losses attributed to the cleaning procedure by exposing a blank specimen of each EN coating type to the same cleaning procedure. Examination was conducted on each sample both visually and under a microscope at various magnifications ranging from 1x to 30x using an unexposed specimen for comparison.

Determination of Corrosion Rates

Average corrosion rates were calculated by the following equation: EON. 1 . . .CORROSION RATE (Mils/Year)= $\frac{534\ W}{DAT}$

W= Weight loss, mg
D= Density of coating, G/cm^3
A= Exposed surface area, inches^2
T= Time of exposure, hours

The corrosion rates listed in the Tables are valid for systems which obey linear kinetics as normally encountered in dissolution--controlled corrosion and yields a conservative corrosion rate for design considerations.(2)

Discussion of Results

Results shown in Table No. III indicate that low phosphorous coatings (1-2%) were resistant to all of the corrodents included in the testing except for Phosphoric Acid (75%) and phosphorous oxychloride. The low phosphorous coating was completely removed in Phosphoric Acid after 30 days exposure, the solution turned green, and the steel substrate displayed considerable attack. The corrosion rate calculated is therefore inaccurate for the coating alone. The corrosion rate in Phosphorous Oxychloride increased from 0.04 mils/year after 30 days to 1.12 mils/year after 60 days exposure, but no color change was detected in the solution. The test specimen exhibited some discoloration (black) over about 50% of the exposed surface. It was decided to continue exposure for a longer time period to obtain more meaningful results.

The medium phosphorous (6-8%) coating was found to be resistant to all of the corrodents except Phosphoric Acid (75%). The increased phosphorous content appeared to contribute to a decreased corrosion rate in Phosphoric Acid (75%) and Phosphorous Oxychloride. The coating exhibited peeling from the substrate and a corrosion rate of 7.60 mils/year in the Phosphoric Acid solution as shown in Table No. IV. The corrosion rate actually decreased slightly from the 30 to 60 day test exposure in Phosphorous Oxychloride with no change in corrodent color and only a slight discoloration on the surface of the EN coating.

The high phosphorous EN Coating (10-11%) showed improved corrosion resistance to Phosphoric Acid (Table No. V) over the lower phosphorous coatings, but the corrosion rate was still increasing with exposure time and flaking of the coating was observed. The corrosion rate was still decreasing slightly, with times in Phosphorous Oxychloride, which is similar to the pattern found with medium phosphorous.

The high phosphorous coating was found to be resistant to the remaining corrodents with only minor surface discoloration evident on the specimens and very little color change on the corrodents when compared to the blanks.

Table No. VI is presented as useful supplemental data to compare the corrosion rates of each EN coating after 60 days exposure, with published data on mild steel and Nickel 200. In most of the corrodents, the EN coatings are equal or better than Nickel 200 and cathodic to the steel substrate as shown by their lower corrosion rates. In Phosphoric Acid (75%) the corrosion rates on EN Coatings were higher than Nickel 200. In Phosphorous Oxychloride, the corrosion rate of the low phosphorous coating (1-2%) was higher than Nickel 200 but medium and high phosphorous coatings displayed lower corrosion rates than Nickel 200.

Conclusion

Electroless Nickel Coatings were found to offer comparable or improved corrosion rates over Nickel 200 in a variety of the corrodents tested. Nickel 200 was superior to all of the coatings tested in Phosphoric Acid (75%) and also superior to the low phosphorous coating (1-2% P) in Phosphorous Oxychloride.

TABLE NO. I COATING CONDITIONS

Corrosion Characteristics of Electroless Nickel Coatings in Chemical Environments

Coating	Hard Rc	Heat Treat	% P	Thick Mils	Density G/CM^3	Plate Rate Mils/ hour	Sulfur Type Stabilizing AGENT	Bright Deposit
1	60	None	1-2	2.0-2.5	8.6	0.4	yes	No
2	48	None	6-8	2.0-2.5	8.4	0.65	yes	yes
3	46	None	10-11	2.0-2.5	8.1	0.4	No	No

Surface Prep

1) Mill Finish
2) Hot alkaline soak/clean @ 180-190°F
3) Water (Di) Rinse
4) Electro activation process cleaning @ ambient, cyanide base solution alkaline side for 5-10 minutes @ 25-50 amps/Ft^2. Periodic reverse current flow (+ to -) 7 second cathodic, 10 second anodic cycle.
5) Sample removed at end of anodic cycle.
6) DI Rinse Water
7) Plate
8) DI Water Rinse
9) Air Dry (Pressure)

TABLE NO. II - CONDITIONS OF TEST

Corrosion Characteristics of Electroless Nickel Coatings In Chemical Process Environments

Corrodents

1. Sodium Hydroxide sample from 1st effect vapor body--Niagara Bldg H-24 45% NaOH saturated with NaCl (about 5%) remainder water.

2. Thionyl Chloride ($SOCl_2$) double distilled final product, Bldg. C-23, 11/26/84.

3. Orthochlorobenzyl Chloride (OCBC) $C_7H_6Cl_2$ — Crude (M-15 Drums) Run 17 8/6/84

4. Orthochlorobenzyl Chloride (OCBC) $C_7H_6Cl_2$ — Final Product (M-15 Drums) Lot No. 84-262-11

5. Phosphoric Acid (75%) from sodium hypophosphite process H_3PO_4 V-84 storage tank

6. Phosphrous Oxychloride ($POCl_3$) Final Product

7. Benzotrichloride ($C_6H_5CCl_3$) Final Product BTC C area storage tank

8. Benzoyl Chloride Final Product (C_6H_5COCl) BOC No. 14 Storage Tank 11/26/84

Temperature: Ambient Velocity: static

Method: ASTM G-31 Laboratory immersion corrosion testing of metals
NACE TM-01-69 Laboratory corrosion testing of metals
Single specimen of each material partially immersed (1/3) in 2000 ml of corrodent contained in 3000 ml resin flask specimen size 6" x 4" x 0.020" thick.

References: ASTM B-733-84 Autocatalytic nickel-phosphorous coatings on metals.
ASTM B-656-79 Autocatalytic nickel deposition on metals for engineering use.

TABLE NO. III CORROSION RESISTANCE OF 1-2% PHOSPHOROUS EN COATING IN CHEMICAL PROCESS ENVIRONMENTS

CORRODENT	Test Duration Days	Corrosion Rate Mils/year	Microscopic Exam. of Coupons 1-30X	Observations of Corrodent
1 NaOH	15 30 60	0.02 0.02 0.01	Slight Discolor Same Same	Uneffected Same Same
2 $SOCl_2$ $(FP)^2$	15 30 60	0.10 0.17 0.13	Sample turned black Darker than above Same	Uneffected Same Same
3 OCBC (crude)	15 30 60	0.14 0.15 0.15	Slight discolor Turned black Same	Uneffected Same Same
4 OCBC (FP)	15 30 60	0.02 0.21 0.21	Slight discolor Same Same	Uneffected Same Same
5 75% H_3PO_4 (FP)	15 30 60	10.91 *45.54 Disc.	Severe attack Removed	Green Discolor Darker ------
6 $POCl_3$ (FP)	15 30 60	0.04 0.04 1.12	Black discolor Same Same	Uneffected Same Same
7 BTC (FP)	15 30 60	0.11 0.11 0.10	General discolor Same Same	Yellow tinge Darker Same
8 BOC (FP)	15 30 60	0.03 0.05 0.04	Discolor in vapor Same Same	Uneffected Same Same

* Sample perforated and substrate attacked therefore corrosion rate not accurate.

TABLE NO. IV.-- CORROSION RESISTANCE OF 6-8% PHOSPHOROUS EN COATING IN CHEMICAL PROCESS ENVIRONMENTS

CORRODENT	Test Duration Days	Corrosion Rate Mils/year	Microscopic Exam. of Coupons 1-30X	Observations of Corrodent
1 NaOH	15 30 60	0.02 0.04 0.01	Slight discolor Same Same	Uneffected Same Same
2 $SOCl_2$ $(FP)^2$	15 30 60	0.09 0.10 0.07	Slight discolor Slightly darker Same	Uneffected Same Same
3 OCBC (crude)	15 30 60	0.24 0.40 0.29	Slight discolor Same Same	Uneffected Same Same
4 OCBC (FP)	15 30 60	0.03 0.50 0.53	Slight discolor Same Same	Uneffected Same Same
5 75% H_3PO_4 (FP)	15 30 60	0.22 0.90 7.60	Slight discolor Attack on bottom Peeling	Green Discolor Darker ------
6 $POCl_3$ (FP)	15 30 60	0.01 0.09 0.06	Slight discolor Same Same	Uneffected Darker Same
7 BTC (FP)	15 30 60	0.16 0.16 0.22	Slight discolor Same Same	Yellow tinge Darker Same
8 BOC (FP)	15 30 60	0.04 0.04 0.03	Slight discolor Same Same	Uneffected Same Same

TABLE NO. V--CORROSION RESISTANCE OF 10-11% PHOSPHOROUS EN COATING IN CHEMICAL PROCESS ENVIRONMENTS

CORRODENT	Test Duration Days	Corrosion Rate Mils/year	Microscopic Exam. of Coupons 1-30X	Observations of Corrodent
1 NaOH	15 30 60	0.05 0.05 0.03	Slight discolor Same Same	Uneffected Same Same
2 $SOCl_2$ $(FP)^2$	15 30 60	0.13 0.14 0.10	Slight discolor No change Same	Uneffected Same Same
3 OCBC (crude)	15 30 60	0.31 0.35 0.28	Slight discolor Same Same	Uneffected Same Same
4 OCBC (FP)	15 30 60	0.04 0.33 0.37	Slight discolor Same Same	Uneffected Same Same
5 75% H_3PO_4 (FP)	15 30 60	0.08 0.33 0.76	General corrosion Flaking Same	Green Discolor Darker Same
6 $POCl_3$ (FP)	15 30 60	0.06 0.13 0.10	Discolor in vapor More than above Same	Uneffected Same Same
7 BTC (FP)	15 30 60	0.20 0.20 0.24	Discolor in vapor Same Same	Yellow tinge Darker Same
8 BOC (FP)	15 30 60	0 0.02 0.02	Uneffected Discolor in vapor Same	Uneffected Same Same

TABLE VI

COMPARISON OF THE CORROSION RATES OF EN COATINGS
WITH NICKEL 200 AND MILD STEEL
ALL CORROSION RATES IN MILS PER YEAR

CORRODENT	NICKEL 200	EN COATINGS			MILD STEEL
		1-2% P	6-8%	10-11%	
1 NaOH	0.10 [1 3]	0.01	0.01	0.03	1.40-2.10 [1 3]
2 $SOCl_2$ (FP)	0.17-0.40 [1]	0.13	0.07	0.10	8.20-9.77 [1]
3 OCBC (crude)	0.50 [1]	0.15	0.29	0.28	N.A.
4 OCBC (FP)	0.50 [1]	0.21	0.53	0.37	N.A.
5 75% H_3PO_4 (FP)	0.30-0.50 [2]	>36.5	7.60	0.76	> 50.00 [4]
6 $POCl_3$ (FP)	0.11-0.62 [1]	1.12	0.06	0.10	2.35 5.68 [1]
7 BTC (FP)	0.20 [1]	0.10	0.22	0.24	0.10-0.60 [1]
8 BOC (FP)	0.20 [1]	0.04	0.03	0.02	0.34 [1]

N. A.-- No data available, product polymerizes when exposed to mild steel.

1) Occidental Chemical Corporation, Materials Engineering reports
2) Huntington alloys, "Resistance to Corrosion," bulletin 15M 5-79 S-37
3) NACE publication 5A271, "Comparison of the Corrosivity of Diaphragm Cell Caustic Soda vs: Mercury Cell Caustic Soda," Materials protection , July 1971.
4) NACE "Corrosion Data Survey," NACE 1974.

CORROSION CHARACTERISTICS OF ELECTROLESS NICKEL COATINGS
IN CHEMICAL PROCESS ENVIRONMENTS

References:

1) "Chemical Nickel Plating Methods and Apparatus," U.S Patent 2, 717, 218, September 6, 1955. Paul Talmey and William J. Crehan, assignors to General American Transportation Corporation.

2) "The Performance of Electroless Nickel Deposits in Oil Field Environments," Corrosion 84 paper, No. 221. R. D. Mack, W. W. Bayes.

3) "Electroless Nickel Coatings," Proposed NACE Technical Report TPC T-6A-53, National Association of Corrosion Engineers, Draft 6 March, 1984.

4) "Enplate Electroless Nickel Coatings for Oil and Gas Applications," Enthone Incorporated, West Haven, CT 06508.

5) "Hooker Industrial Chemicals for Basic Industries," Bulletin 100-1980-81.

6) "Resistance to Corrosion," Huntington Alloys, Bulletin 15M 5-79, 5-37.

7) "Comparison of the Corrosivity of Diaphragm Cell Caustic Soda vs: Mercury Cell Caustic Soda," NACE Publication 5A271, Materials Protection, July 1977.

8) "Corrosion DATA Survey," National Association of Corrosion Engineers, 1974.

9) "Materials Engineering Reports," 1950-1985, Occidental Chemical Corporation.

10) "Laboratory Immersion Corrosion Testing of Metals," ASTM G-31.

11) "Autocatalytic Nickel-Phosphorus Coatings on Metals," ASTM B733.

12) "Autocatalytic Nickel Deposition on Metals for Engineering Use," ASTM B656.

13) "Laboratory Corrosion Testing of Metals for the Process Industry," NACE Standard TM-01-69.

14) "Corrosion," Volume 2, L. L Shrein, John Wiley & Sons, 1963.

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K-4

Electroless Session K

The Corrosion Behavior Of Pulsed Electroless Nickel-Phosphorus Deposits

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THE CORROSION BEHAVIOR OF PULSED ELECTROLESS NICKEL-PHOSPHORUS DEPOSITS

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Extended Abstract

Several investigators have reported that the physical and chemical properties of electrodeposits can be altered by plating with a pulsed current or pulsed potential. In a recent paper,* the effect of pulsed current on the properties of electroless Ni-P deposits was discussed. The superposition of pulsed current on the EN reaction produced deposits with physical properties similar to normal EN deposits with one significant advantage; they can be deposited several times faster. In this study, the corrosion behavior of EN deposits formed under the influence of pulsed current was compared to that of "normal EN deposits.

The corrosion resistance properties of both pulsed and normal EN deposits were compared in neutral 5% salt spray (per ASTM B-117). Additionally, the corrosion behavior of the deposits in a salt water environment was investigated using electrochemical techniques.

Experimental

The experiments were performed at three pH values 4.4, 4.7 and 5.2 in both the pulsed and "normal" cases. Two duty cycles were used during the pulsed current tests; 9.1% and 50 %. Deposits were also produced at 100% d.c. The experimental plating bath was similar to that used in the earlier study. The deposits were plated onto zincated aluminum and mild steel. The temperature was maintained at 87°C ± 20.

Stress

The corrosion behavior of EN deposits has been shown to be dependent on the internal stress of the deposit as well as other factors. In general, it was found that compressively stressed EN deposits showed enhance chemical resistance when compared to deposits with tensile stress. The stress of all "pulsed" deposits was tensile in nature. At pH 4.4, 4.7 and 5.2 and 9% duty cycle, the internal stress was nearly constant at 8500 psi tensile. The stressed remained in the range 8500 - 9000 psi except at pH 5.2, 50% duty cycle and 100% d.c., ie., 15,000 and 30,000 psi respectively.

The stress of the "normal" EN deposits plated at pH 4.4, 4.7 and 5.2 were -250 psi compressive, 1500 psi tensile, and 4000 psi tensile respectively.

Salt Spray Results

When direct current is superimposed on the EN reaction, the resulting deposits showed varying degree of porosity. The corrosion resistance of the pulsed EN deposits in neutral 5% salts spray showed marked improvement as the pH of the plating bath was increased from 4.4 to 5.2 for any of the experimental duty cycles (9%, 50%, 100%). That is, for example, the porosity of pulsed EN deposits is greater at pH 4.4 than at pH 5.2 when the duty cycle is, say, 50% (salt spray testing of nonsacrificial coatings is a measure of deposits porosity). The corrosion behavior of these same deposits is vastly improved when the duty cycle is decreased from 100% to 9%.

The deposits formed at pH 5.2 with duty cycle 9% showed similar salt spray resistance to "normal" EN deposits with low tensile internal stress. Pulsed EN deposits do not behave, corrosion-wise in salt spray, as well as compressively stressed EN platings. The above results were observed to be independent of plated substrate, e.g. zincated aluminum or 1010 mild steel.

Electrochemical Corrosion Measurements

The electrochemical corrosion behavior of pulsed and normal EN deposits in 1% salt water was investigated using electrochemical techniques. Results were obtained for the active potential region, which is characteristic of general nonlocalized corrosion; and for the passive potential region, which is characteristic of crevice or pitting corrosion. The corrosion rate given in mils per year for the pulsed deposits, was similar to that found for typical EN deposits, i.e., in the range 0.7 - 1.2 MPY. The normal EN deposit plated at pH 4.4 had a corrosion rate of about 0.5 MPY. The corrosion rate of the other normal deposits fell in the range given for the pulsed deposits.

The breakdown potential or minimum potential for initiation of pitting corrosion of pulsed deposits was similar to that found for normal EN deposits, which occurred at aobut 350 mV, vs. SCE.

Conclusion

The corrosion behavior of pulsed EN deposits was found to be quite similar to that of normal EN deposits obtained from the EN plating bath used in this investigation.

Pulsed plating from an EN solution may be useful in such applications as salvage work, heavy build-up, etc., without any loss in the physical and chemical properties of the Ni-P deposit.

* G. Mallory, V.A. Lloyd, "The effect of Pulsed D-C Current on Electroless Nickel Plating", PROC., AES 71st Annual Tech. Conf., 71 (1984)

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Electroless Session K

Advancements in Electroless Nickel Plating Technology for Printed Circuits

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ADVANCEMENTS IN ELECTROLESS NICKEL PLATING TECHNOLOGY FOR PRINTED CIRCUITS

By

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The printed wiring board (PWB) industry is developing a number of new manufacturing methods to meet the increasing demand for close dimensional tolerances found in densely packed circuitry. Surface-mount devices (SMDs), for example, require fine lines, tiny "vias", and close spacing; and large-scale integrated circuits require a large number of leads on tightly spaced centers. Some of the current industry trends are:

1. Complete automation of the PWB manufacturing process
2. Composite substrates for leadless ceramic chip carriers
3. New P.W.B. substrate materials such as extruded or molded thermoplastics
4. Permanent resists to protect fragile fine lines
5. Dry, thermomagnetic resist process
6. Laser exposure of artwork and resist-covered boards
7. Multi-layer boards
8. New processing steps and materials such as additive/semi-additive circuit production and special electro-/electroless plating materials

This paper will discuss special electroless nickel plating processes which provide the finish required for surface mount technology, multi-layer P.W. boards, PWB contact surfaces, and boards exposed to high temperatures.

SURFACE MOUNT TECHNOLOGY

In order to provide a surface which can be used for surface mount components (direct mounting and connecting of microelectronic components), the P.W. board finish must be receptive to effective wire bonding, die bonding, and soldering. Very few finishes can provide a suitable surface capable of all three attachment processes. Gold, for example, which is most widely used, is not ideal for soldering or wire bonding. Gold in a solder joint causes a dull, weak joint and will contaminate the solder pot to the extent that it must be discarded (reclaiming the gold where possible) periodically.[1]

Wire bonding to gold will sometimes have voids under the wire (Kirkendahl voiding) resulting in a weak bond.[2,3] Die attachment using gold/silicon pre-forms is excellent, but less satisfactory if epoxy die attachng is used.

Other metals commonly used for P.W. finishes have similar shortcomings. Tin and tin-lead deposits, for example, solder well but cannot be wire bonded. Electrodeposited nickel does not solder well after aging, even for a short time. Copper solders well if pre-cleaned after aging, but does not wire or die bond well.

Specially formulated electroless nickel deposits, on the other hand, are capable of providing excellent bonding characteristics for wire bonding by ultrasonic or thermalsonic methods, die attachment by gold/silicon or epoxy methods, and are solderable using RMA fluxes.

Table I shows typical bond strength data for aluminum wire bonding to electroless nickel-boron deposits.

Table 1. Ultrasonic Bond Strength of .001 in. dia. Aluminum Wire on Electroless Nickel-Boron Deposits .3% Boron

Deposit Thickness μ In.	Wire bond strength - grams
12.5	6.24 ± .41
24.4	6.38 ± .42
49	6.51 ± .38
65	6.0 ± .27
86	6.51 ± .34
114	6.4 ± .26

Solderability was tested on steam aged plated panels using a meniscograph with a Soltec recorder. The solder was 63/37 tin-lead at 240° C. A time of 1 second is considered excellent with 2.5 seconds satisfactory.

Table II. Solderability Test Results for Nickel-Boron Alloys

Boron Content %	Bath pH	Treatment	Flux	Average Value in Seconds To Reach Zero-Force Axis
.2	6.5	Steam aged*	RMA	2.3
.2	6.5	Steam aged	RA	0.73
.2	6.5	Degreased	RMA	1.18
.3	6.5	Degreased	RMA	1.18
3	6.0	Degreased	RMA	1.13
3	6.0	Steam aged	RMA	1.65
3	6.0	Steam aged	RA	0.8

Table III. Solderability Test Data for Nickel-Phosphorus Alloys

Phosphorus %	Bath pH	Treatment	Flux	Average Value in Seconds To Reach Zero-Force Axis
4	9.5	Degreased	RMA	1.98 slidewetting
8	4.8	Steam aged	RA	1.10
8	4.8	Steam aged	RMA	2.7 slidewetting
11	4.8	Degreased	RMA	1.85
11	4.8	Steam aged	RMA	1.75
11	5.2	Degreased	RMA	1.89

The steam aging was conducted for 1 hour in accordance with MIL-STD-202, Method 208.

These tests show that electroless nickel-boron deposits exhibit good solderability using RMA flux, or stronger, even after steam aging.

Die Bonding-Pre-form processing using electroless nickel-boron is replacing spot gold plating for die attachment in numerous applications. Gold-silicon pre-forms bond well to nickel-boron deposits, as do conductive and non-conductive epoxy die attachment compounds.

Cox and Dean[4] reported difficulty in die bonding to alloy 194 copper lead frames with electrodeposited nickel. "No problems were experienced with electroless-nickel plated frames." The mode of failure from electroplated nickel was dewetting of the gold-silicon eutectic from the lead frame. No de-wetting was observed when 50 micro in. of electroless nickel was plated onto the copper alloy.

MULTI-LAYER PRINTED WIRING BOARDS

The requirements for small hole diameters and a large number of layers creates exacting demands on present plating interconnect processes. The limitation of current distribution, causing low current density inside small diameter holes (which are also deep due to the several layers stacked) results in either thin copper deposits or voids. The voids result from either incomplete electroless copper deposition or burn-out which occurs when current is applied but no electroplated copper is deposited. The thin electroless copper deposit is dissolved by the copper electroplating solution.

Certain electroless nickel systems of low phosphorus or boron content can be plated easily to greater thickness and with complete coverage than with most electroless coppers and are capable of surviving the plating conditions, allowing electroplated copper to deposit. In some cases the electroless nickel deposit can be the entire interconnect conductor. For example, multilayer printed wiring boards have been successfully produced which had twenty layers with holes of .010" diameter, others with 40 layers and holes of .020" diameter. These are used in high frequency circuits where low background noise is required. Electroless copper was not only incapable of interconnecting all the holes in the PWB, but the few successful connections resulted in high noise (low signal-to-noise ratio).

The electrical resistivity of electroless nickel is higher than that of electrodeposited copper (18-12 μ ohm/cm for electroless nickel and 1.7-4 μ ohm/cm for copper). However, for low current, high frequency applications the difference is negligible.

PWB CONTACT SURFACES

Contact surfaces such as plug-in "fingers" require good wear resistance, low electrical resistance, corrosion resistance, and heat resistance. Electroless nickel-boron and some low-phosphorus deposits meet these requirements either alone or overplated with a thin (up to 5 micro inches) layer of gold.

HIGH TEMPERATURE EXPOSURE

Because electroless nickel deposits are good diffusion barriers compared with electrodeposited nickel and most other metals, electroless nickel-plated copper circuits and contacts can withstand high heat environments such as "burn-in" products. "Burn-in" cycles are typically run from room temperature to 93.3° C (200° F) alternately for from 1 day to 1 week.

Isolated copper circuit areas can be plated electrolessly by using a special electroless nickel poly-alloy strike followed by more conventional electroless nickel deposits. (Copper is not considered catalytic to electroless nickel-phosphorus deposition.) This unique property provides great versatility in the use of electroless nickel for printed wire boards.

CONCLUSION

As the printed wiring board industry develops smaller, higher density, and more complex circuits with tiny vias, hole pads, and surface mounting areas in close proximity and with small diameter through-holes, the performance requirements of plated deposits will become more critical and have tighter tolerances. Electroless nickel formulations of low phosphorus or boron content can fulfill all of these requirements, often without the need of any additional plated deposits.

On PWB's requiring copper deposits, an overplate of these electroless nickel alloys will provide the multiple properties of solderability and wire and die bondability that are prerequisites for successful surface mounting of components. The versatility and excellent deposit characteristics of electroless nickel deposits will continue to meet the needs of the advancing state of the art.

REFERENCES

1. H. Manko, Solders and Soldering, 2nd Ed, McGraw-Hill Book Co, New York, NY, 1969; p 76
2. E. Philofsky, Solid State Electronics, 13, 1391 (1970)
3. C. W. Houting, Proc. of 10th An Reliability Physics, IEEE, 155 (1972).
4. B. T. Cox and S. W. Dean Jr., "Analysis Of Die Bond Failures On Alloy 194 Lead Frames," *Proc. of Technical Program of NEPCON,* 1976, pp 111-118.

K-6

Electroless Session K

Advanced Manufacturing Techniques In Plating Using Computer Technology

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Advanced Manufacturing Techniques in Plating using Computer Technology

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The last fifteen years of this century will see the extensive integration of computers into the manufacturing process. This paper describes the use of computer software to do on-line statistical quality control, track the effect of corrective actions and acquire and monitor information about the process.

By developing an integrated solution to the plating process it will be possible to develop and control all major aspects of the system.

A revolution in manufacturing is beginning which will see an integration of man and machine through computerization. At the center of this revolution is computer technology and distributed communications systems. This revolution will produce new industries and disciplines requiring a new type of specialist who can use these powerful tools.

For process engineers and platers to realize this revolution, they will have to call upon several sciences. These sciences include chemistry, statistics, metallurgy, systemation and process engineering. Because of the complexities and diverse requirements, the integration will only come after each of these sciences is analyzed and a method is chosen which is common to them all.

There are several reasons for this revolution. The major reasons are: the reduction of direct manufacturing cost, the improvement in performance of finished goods, and the capability of producing a greater variety of goods from the same equipment. To achieve these goals a new manufacturing philosophy must be developed. This philosophy has at its center the concept of flexibility of machines through automation. With this type of system, production can be adjusted by changing production programs building only for current demand. These techniques will improve productivity by reducing inventory, reducing start-up on new products, increasing product range and reducing direct labor costs.

Metal finishing represents a key manufacturing technique in achieving

the design flexibility goals of these new systems. Metal finishing advances also represent a significant enhancement in product value with coatings like electroless nickel and ion implanation. These coatings make is possible to build new levels of performance fraction of the cost of the exotic materials currently being used.

With the advent of this new philosophy and the desire to have more information about the metal finishing process, a more integrated information system must be developed.

The technology requires that the information system provide current facts on process and production conditions. This information would be available for engineers to quickly modify machines and process conditions to produce different products. This system also requires that historical process and production information be analyzed to determine quality. This change will take place over the next 20 to 30 years. To remain vibrient and competitive, many industries must accept this challenge For some metal finishing operations this challenge may never come, for others it is already here.

Large captive facilities producing tens of thousands of similar parts will want a statistical system to trap rejects without increasing inspection cost. Job shops may have hundreds of processes and batches which require monitoring on a daily basis. What ever the reasons, the computer and specialized hardware must be available which can be used to achieve these objectives

Some of the major requirements for a metal finishing computer system are:

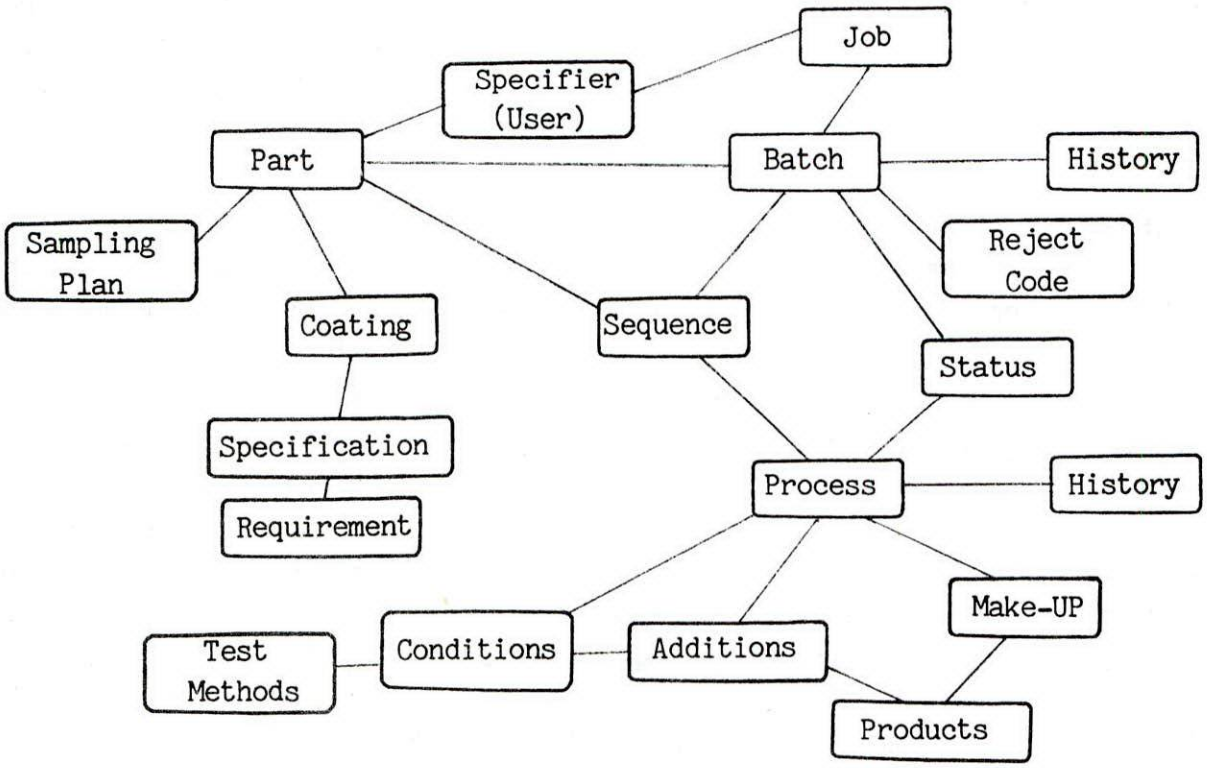
Analyze Quality
Control Quality
Monitor Cost
Control Process
Communicate to other computers

There are two choices for hardware at the present, the mini-computer and the micro-computer. Each tool can be programed to do the job and provide the information and ultimately help implement the philosophy.

At the center of either type of hardware system is the software. The software for these systems must be designed and implemented to relate all the information in an organized way. Within the computer software this function is called the data base which includes items like process conditions, reject codes and sequences numbers.

Parts or batches of parts, process, and activities are the critical items of the metal finishing system. From there, several other key items are required. The broad catagories of a data base are represented below and are organized as one might in a metal finishing system.

Metal Finishing Relational Data Base



Programs that are written to collect and share this information can provide past, present and future advice on the operations of the metal finishing system. With additional software, infromation from test points on equipment and processes can be collected, as well as communication of production and quality information to other systems.

To produce a system which will provide this type of integration, a fairly complex computer software solution is required. For metal finishing, a problem like controlling gold thickness is dependent upon the dynamic efficienty of the process, the surface area of the part, the current density, the density of the gold deposit, and the uniformity and distribution of gold on the part. With all of this information available, the computer can provide the operator

with the amp-seconds to produce the coating or commnd the hoist to move the batch of parts into the gold tank, turn on the rectifier for the exact time and voltage to achieve the required thickness on the significant surface, and then remove the batch to the next step. The reason for this type of sophistication would be to control the gold density and thickness, ultimately to reduce cost and rejects. Processing errors can be very expensive - reject parts and loss of gold.

Providing advice on the metal finishing process could take the form of checking for process tests which were over due when checked against the last time an input was made, and the frequency for the test. Another example could be the mean thickness or alloy for a particular part over a period of time.

The third type of program is used to communicate to other systems. These programs can take quality information and send it to other computer systems. With a properly written system, design information like specifications and process conditions can be communicated to the metal finisher for his use.

To produce a group of programs which work together and provide control, advice, and communication in the metal finishing environment, several criteria must be examined: How many people will be using the system when it is in full operation? How easily will it be to modify as new requirements become identified? What is the economic value of the system? Is it going to be integrated into a computer aided design system? What test points are dynamic to my system? What kind of equipment shall I use? These answers and others should be carefully considered before a a computer system is purchased.

The logical choice for equipment is the micro computer (PC) using Local Area Networking (LAN) techniques. This type of equipment provides for a highly flexible and cost effective hardware solution. This differs from the mini computer and main frame approach of earlier this decade.

Today there are hundred of peripheral suppliers who can provide printers, plotters, bar code readers and more for the micro computer. In addition there are thousands of programs ready to run which can be used to get answers now to current questions. This supply of equipment means that the hardware can be configured quickly to achieve the desired function.

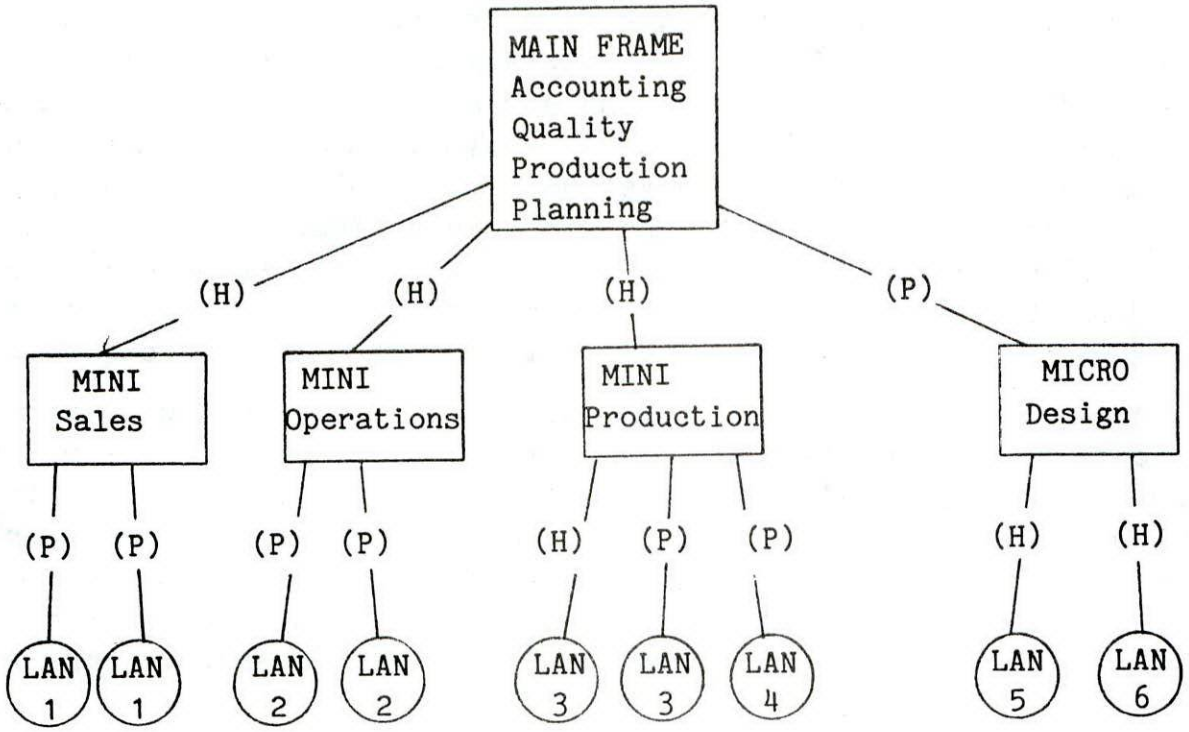
The Local Area Network is a new way of communicating between micro

computers. This technique uses a single strand cable and transmits FM pulses between the micros. The rate of transfer of information is 5 to 10 times faster than the disc transfer in most cases which provides for high performance on a small system. With the LAN the micro computer does the processing and sends the results to one of the other micro computers which has a system disc. In this way each micro has access to the system information and at the same time it can be free to do independent processing. This means the system is not subject to the typical strains main frame computers have when too many users are making requests. This can be critical when a rectifier must be turned off or a hoist is to start a sequence.

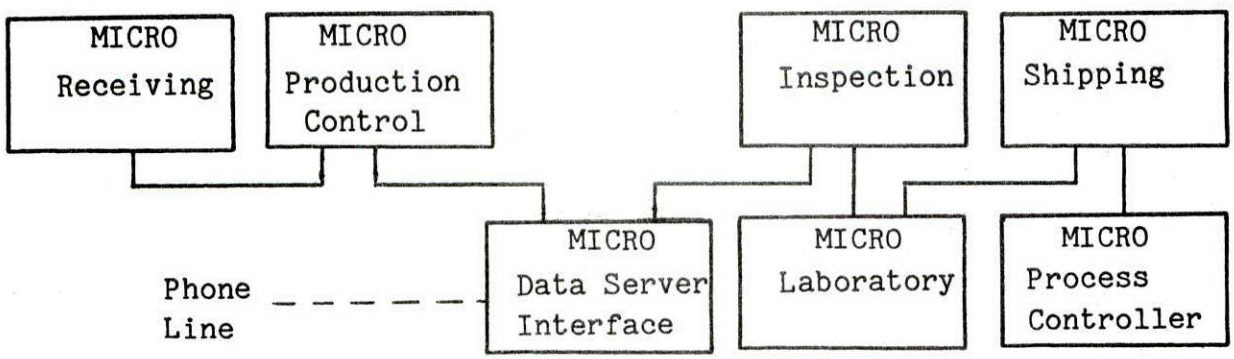
In these control problems the local processor is low cost and dedicated to a single task. The output from this process micro would be through the LAN to the system disc. Other micros on the LAN would run programs requesting input and printing reports, each time updating the disc. Dependent on the organization, the quality information being generated within the system could be printed in a report, statistically analyzed or transmitted to another computer system.

With this type of computer design a layering of services and capabilities can be provided which will quickly and efficiently organize the information (see page 6).

COMPUTER SYSTEM DESIGN



LOCAL AREA NETWORK



KEY

1. Remote Sales Offices
2. Remote Distrubution
3. Machining System
4. Metal Finishing System
5. Computer Aided Machine Design
6. Computer Aided Metal Finishing Design

LAN	Local Area Network	MINI	Mini Computer System
MICRO	Micro Computer	MAIN FRAME	Large Computer System
(P)	Phone line	(H)	Hardwire connection

With local data bases the highly detailed process information which is needed locally for control would not be distributed to the main frame unless requested. Local back-up would be maintained and be transportable for off line analysis and design function if desired.

The concept of traceability is a key aspect of the computer system we are discussing. The tracking of batches and inspection results to process conditions at the time of plating becomes the important task of the computer system.

The least expensive and most flexible means of tracking the work is by producing a traveler which can be read by an optical code reader (OCR) like those used at department store check outs.

The use of a reader is an important consideration because it increases reliability over keybound operations. By using a traveler system the detailed instruction for process and inspection can be printed for the plater and inspector. Travelers for batches can be prepared in advance of processing and the reader used to point the computer to the set of steps and operator is completing. The reader and traveler provide the computer system with the capability of connecting the part to a specific process and establishing the critical traceability. Without traceability of the processing time and operator and current process conditions the ability to identify critical variation in the quality will be missing.

Continuing the application of computerization in metal finishing the area of inspection is important. It is here that the actual quality is recorded. Through the use of sampling plans, specification and requirements a complete detailed report on the batch of parts can be produced. By checking the requirements and identifing the mean values for each batch of parts, a record of the quality will be generated.

Process information, in most cases, is already available from the process engineer or chemists. This information can be entered into the system with little effort. With some dynamic or critical processes monitors and controllers can be used.

In these applications sensors and analyzers are used to collect information, and using micro computers provide closed loop control on the process by feeding back the material consumed. Only dynamic or critical processes should be controlled in this maner. If the temperature is determined to drift on a process a more responsive and accurate temperature controller should be examined before

computerization is attempted. Pumps and valves can be accuated with level switches much more conveniently and reliably than with computerization in many cases.

Any computer control problem should be evaluated by the following questions: How reliable does the system have to be? What will the cost of developing it be? Who will maintain it? What effects on quality and production is this control point?

The use of industrial analyzers and process controllers can offer reliable manufacturing solutions. Typical cost for ruggedized analyzers are $20K to $80K. These units can analyze several process chemical conditions continually. This compares to a chemist who is flexible and able to analyze and control 40 or more process daily for $20K to $30K annually,

In the future factory, the programs for the analyzer and hoist will be generated by the micro computer and interfaced, down loaded, to the local unit to work until another program is down loaded. Only critical operations which are subject to variations like rectifiers, waste water controls, dynamic processes and hoist and robot systems will need to be computer controlled. Information about the processes like boiler pressure and cleaner temperatures would be monitored and used to identify potential maintenance problem and track the effect of correction measures taken by the process engineer.

The collection of useful process information is a primary goal of the computerized metal finishing system. The examples discussed below provide some guidelines on what conditions should be controlled and monitored.

Dynamic Processes - these are chemical or mechanical systems which will have variation (noise) that can effect the quality. They are generally not controllable by normal human systems. This may be due to the redundant analyses or dynamic nature of the process.

Electroless poly alloy solution can require 100% additions of control additives within 10 minutes of processing. Sampling, analysis and replenishment might take 5 minutes manaully and therefore not be adquate when trying to control the process. Electroless copper solutions also can require automatic analysis and feed in large automotive and electronic applications.

In these dynamic processes the micro computer is used to provide

all the primary control through input and output. Most process controllers also provide the status and test results which can be interfaced to another micro computer used for communications and data basing. These interfacing micros also store the instruction used in the process controllers. Depending on production or process requirements, the instructions are down loaded to the process computer changing the parameter and establishing new set points for conditions.

Motion - Hoist and robots may be controlled by a computer. In this example, the process sequence may be altered to control the specific step or timing. These changes would be determined by variations in the type of work being processed and the process conditions.

From calculations made from thickness tests the time within the plating process would be altered. This would be accomplished by having the interface computer generate a new set of instructions and down load them to the micro controlling the hoist or robot.

Monitor - Process information which would require monitoring should be dynamic to the quality. Temperature of the oven, etchs, soak cleaner, and plating process should be considered. Other information like rinse water temperature and specific gravity of zincates and activators should not be considered unless they vary rapidly and cannot be tested easily.

The information collected would be checked for accuracy using several probes and voting techniques. The software would then record the changes via the LAN to the system disc.

All of the equipment for producing an integrated computer system like the one we have described is available and ready to be built. The cost of the hardware has been dropping and has reached a level which will not change considerable over the next few years. Additional features will maintain the cost somewhat constant while adding greater capability.

It is our hope that the technologies and phillosohpy described in this paper will stimulate interest and discussions within our industry. The result of these discussions and the implementation of these technologies will improve the confidence and acceptance of metal finishing as a tool for adding value and performance in many more applications.

L-1

Statistical Methods I
Session L

The Step Test — A Systematic Evaluation Of Current Equipment And Standards Using Statistical Methods

Mr. D.L. Davidson, Chrysler Corporation
Mr. L.W. Wiedmayer, Ford Motor Company
Mr. G.G. Perrin, Jr., Ford Motor Company

THE STEP TEST - A systematic evaluation of current equipment and standards using statistical methods.

Mr. D. L. Davidson, Chrysler Corporation
Mr. L. W. Wiedmayer, Ford Motor Company
Mr. G. G. Perrin, Jr., Ford Motor Company

The step test for evaluation of deposit thickness and electrochemical potential difference introduced by Chrysler Corporation in 1980 has generated considerable interest in the Automotive Industry materials engineering community. At Ford Motor Company this interest lead to the development of a Ford Laboratory Test Methods (FLTM) to support a proposed engineering specification (material preference) requirement. To effectively evaluate the FLTM which varied in several respects from Chrysler's recommended practice, a round robin was conducted. The round robin was proposed by the Electroplated Parts Quality Task Force (PPTF) to provide information on repeatability and reproductibility of the measurements for thickness and electrochemical potential difference. Sample plaques were prepared by W. A. Donakowski, Ford Manufacturing Process Laboratories, and sent to four (4) locations for evaluation (Saline Plant, Sandusky Plant, Udylite and Central Laboratory Services). The outcome of the round robin evaluation caused considerable consternation and confusion since the results were so anomalous.

In an attempt to resolve the anomalies the Test Methods and Specifications Committee of the PPTF prepared a cause and effects analysis to determine the possible sources of the measurement variance within laboratories and between laboratories. The results of the cause and effects analysis and supplemental information on thickness measurements indicated serious shortcomings in the thickness determination that were not resolvable in the estimation of the Test Methods and Specifications Committee PPTF. The anomalies noted in the potential difference portion of the method were considered resolvable by the Test Methods and Specifications Committee PPTF. At this juncture it was decided a more rigorously controlled round robin should be conducted. This paper will deal with the results of that round robin on the potential difference measurement using Step Test equipment.

The first effort of the Test Methods and Specifications Committee PPTF was to prepare a standard procedure for conducting potential difference (E) measurements (See Illustration I). The next step was to return to the cause and effects analysis and attempt to provide blocks for all possible variation in measurement. This was partially accomplished by using a single test solution prepared at Ford Motor Control Laboratory Services based on recommendations from Chrysler Corporation's Electroplating Section Metallurgical Engineering. The discussions with Chrysler also produced changes in the standard procedure for conducting the test. The Electroplating Section Metallurgical Engineering Chrysler Corporation provided seven (7) E standard coupons marked 130 millivolts (See illustration II).

The round robin was conducted with a Ford Motor representative attending the evaluation to assure that the instructions were followed per the outlined procedure. The program was originally scheduled to have eight (8) locations involved. The locations involved were suppliers to Ford Motor Company and Ford Motor laboratories. Four (4) of the locations provided measurements on the standard panels and an interim review of the results indicated that a large variation existed in the results that was not anticipated and the program was terminated until adequate statistical analysis could be performed.

An analysis of variance table was constructed to compare the results of the E measurements and is contained in illustration III and IV. The conclusions drawn from this statistical analysis are that the instrumentation was not statistically different location to location but that there is some statistical significance in the difference in the standard coupons.

L-2

Statistical Methods I
Session L

Pulse Plating Of Cyanide Evaluation of Current Equipment And Standards Using Statistical Methods

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PULSE PLATING OF CYANIDE EVALUATION OF CURRENT EQUIPMENT AND STANDARDS USING STATISTICAL METHODS

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There has been much discussion over the last few years regarding the advantages of acid copper as a base metal deposit over zinc alloy castings as a deterrent to field corrosion failures. The advantages of this process are the increased thickness of the copper layer and the "Levelling" effect of acid copper over casting defects by providing a "seal" over the base casting. In effect, acid copper is perceived to add a margin of safety against field corrosion when plating inferior castings.

We at Siegel-Robert feel that an alternate approach is in order. Regardless of the copper plating system, the quality of the casting is directly related to the field longevity of the plating part. For that reason, castings with known defects such as cold shot, should not be plated. Proper control of diecast parameters, adequate manufacturing control and quality control can provide good castings to the plater.

This leaves us with sporadic parts that occur within casting runs with defects that are either very difficult to see, or so limited in number that they would not be picked up under normal inspection. These castings can be helped by increased thickness of the copper deposit. It is our feeling, backed by the statistical evidence attached, that pulse copper is a far superior method of depositing this additional plating thickness.

Pulse Copper

The attached data is documentation of extensive plate thickness distribution testing, comparing pulse copper plating with acid copper plating. For this experiment, a thickness checkpoint was picked in a relatively high current density area, designated "back outside" and this was the point that was plated to specification (.0008"). No attempt was made to plate the low current density areas to specification. This was done to provide information on the overall distribution range of the copper deposit, using pulse relative to acid copper. By increasing the plating time, specified thickness of the pulse copper can be achieved in the low current density areas.

In analyzing the data from this experiment, the following things become evident:

1. Pulse copper is far superior to acid copper in its ability to evenly deposit copper thickness across all density areas of the part (Charts A & B).

2. Pulse copper has the ability to plate the back, or non-show areas of the part, more evenly, with more thickness, than acid copper, thus providing additional corrosion protection.

The number one finding of this study, which we feel is significant, is even plate thickness distribution. The frequency distributions in Charts A & B graphically demonstrate the even distribution capabilities of pulse copper versus acid copper. In comparing the frequency distributions in Chart A, for pulse, and Chart B, for acid copper, it is readily apparent that pulse is far more capable of obtaining consistent, even thickness from part to part, regardless of current density and rack position. While the process averages are close to the same, .00097" for pulse, .00091" for acid copper, the real story lies in the three standard deviation spreads. The bell-shaped curve for the distribution of pulse readings, while slightly skewed to the left, much more approximates the normal.

As mentioned earlier, additional plating time with pulse copper can provide specified thickness in the low current density area. Certainly this is also true of acid copper; however, because of the differences in the distribution spreads, there is a real problem with acid copper in this regard. Shifting the process average of acid copper far enough to become capable of plating to specification in the low current density areas, would result in readings in excess of .00451" copper in the high current density areas of the part, which compares with .00016" using pulse. In other words, to plate to the specified copper thickness using acid copper, it takes roughly four times more thickness in the high current density area using acid copper, than with pulse copper. Chart F demonstrates the comparative differences between the averages of the absolute lowest current density and averages of the absolute high current density readings of pulse and acid copper. By using pulse, we have obtained more consistently uniform thickness without the dramatic high and low thicknesses observed by using acid copper.

In summary, we feel that the evidence shown here, along with test results in accelerated corrosion testing, support our position that pulse copper plating is a viable, if not preferable, alternative to acid copper plating.

L-3

Statistical Methods I
Session L

Environmental Degradation: Do Present Accelerated Corrosion Test Methods Act As Adequate Determinors?

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ENVIRONMENTAL DEGRADATION: DO PRESENT ACCELERATED CORROSION TEST METHODS ACT AS ADEQUATE DETERMINORS?

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Numerous reviews of automotive bright trim hardware in the Northeastern United States and Eastern Canada conducted during the previous five (5) years have surfaced a particular concern related to duplex nickel chromium electroplated plastic, zinc diecast and steel parts. The concern is focused on the considerable incidence of corrosion failures at low service mileage (less than 250 miles) and moderate environmental exposure duration (6-12 months), at no service mileage and extended environmental exposure duration (12-24 months), or at moderate service mileage (1000 -2000 miles) and short environmental exposure duration (1-6 months). The corrosion failure incidence is approximately twenty percent (20%) averaged over all vehicle lines and components (North American, Japanese, and European Manufacture) sampled during the prior five years. In specific instances for a given vehicle line (car, light and heavy truck) and component the corrosion failure incidence approaches one hundred percent (100%) within the first year of environmental exposure or approximately five thousand (5000) miles based on the field evaluation samples.

Several explanations may be offered for this serious performance degradation versus performance expectation for duplex nickel chromium electroplated automotive bright trim hardware. The first explanation is that the electroplating systems currently extant are inadequate to meet the stated performance expectations of the various automotive companies. The second explanation is that the manufactures of the various trim hardware components do not understand the technology sufficiently to correctly manufacture the various components which will meet the stated performance expectations. The third explanation is that the various automotive manufacturer performance specifications and their associated evaluation methods will not act as adequate controls or measures of field performance. A fourth explanation is that current component design practices exceed the bounds of available technology for the electrodeposition of metal films such as duplex nickel chromium systems by violating established standards for feasibility of design. A fifth explanation is that the theoretical knowledge of field corrosion mechanisms is not adequately developed to state appropriate models and thus provide adequate test methodologies. A sixth explanation is that the theoretical knowledge exists but is poorly understood by the materials performance specification and design engineering communities and is therefore in some instances improperly used or misapplied. A final explanation is that the real situation is some combination of the previously noted explanations. Considerable evidence exists implicating component manufacturers 1) inability to meet specification requirements, 2) poor quality systems, 3) poor technical systems (as measured by the Ford Motor Company Electroplated Parts Quality Task Force systems and facility reviews) and implicating misapplication of theoretical

knowledge in the development of corrosion evaluation methods. The other explanations are not currently supported or refuted by substantive evidence derived from adequate statistical analysis.

The focus of this paper will be existing corrosion evaluation methods specifically accelerated cabinet corrosion tests. Those tests dealt with will be salt spray, acetic acid accelerated salt spray, copper acetic acid salt spray, kesternich, and corrodkote. Several criticisms of these test methods are regularly voiced when the test fails to act as an adequate predictor of expected field performance. The complaints or contentions of the customer and producer are much the same - The test results indicate no failures; yet, failures occur in the field, why? Once again, speculation leads to many conclusions several of which are supported by substantial evidence. The supported evidence consists of the following: 1) Lack of adherence to all the provisions of standard methodologies, 2) Failure to evaluate the parts tested using the stated requirements outlined in the various engineering or standards association specifications, 3) Use of equipment improperly installed and maintained, 4) Improper preparation of test solutions or pastes used in the conduct of the tests. The conjecture unsupported by adequate statistical evidence but based on established chemical and physical principles is as follows: 1) The individual tests are at best coarse approximations of field service conditions, 2) No single test adequately measures the combinations of conditions inherent in lots of parts, 3) Any stated time frame relationship suggesting correspondence between cabinet exposure and field exposure has no strong correlation and should be ignored.

The discussion of the supported evidence centers around the operating parameters of the various test cabinets. Placement of aspirator towers, fog collection devices, and corrosion panels are crucial. When more than one tower is used in a cabinet, the towers are rarely balanced so that each tower has an equal effect on fog distribution. Fog collection devices are poorly positioned or the minimum number specified utilized, sometimes both previous situations are combined; corrosion panels are rarely used. Solution or paste preparation is improper or exceeds the age limitations. Part placement in the cabinet does not follow recommended practice. Venting of the cabinet does not meet the recommended practice. Cabinet or solution reserviors are not cleaned on a regular basis allowing the growth of algae and bacteria whose by products may compromise test results. Heaters are not checked for function on a periodic basis. Cabinet jackets are not kept full thereby creating temperature gradients in the cabinet; aspirator nozzles are not examined for erosion and clogging. Records of the ongoing performance of the cabinet are not maintained in most instances. Statistical control charts on certain crucial parameters are not used. The list of abuses is endless. These abuses all contribute to our collective inability to understand what an accelerated corrosion cabinet is describing in terms of part performance. The resulting confusion maifests itself in the comments mentioned earlier, "test results indicate conformance yet field performance contradicts; Why?"

The discussion of the unsupported conjecture centers around applicability and efficacy of the test methods involved. Since the history of cabinet salt spray testing has been evolutionary in nature and that evolutionary process has been forced upon the plating and surface finishing industry by circumstance rather than by rational logical design, it is not surprising questions regarding efficacy and applicability arise. Certainly, one must question why there are varying exposure times for each specify-

ing organization; when single exposure periods as short as sixteen hours are compared to single exposure periods of forty four (44) hours, it becomes difficult to understand the rationale unless one presumes that the specifier has been mislead by some cabinet performance versus field performance correlation statement without questioning the validity of that statement. Another question that arises is why do ASTM and two (2) of the big three (3) automotive producers require wiping of parts to be tested in CASS with a magnesium oxide slurry and one (1) producer does not require the use of the slurry. Similarly, why on diecast and steel parts does one manufacturer require corrodkote and the others require CASS or a mixture depending on circumstance? A rational argument exists for the choice between one of the salt spray tests and the corrodkote test; which one truly represents the set of conditions experienced by the component in question. Do high humidity high temperature situations really represent the most corrosive environmental situaton as a model or is some more adequate model yet to be discovered by the test methods and specifications community? Are there hidden galvanic effects not considered as part of the model yet operating on components in the field? Do concentration cell effects play an important role in the cabinet versus field performance model? Do some transport effects contribute to the cabinet versus field performance model? Certainly none of the above questions are answered when one looks analytically at the existing test procedures; yet, all of those effects contained in the preceding questions probably play an important part in the field exposure situation and are not accomodated in the test procedures. An important observation also regarding salt spray and corrodkote testing is the lack of ongoing review and revision of these test methods which now are more than twenty five (25) years old. The preceding statement alone should provoke an effort in the engineering and scientific community to review these methods particularly since the knowledge of electrochemical mechanisms has increased manifold during this time period. The preceding questions and comments can no doubt be aligned with the earlier statement "test results indicate conformance yet field performance contradicts, why?"

There is fortunately a way to resolve the dilema currently extant. The use of a specific statistical method, experimental design, should provide the tool to most effectively resolve some of the mysteries that exist and return some semblance of order to the seemingly chaotic situation that is currently plaguing supplier and customer. A portion of the necessary work is currently being carried out by Ford Motor Company, Body and Chassis Engineering Materials Laboratory and Harshaw/Filtrol as a cooperative effort. A fractional factorial design (3 level 8 factor reduced by 3 factors) is being conducted to evaluate various combinations of plate thickness, step potential, pretreatment of basis metal and intermediate metal layers. While the design does not take into account the test methods, the panels in question will be subjected to environmental exposure and accelerated cabinet corrosion testing. This will provide some insight into correlation between cabinet and field performance but not sufficient insight because of confounding of effects. A fractional factorial design including all the test methods and field exposure should be conducted. The most successful design in terms of cost time versus information probably is a two level N-K factor reduced designed N being between twelve (12) and fifteen (15) and K between four (4) and six (6) with replication. That design should in two years indicate whether further work is necessary and in what direction that effort should be conducted.

L-4

Statistical Methods I
Session L

Process Control Improvement In The Plated Parts Supply Base

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PROCESS CONTROL IMPROVEMENT IN THE PLATED PARTS SUPPLY BASE

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Reviews of automobiles at used car auctions, shopping center parking lots and rental car lots have shown that a high percentage of plated exterior automotive trim parts do not maintain the initial bright appearance which was intended to give these vehicles an initial appearance of quality. While the intent of plated parts was to enhance the appearance of the vehicle, significant deterioration has, in many instances, resulted in detraction from appearance. Reviews conducted at dealer lots in Montreal by the Ford Survey Team have also shown significant corrosion on plated parts on new vehicles awaiting customer acceptance.

The causes of deterioration of plated trim parts can be grouped into two broad categories; parts poorly designed for plateability and supplier quality. In order to improve the durability of plated trim parts, Ford Motor Company established an interdivisional Plating Task Force in 1980. Many of the actions of the Plating Task Force are summarized in Attachment I. While the list of actions deals with both design and quality concerns, the balance of this paper concentrates on those activities which relate to the plating processes.

Among the earliest activities of the Plating Task Force were establishing supplier evaluation criteria and conducting reviews of supplier locations for rating purposes. After reviewing several plating supplier locations, a recurring weakness became apparent. This recurring weakness was an inability to maintain the process according to the process specification. While there were usually available process specifications which defined how the processes were to be maintained with respect to tank composition, temperature, pH and contaminants, and there were usually available test equipment and meters for measuring these operating parameters, a review of the actual results of the testing showed a high percentage of results not conforming to specification requirements. In some instances, out of specification results did not result in any corrective actions.

In order to improve the capability of plating suppliers to control their plating processes, a statistical technique was sought which would indicate the capabilities of the control strategies and any out-of-control conditions. After some investigation, the individual and moving range chart was selected as the type of control chart most suited for evaluating the data in the form as collected by platers. The individual and moving range chart has been used for years in the chemical industry. $\bar{X}$, R charting can also be used for those parameters which are measured more than once per day.

In order to provide training material for plating suppliers, laboratory test results were obtained from four supplier locations and charted. This provided examples of actual plating data to demonstrate the purpose of the charts. Two training sessions were held for plating suppliers to demonstrate use of the individual and moving range charts and train in their use. Each Ford supplier location was assigned to apply the individual and moving range chart to two difficult to control parameters at its respective location. A sample individual and moving range chart used during the training sessions is shown on Attachment II. Sample calculations for the statistical control limits is shown on Attachment III.

This particular control chart indicates that the process was in statistical control, all data points falling within the control limits. The upper and lower control limits shown on the upper graph are the ± 3 sigma expectations of the control strategy as calculated from the moving range shown on the lower graph. The moving range is used as an indication of the process variability. While the control chart indicates that the process was in statistical control, it also indicates that the process was not "capable", the width between the upper and lower statistical control limits being considerably wider than the process specification limits.

As of today, some 30 plating suppliers are using statistical control charts on some parameters of their plating processes. The degree of implementation varies from location to location, from the original two parameters at some locations to as many as 70. The degree of improvement resulting from using the control charts to indicate out-of-control conditions and non-capable processes also varies considerably from location to location.

For example, the supplier whose data was charted on Attachment II required two follow-up visits before any significant improvement resulted. On the first review, the data was being charted but no changes to the control strategy had resulted from finding the process to be not capable. The charts continued to look about the same. By the second review, the test frequency had been increased but tank feeding strategy needed improvement and the charts continued to show low capability. In order to noticeably improve the process capability, it was necessary to both increase the test frequency and reduce the feed increment. A more recent control chart of this parameter is shown on Attachment IV. While the specification has since been changed, the significant change is that the variability has been reduced in half which can only result in a more consistent product.

The bar graph on Attachment V shows a summary of results of the last three Montreal surveys for a few plated commodities. The values shown are the average for that part type for all vehicle lines. Some individual car lines experienced much higher corrosion rates as did some components not graphed here. The Montreal survey is conducted in April

of each year. The survey is conducted at dealer lots and the degree of corrosion is determined on the new vehicles at the dealerships. Most of the vehicles surveyed had less than 100 miles on the odometer although a few demonstrators are included. The data shows a downward trend in percent corrosion for the last three years. However, levels of five or ten percent corrsion are still considered unacceptable when you consider that these are the corrosion rates on new vehicles which have not been delivered to customers. The percentage and degree of corrosion will get worse with further exposure by the customers. The Montreal area was chosen for survey purposes because it is a large metropolitan area to provide significant sample sizes of various vehicles and because it is a sufficiently severe environment to provide an early indication of plating weakness.

While there has been improvement in plated part quality over the last 5 years, further improvement is still required if plated parts are to achieve long term customer satisfaction. Improvements to date can be attributed to a number of factors including the following:

- Reduction in the number of parts non-feasible by design
- Improvement in plating thickness capability
- Elimination of the poorest quality suppliers
- Institution of the S.T.E.P. test to determine electro potential between nickel layers
- Improvements in supplier process control.

ATTACHMENT I

PROGRAM TO UPGRADE CHROME PLATING SUPPLIERS

I. Plating task force in depth facility reviews

II. Plating task force supplier ratings

III. Montreal bright trim surveys

IV. Revision of design guidelines book

V. Development of design standards individual plated components

VI. Development of training material

A. Plating process
B. Microscopy training

VII. Step test development

VIII. Specification review

IX. Test method review

X. Paint on bright capability reviews

XI. Paint on bright development

XII. Statistical process control of plating

XIII. Statistically designed experiments - die casting and plating

XIV. Plating chemical and equipment supplier recommendations

XV. Plating process

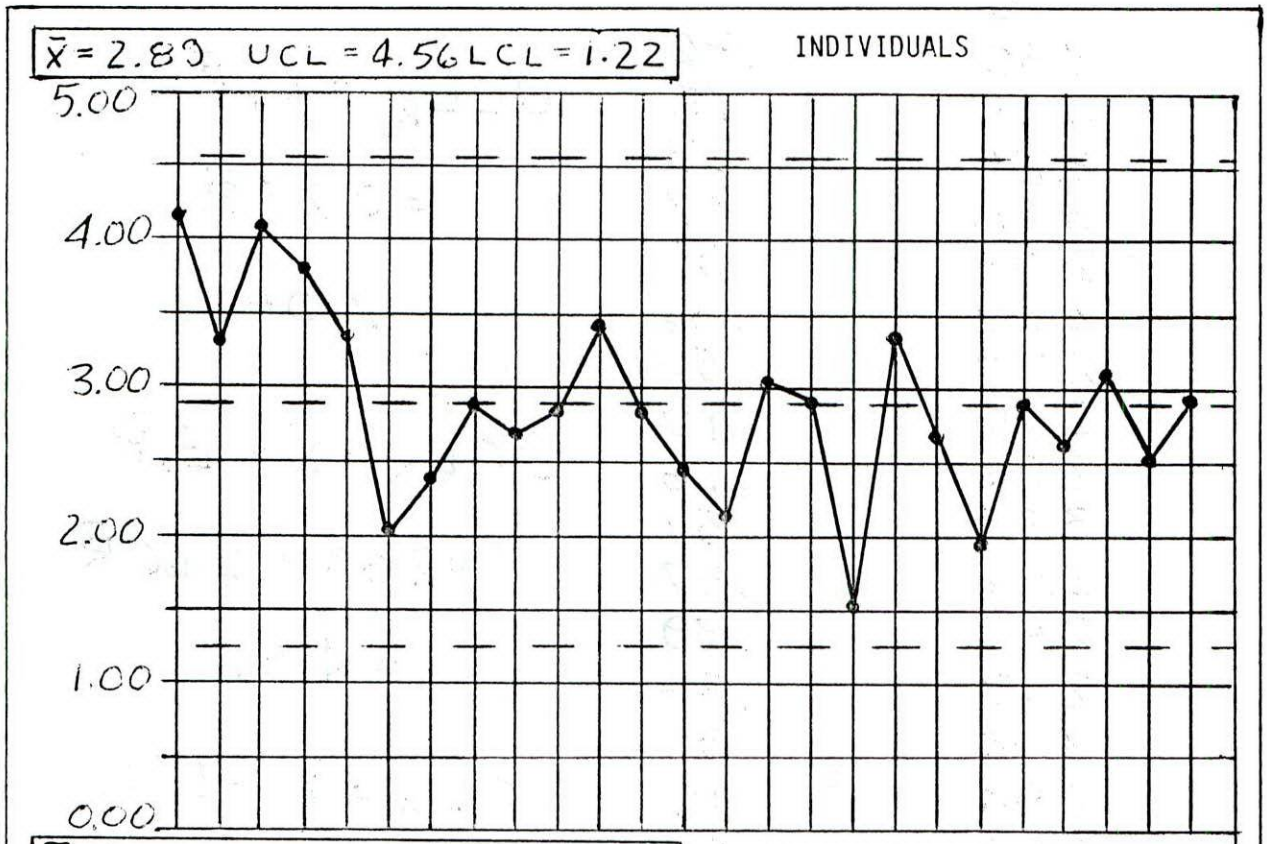
XVI. Technical society presentations

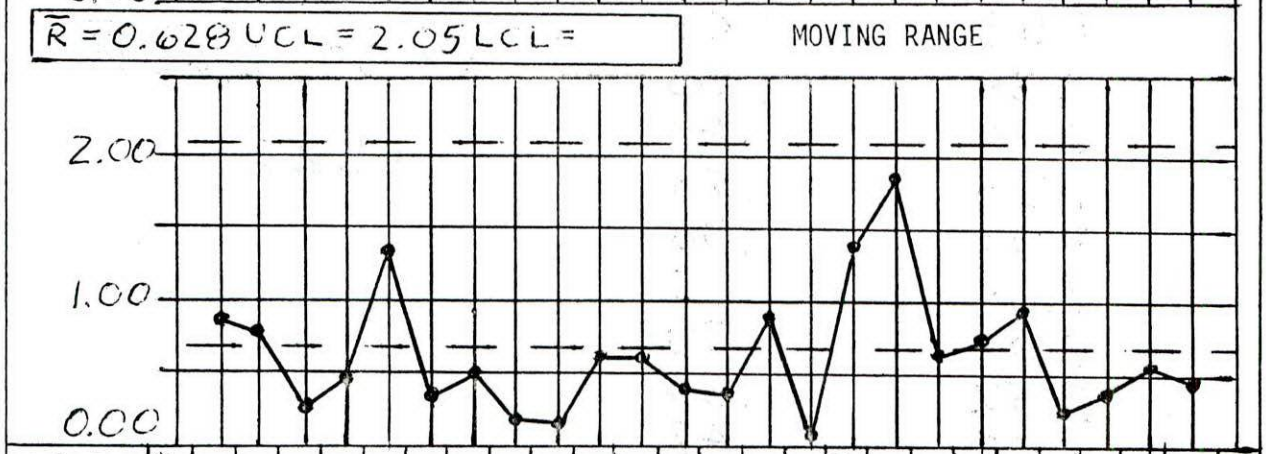
XVII. Racking capability studies

ATTACHMENT II

COPPER STRIKE - FREE CYANIDE

SPECIFICATION 2.5 - 3.5





DATE	4 1	5	6	7	8	13	14	15	19	20	21	22	26	27	28	29	5 3	4	5	6	10	11	12	13	17
	4.16	3.30	4.08	3.85	3.38	2.03	2.39	2.89	2.70	2.86	3.43	2.86	2.47	2.13	3.04	2.14	1.53	3.38	2.70	1.95	2.91	2.68	3.07	2.52	2.99
R		.86	.78	.23	.47	1.36	.36	.50	.19	.16	.57	.57	.39	.34	.91	.10	1.41	1.85	.68	.75	.96	.23	.39	.55	.47

ATTACHMENT III
CALCULATIONS

4.16	
3.30	.86
4.08	.78
3.85	.23
3.38	.47
2.03	1.35
2.39	.36
2.89	.50
2.70	.19
2.86	.16
3.43	.57
2.86	.57
2.47	.39
2.13	.34
3.04	.91
2.94	.10
1.53	1.41
3.38	1.85
2.70	.68
1.95	.75
2.91	.96
2.68	.23
3.07	.39
2.52	.55
2.99	.47
$\sum X = 72.24$	$\sum R = 15.07$
$\bar{X} = 2.89$	$\bar{R} = 0.628$

$$UCL_{\bar{R}} = D_4 \bar{R}$$

$$= 3.27 \bar{R}$$

$$= 2.05$$

$$UCL_X = \bar{X} + E_2 \bar{R}$$

$$= 2.89 + 2.66 \bar{R}$$

$$= 4.56$$

$$LCL_X = \bar{X} - E_2 \bar{R}$$

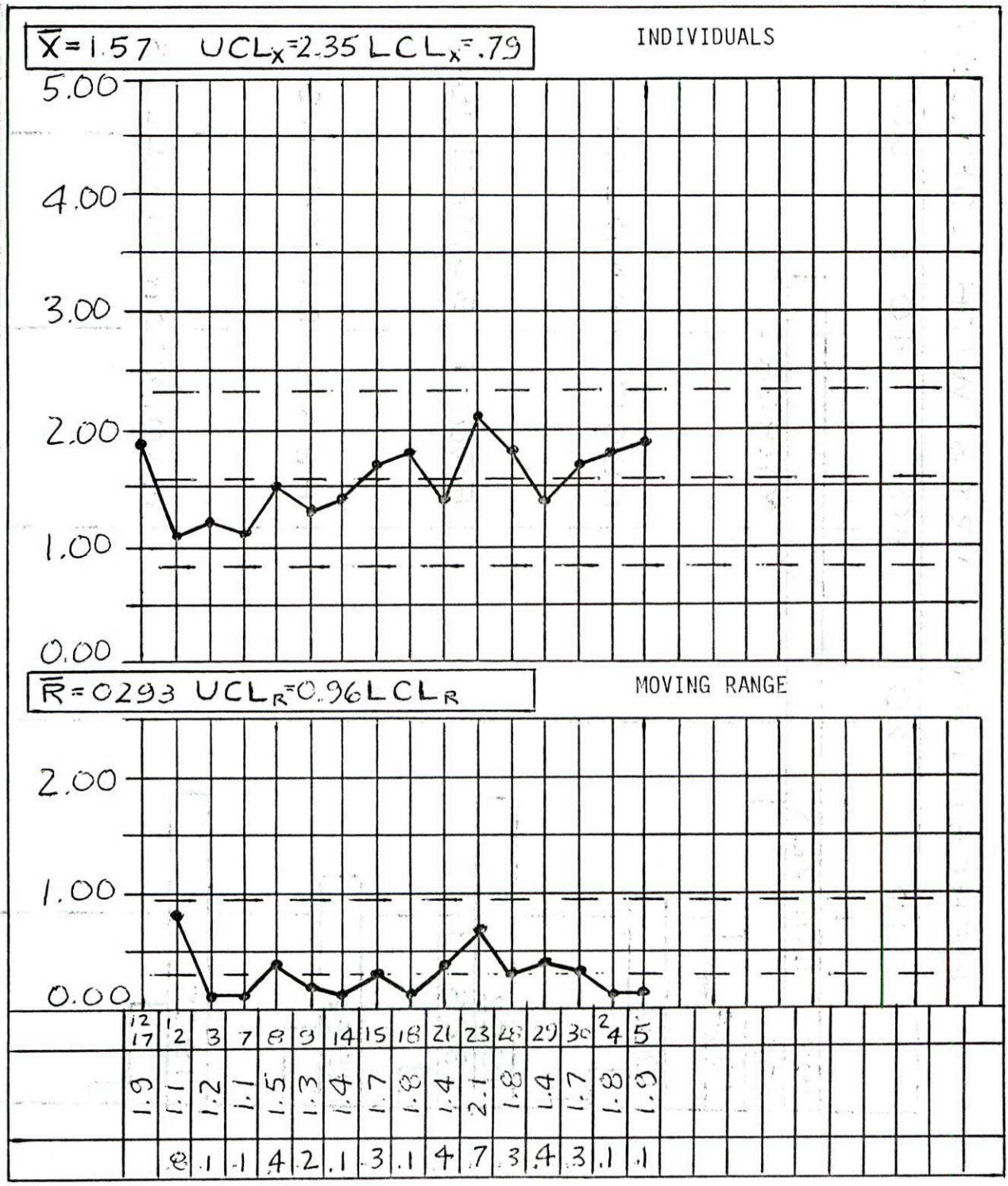
$$= 2.89 - 2.66 \bar{R}$$

$$= 1.22$$

ATTACHMENT IV

COPPER STRIKE - FREE CYANIDE

SPECIFICATION 0.5 - 4.0



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	1.9	1.1	1.2	1.1	1.5	1.3	1.4	1.7	1.8	1.4	2.1	1.8	1.4	1.7	1.8	1.9
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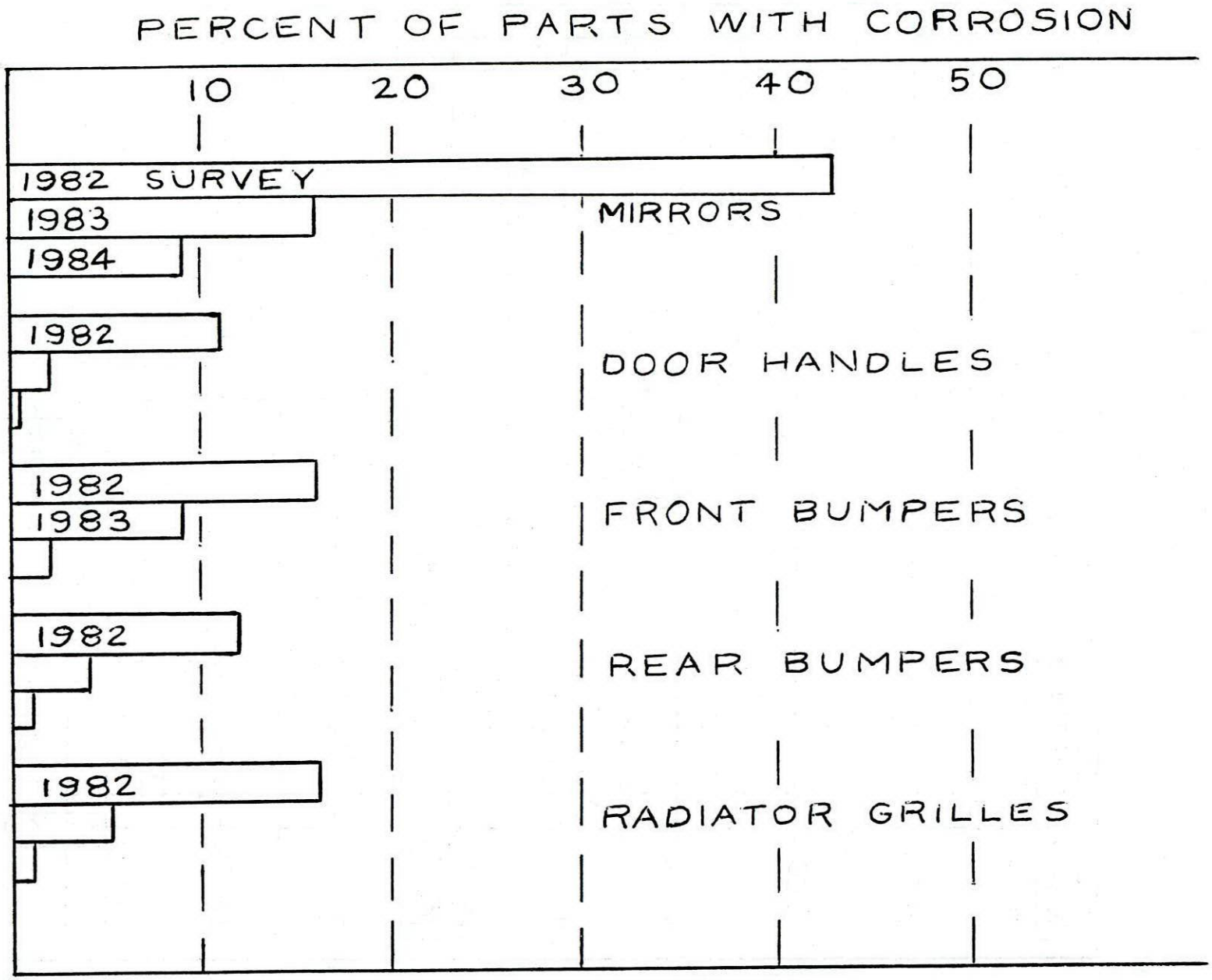

ATTACHMENT IV

M-1

Organic Finishing
Session M

Coating Down Under — The Australian View

Robin Isaacs, Director
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COATING DOWN UNDER - THE AUSTRALIAN VIEW

Robin Isaacs
Director,
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It has been generally assumed by most Australians that "what is good for the U.S.A. must be good for us", and through the immediate post World War II years one could readily see that the attractions of having a licensing arrangement with and American company were not to be taken lightly and there was an exodus of Australian Industrialists to the U.S.A., thirsting for new technologies, processes and equipment.

In the case of my own organisation we were delighted to be able to secure a licensing arrangement for the Kalcolor anodising process developed in Kaiser Aluminum's Spokane Research and Development Laboratories. The year was 1963 and we are still, nearly twenty-two (22) years later, happily sending back our royalties to Kaiser Aluminum and Chemical Corporation.

Since those days, however, most Australian companies, and here I am referring specifically to the coatings industry, have set up their own research divisions and have used these, not only to fine-tune U.S. processes for Australian conditions, but to institute and develop techniques which are now, in turn, licensed to international operators, especially those in the U.S.A. and South East Asia.

The Australian Industrial coating market peaked in 1981 and had declined 8% in the next year. A further decline took place in 1983 and in the paint industry, the total national production by the commencement of 1984 had dropped to 29,000,000 litres.

1984 was a static year, and the latter half of the year was to prove the start of an economic turn around for almost all facets of industry. This period was also coincidental with the breaking of a long and severe drought in the rural sector, and the election of a Labor Government, spearheaded by a (relatively) young and enthusiastic Prime Minister.

We believe that 1985 through 1990 will see a pattern of steady growth.

The Architectural coating market is undergoing a transformation that has been welcomed by the major paint manufacturers, who also see the advantages of allying themselves with established American Paint Manufacturers.

The thermosetting acrylics, so popular world-wide through the 1960's and 70's are now finding competition from the high technology coating systems, some of which were developed in Europe, and some in the U.S.A. They comprise:-

(1) Thermosetting modified acrylics.
(2) High solid coatings.
(3) Liquid polyesters.
(4) Vapour-cured coatings.
(5) Powder coatings.
(6) Fluoropolymer coil coatings on steel.

(7) Fluoropolymer architectural coatings for sheet and extruded aluminium.
(8) Three (3) coat Fluoropolymer systems.

Leading paint companies have instituted comprehensive testing programmes both in weatherometer type cabinets or by long term exposure to aggressive environments to find the ultimate primer/paint system.

Conclusion.

New products, new colours, and new application techniques are providing designers with a staggering range of classic and durable coatings.

There is a sudden awareness in the industry that quality coatings on metal substrates are eminently suitable for preserving and beautifying monumental buildings. The next ten (10) years will see the introduction of systems that will provide new textures (closely resembling stone, timber and metal) with even greater life expectancy, and obtained with little or no danger to our environment.

M-2

Organic Finishing
Session M

Condensed History of Phosphate Coatings

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CONDENSED HISTORY OF PHOSPHATE COATINGS

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The suseptibility of some metals to attack by the environment and or use has stimulated the development of many types of surface treatments to protect the surface during the designed life or use.

Protective barriers such as chemical coatings, metallic deposits, and even oils have only limited resistance to the harshness of exposure during use. Man has tried to devise a better surface and at the same time keep the cost low and profitable. Nature has its own way of protecting itself from the elements of the environment, and nature has its own way of destroying or decomposing matter and especially metals.

Thus with each step of progress we find improvements in the development and use of both organic and inorganic coatings or depositions. The questions are still being asked: Which is best? What do we use? For what? and Why?

The three basic surface coatings or protection are as follows:

1. Organic coatings such as paints, waxes, oils, etc.
2. Inorganic coatings such as metallic plating deposits
3. Chemical conversions using both organic and inorganic solutions to form metallic salt deposits.

The third condition is known today as chemical conversion coatings such as phosphates and chromates as a chemical physical conditioning of metallic surfaces. It owes most of its modern beginning to Thomas W. Coslett who in 1906 was granted a British patent based on the use of Phosphoric acid for the protection of iron and steel. He put iron fillings in the phosphoric acid bath. Raised the temperature to around 225 degrees F. and heated the metal to be treated to a red hot condition and presto!...he had formed a Ferrous Di-Phosphate Coating on the steel.

In 1909, A.D. Liebski, a German did the hot metal bit also. With a solution of Phosphoric acid he added Ferric Chloride and a Calcium salt. This solution allowed a reproducible coating to be formed. The concentration of the chemicals allowed for some means of control. The solution life was very short, but back in their times who seemed to be concerned about pollution when the baths were dumped frequently...there was an industrial revolution going on and money to be made.

However, these two men were not the first to use phosphates for corrosion protection. It has been suspected that the Romans used a crude form of phosphating in making their weapons. They would heat the metal up to the red hot condition and plunge it into a bank of sand which was thought to be a natural phosphate mixture. This would have given them a molten layer of the phosphate and a hardening of the iron. It is not known if they realized that the phosphate was giving them any form of corrosion protection when the

tool or weapon was hand polished. This was probably some recognizable phenomenon as we find in research programs today.

Even around 1879, Aaron and Wendell Brown using an alkaline phosphate under high heat formed a precipate coating which was powder like on steel and copper. This aided the drawing of parts and wire by acting like a flux and was used to prepare metals for coatings as well as some plating work. A U.S. patent was granted on January 9, 1898. Very close to this Otto Strecker in the U.S.A. developed a process of preparing metal plates with a phosphate for the preparation for litographic printing. The method consisted of submitting ground plates to a phosphoric acid and phosphate salts to form insoluble compounds with the metal which developed an insoluble hydroscopic layer that was firmly adherent to the plate and gave an excellent base for printing plates.

Acid Iron Phosphate solutions were the predominant solutions used by the early researchers and developers. These simple solutions were not self-regulated and usually displayed poor adhesion with a minimum corrosion protection. Many were not reproducible or suitable for production operations and very little was known about the HOW, WHAT, IF, as well as the concentrations which varied along with temperatures and pH range. By 1919, the use of Zinc Oxide, Phosphoric acid, and Calcium salts were making use of Hyper-Phosphates in Zinc and Manganese solutions. This was done by heating Phosphoric acid to above 322 degrees F. to decompose the acid into Pyro and Meta Phosphates. Cleaners were using combinations of these materials to compound new formulas to aid in the preparation before conversion coatings. Caustic Soda and Soda Ash had met its match in these new phosphated cleaners. It is very interesting that these were developed because of the shortage of German Potash during World War 1 and today we are trying to get the phosphates out because of waste treatment requirements to meet environmental discharge regulations.

Most of the developments since these early solutions have been along the lines of trying to speed up the reaction time from the average of 2 hours to todays time cycles of 15 to 60 seconds for excellent conversion coatings. Also, to stabilize the baths for longer production life to reduce cost and dumping frequencies. Today the first reactions in a bath takes place in 2 to 3 seconds of contact after removal of soils such as oils, etc. This is usually called the activation or reduction step. Next is the oxidation step of physically converting the reaction salts to form the insoluble metallic phosphate coating. A large number of developments today are being covered by patents which are mostly minor modifications of the original process. Many may not be production practical, but they meet special requirements for the demands of production, quality, and corrosion engineers.

In the early 1920's to make more stable solutions that could be controlled, the use of ferrous manganese hyper phosphate and potassium chlorates were developed. By 1927 the use of Manganese oxide plus Phosphoric acid with dissolved iron plus iron fillings were used to obtain a coating of Manganese Iron complexed as a phosphate. Then it was found that Boric acid and Borax added to a Zinc oxide solution gave a heavy coating where oils, mixed with

gelatin or paraffins give good corrosion protection and lubricating properties.

In 1929, a development using electrolytic deposition of iron followed by immersion in a weak or dilute solution of Phosphoric acid with salts of aluminum, copper, chrome, iron or manganese as metallic phosphates would form insoluble phosphates. This led to the discovery that when metallic salts of Phosphoric acid such as Sodium Hyper-phosphate complexed with ammonia and/or nitrogen compounds they could form self-regulating baths similar to the types used today. Soon the use of alcohols and other additives with monosodium phosphates gave very thin coatings of phosphate conversion. These were excellent for low quality pre-paint treatments.

During the 1930's the use of phosphates in cleaning and pickling of metal was growing. These new formulas gave quicker cleaning cycles and increased the demand to provide conversion coatings that were designed for higher production schedules. By 1936 the development of Zinc Phosphate baths using Sodium Nitrate to maintain a self-regulating solution were beginning to be used. When a small amount of copper, tin, or nickel salts were added, the speed of activation or acceleration was increased. In 1937 the spray process for Zinc Phosphate was developed and new possibilities for higher speed production was promoted.

Because of the need for greater production and shorter processes in the early 1940's, there was a development of adding cleaning agents to the phosphoric acid/phosphate conversion solutions. This allowed a shorter process...from the normal five stages down to three stages. In some installations four stages were used, with the first two stages being an iron phosphate cleaner solution, followed by a fresh water rinse and a final acidified chromic acid rinse. In 1944, the use of flourides as a neutral salt with the phosphates and chromates at saturated solutions allowed for lowering the temperatures from the normal 140 to 180 degrees F. down to a range of 90 to 120 degrees F. This opened up new possibilities for higher quality coatings and faster reaction deposits with lower energy cost.

By the 1950's, there were five main generic types of commercial phosphate coatings being used. They were solutions which deposited insoluble metallic salts of Manganese and Iron; Zinc and Iron; ZINC; IRON; along with Aluminum and Chromium. These were used according to their characteristics such as thickness, crystalline structure and chemical composition. The method of cleaning before treatment, along with the equipment or system for applying the phosphating solution, the time cycle, and bath composition with pH ranges guided the end results or the purpose the treatment was designed to provide. The choice of the type of coating to be used and the application of the product depended upon the metal to be treated and the purpose the coating was to serve.

The important functions of phosphate coatings are as follows:

1. To retard electrochemical corrosion under a paint film by forming an insulating effect to restrict attack to an area where the film might be damaged.

2. The physical form of the phosphate crystal layer serves to lock an organic finish to the surface.
3. A chemical bond is formed between the paint and the surface to provide a better adherance.
4. The absorptive characteristics of phosphate coatings and their affinity for oils and lubricants lead to corrosion resistance and reduced wear.

Today with the new Painting Systems and the many types of paints, we have to make decisions or compromises to get the quality of pre-treatment and economy demanded. New developments are coming forth but most of them are modifications of many of the older formulas and processes. Even so, there are many questions that should be considered before installing a pre-paint treatment or a phosphate conversion coating.

How much production will we need tomorrow - not just today?
What are we doing now that we want to change?
What are we doing today that we must change - EPA, OSHA, etc.?
What soils do we need to remove - from what metals?
What systems would we like to use...spray, dip, barrel, etc.?
What will be our labor cost, energy cost, waste disposal cost, etc.?
And many others...evaluate any past history and plan based on the best guidance available from inside and outside organizations. Even the best advice and benefits fail when the preventative maintenance program takes a back seat to production and neglect.

In operating a phosphate system we will get causes and effects. Some may call them problems, or they may feel that they have gone from a historical situation to a hysterical condition. Some of the tears and sorrow will come from neglect in controlling a process specification such as concentration, pH, temperature, spray pressures and patterns, scaling of heating elements, pump deterioration, etc. Solving one problem does not always solve the condition that seems to be creating either a visual problem or a quality control specification. The important thing to remember about any and all conversion coating operations is: Approach it with an open mind and take one thing at a time to be assured that everything is correct or operating at its best condition and then control...

SOME OF THE CAUSES AND EFFECTS ARE:

Cleaning: If it is slow or ineffective...then the phosphating will not take properly. Streaking or patterning appearances may show through the paint. Excessive or heavy phosphate coatings may develop in areas and little or none in the areas that did not clean properly. Slow cleaning can also be the cause of flash rusting...leaving salts of the cleaners and soils which may oxidize between stages to form a rust bloom. Poor rinsing may be evident from slow cleaning or contaminated rinses. If the part is removed from the cleaning stage before it is completely clean, then selective activation or poor activation may cause a reacted deposit to form that will be powder like...these loose partially reacted phosphate salts will not provide the proper surface condition for good paint adhesion. In operating an iron phosphate cleaner this is very important as the cleaning and the phosphating is done simultaneously in a single stage. In a five stage process the contamination of residual cleaner can neutralize the phosphate

solution as it contacts the surface and the activators or accelerators may not react to form a true conversion. Oxidized oils and drawing compounds can form a varnish like deposit under the conversion coating and may re-liquify when exposed to heat before and after painting...sometimes bleeding through or causing blisters or rupture with pin holes to allow corrosion to start. Even rough edges from shearing, punching, or machining operations can hold soils from poor cleaning.

Smuts: What color are they...black, brown, or grey? A conversion coating may have formed over a smut or with a smut. The smut is usually a carbon disposit that may have been formed during the etching action of the cleaning or phosphating process. These are usually black in color unless mixed with oils, etc. which were not removed during the cleaning phase. Smuts have a tendency to be very tenacious...even though they may be rubbed off with the hand. Oils and grease soils usually show up as brown smuts after conversion coatings and the coating may be very light in weight and show up as a light blue or grey appearance. Fast and thorough cleaning is required with little or no attack to the metal to eliminate or reduce the smut formation from the soils and the carbon that may be in the metal. An excessively low pH or high free acid condition can cause a very active attack to steel and pull the carbon to the surface faster than the cleaner solvents or surfactants can handle before the conversion can be formed and the quality or weight of the coating will be noticed. STAINS can be caused when oxides are present or when the pH of the solution is too high for the process. Also, in the final rinse contamination of the dissolved phosphate can be deposited and dried on the surface and will have the same effect as smuts in quality. Some phosphate solution may remove light rust bloom when the pH of the solution is operated at the low end of the range, but this can cause the etching effect that may cause carbon to be drawn out and deposited as a smut. The grey smuts are usually deposits of the phosphate which did not react to the insoluble state.

Color: What is the color of the conversion coating? Is it grey, blue, blue-purple, purple iridescent, gold iridescent...OR? Zinc Phosphates range from light greys to dark grey or almost a charcoal black. This will vary as to time, temperature, crystal structure and coating weights. The Iron Phosphates will vary from light blues through purples to gold. This too will vary according to the operating conditions. Color in an Iron Phosphate can be controlled by adjusting the pH, concentration, temperature and time. By lowering the pH more phosphate can be deposited with finer grain structure and the color will move toward the cold-iridescent. This usually gives better corrosion protection under the paint. By raising the pH in a cleaner-phosphate better cleaning is produced, but the phosphate coating will be less and the color will be in the grey to blue range. The light grey colors are not considered good quality in iron phosphate unless you are looking for heavy coatings for oil retention properties. Then lowering the temperature, increasing the concentration and raising the pH of some baths will give you heavy coarse crystalline structure for greater porosity absorption of oils. If the pH is too high all you may get is excellent cleaning and no activation for conversion coating, and you may get a precipate of phosphate on the surface which will rub off easily.

Rinsing: Is very important as it removes soluble soils, salts, and most solid matter by spray or agitation. Modifications to rinsing stages can improve the rinsing and reduce the volumes of water required. These are counterflow rinsing stages, spray risers on top of tanks and at the entrance and exit of spray rinse systems. Contaminated rinsing is probably the greatest cause of problems in a cleaning system. Not just from the removal of soils that accumulate, but from the condition of the water that is being used. Water salts and water pH has changed in the last few years along with additives that have been approved by health departments to be added to fresh water lines to help retard the corrosion in the pipes. Checking the condition of the incoming water is as important as checking the condition of the rinse tank contamination. Final rinsing with acidified rinse additives remove the insoluble salts or unreacted salts to improve quality. Yesterday we did a lot of things we cannot do today. Most of this is helping us to improve our operations, reduce cost, and be more concerned about what and how we are doing. When we used to dump frequently to avoid problems, today we should be controlling the operating conditions. Filtering so we can recycle water is going to be a must in the future both from an economical and ecological position.

Remember...as research moves ahead to provide better phosphate solutions, it will be necessary for each of us to be aware of the opportunities to do things better...so, keep ahead by looking for the new. This does not mean jump, but it means that as we learn more about the past, we should also learn more about the future possibilities.

M-3

Organic Finishing
Session M

Simplified SPC Guidelines for the Organic Finisher

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SIMPLIFIED SPC GUIDELINES FOR THE ORGANIC FINISHER

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ABSTRACT:

This paper details various simplified versions of a workable Statistical Process Control system that can be implemented into an organic finishing process. This paper critques the advent of SPC controls, the reason for the "New Found" popularity, steps towards implementation, and the advantages of a workable SPC system.

INTRODUCTION:

The usage of paint has been with us since antiquity. Cavemen originally used paint for art and decoration, as evidenced in many cave drawings.

Over the centuries, paint formulations were carefully guarded secrets of a few masters. The advent of the British Patent Act of 1907 and similiar laws in the United States, allowed for the publication of formulations.

Not only did the patent law make it mandatory to disclose certain basic facts, it encouraged the exchange of information, maybe through the hope of finding liscencees for an invention. This exchange of information led to rapid development of the coatings industry.

The concept of Statistical Process Control was developed by Dr. W. Edwards Deming during the WW11 era. He is best known for his work in Japan, which commenced in 1950, and created a revolution in quality and economic production. The Japanese manufacturers created the annual Deming Prize in his honor.

SPC: WHAT IS IT?

SPC in short is a tool that will improve process performance. This tool is a method in which the total process information can be plotted statistically to increase productivity, eliminate rejects, and reduce costs.

SPC is a tool that requires both employee involvement and management support. 85% of all processing problems are managements responsibility.

INTRODUCTION TO PAINT:

There are hundreds of applications that employ organic coatings as the final finish for the product. Organic coatings are composed of pigments suspended in a vehicle. The vehicle or carrier consists primarily of a resinous binder dissolved in solvents, together with small quantities of driers, plac-

ticizers, and stabalizers, as required. As the paint film dries, the vehicles change from a liquid to the solid film by one or more of several mechanisms.

1. Evaporation of solvents
2. Oxidation (of a drying oil)
3. Polymerization through the application of heat, addition of a catalyst, or combination of reactive components.

"Paint usually refers to materials applied primarily for their decorative effect. The term "coating" or"protective coating" on the other hand, generally is reserved for use when protection is the primary consideration.

THE SPC (QUALITY) HAMMER:

It is common knowledge that the American automotive industry is facing stiff competition from the Japanese.

In order to market a better automotive product for the consumer, every step in the design and manufacturing of the vehicle has undergone a critical examination and evaluation.

Protecting iron and steel from corrosion has become more and more important in very aggressive environments with the use of salt to de-ice streets and freeways, automatic car washes with high pressure detergent sprays and acidic sulphur dioxide in the air.

General Motor's objective is World Class, acknowledged Quality Leadership, by the consumer in the 1988 model year, fleet wide. A solid SPC program by all suppliers must be in effect by model launch. Without a solid SPC program there can be little hope of future growth.

SPC: WHO'S RESPONSIBLE?

Everybody! Every employee, including process operators, secretaries, engineers, sales personnel, management, and the company president. Each person must be held responsible for the execution of their part of an integrated quality system, in order for the controls to work.

ORGANIC FINISHING VARIABLES IN SIMPLE TERMS:

Organic finishing is a misnomer, often leading designers, engineers, and production people to focus on the last coat of paint to the exclusion of the substrate, cleaning, conversion coating, and the organic application. A better

approach is to consider each element in the total coating system in its relation to all the other unit materials and processes.

Once a system has been designed that assures compatability of consistent interaction of all units, the variables can be simplified into three concepts.

TIME TEMPERATURE CONCENTRATION

SYSTEM COMPATIBILITY:

In order to insure system compatibility, one must know the product or products to be coated and the various options that are characteristic to organic finishing.

DIP COATING:

Accomplished by immersing the parts to be coated in a tank of paint with the excess paint draining back into the tank as the parts are withdrawn, followed by drying or baking.

FLOW COATING:

Involves flowing paint over the object to be coated as it is held over the tank.

CONVENTIONAL SPRAYING:

Compressed air is supplied to the spray gun and to the paint container. The pressurized air mixes with the liquid paint causing it to be atomized at the gun, and then propels the atomized paint from the gun nozzle to the object to be coated.

ELECTROSTATIC SPRAYING:

Electrostatically charged paint directed by air and attracted to the grounded parts to be coated.

ELECTRODEPOSTION:

In one version, negatively charged paint particles in a tank of liquid paint are electrically plated out of water-suspension to deposit as a film on a conductive object.

SELECTION OF COATINGS:

The important consideration in the selection of coatings are: Purpose, use, cost, expected useful life, and the environmental exposure of the item.

THE COATING PROCESS:

A typical sequence of a coating operation involves:

Surface preparation (pretreatment)

Coating application
Curing

All three phases incorporate the time, temperature, and concentration principals.

INITIAL STEPS TOWARDS SPC

1. Equipment Design:

It must be assumed that the coating system equipment has been designed to meet all the desired specifications. Once the equipment has been proved to be consistent, a process manager or engineer must decide on a choice of pretreatment chemicals and organic coatings.

2. Choice of Chemicals and Coating PITFALLS:

It is extremely important to establish a firm working relationship with your chemical vendors. One major problem that exists in industry today, in many instances, is the antogonistic relationship between the purchasing and material processing factions. If a company's purchasing and processing personnel cannot develop a strong working relationship there is no point in going any further.

Every metal finisher must be able to make a rational choice of vendors, based on Quality and consistency of the product, services and time frame per order, and competitive price structures.

OTHER VENDOR PARAMETERS:

Parameters must be established regarding the quality and consistency of paint and chemicals as received. Quality standards should be set with each individual vendor prior to shipment of the first lot of chemical.

EXAMPLE:

In regards to the organic coating, many variables can be established such as the dissolved solids percentage, viscosity of incoming material, hiding parameters, etc.

Spot testing should be conducted on a random basis to insure the consistency of the product. The manufacturer should be instructed to hold retain samples of each shipment, should further testings be required.

VENDOR SURVEY:

A vendor survey should be conducted prior to the first shipment of material. These surveys should be reevaluated periodically to insure ongoing consistency of the incoming

materials.

Among the many assurances you should receive from your vendor are:

1. Are batch formulations identified as per lots?
2. Are retain samples pulled from each manufactured lot?
3. How long are retain samples kept?
4. Are records kept of each manufactured lot?

PRODUCT TO BE PAINTED:

A program of consistency must be developed with your customer or manufacturing department in order to insure the consistency of finish. Unfortunately in many instances, it is assumed that the metal finisher is responsible for curing the many ills that can occur in the manufacturing.

Among the many problems that can occur are:

1. Rusty or scaled parts.
2. Parts that are excessively burred.
3. Parts that are excessively oily.
4. Parts that are damaged prior to your receipt.

An incoming visual inspection of all incoming parts should be conducted. The customer (manufacturer) should be notified of any discrepancy that could relate to the final finish.

QUALITY MANUAL AND GUIDELINES:

A firm written policy should be established and adhered to. Copies of this policy should be made available to all in-plant personnel, all vendors, and all customers. This policy should be written as to designate every person's area of responsibility. These areas of responsibility are essential in developing a sound SPC program.

TOTAL SYSTEMS APPROACH:

Once the total guidelines and parameters have been set, an overview of the entire processing system will have been established. At this point the day-to-day SPC controls can be initiated.

TYPICAL 5 STAGE PRETREATMENT AND FLOW CHART:

Stage 1 Clean:

1 minute contact Time
140° F. Temperature
4 ozs. per gallon Concentration

Stage 2 Rinse:

1 Minute Contact Time
Ambiant Temperature
Overflowing Concentration

Stage 3 Phosphate:

1 Minute Contact Time
140° F. Temperature
Ratio Free Acid Concentration
Total Acid

Stage 4 Rinse:

1 Minute Contact Time
Ambiant Temperature
Overflowing Concentration

Stage 5 Seal:

1 Minute Contact Time
120° F. Temperature
1 oz per gallon Concentration

Dry Off Stage:

Drive off Water Time
325° F. Temperature

Paint Application:

Delivery Systems Time
Various Viscosities
and delivery
patterns Concentration

Curing:

10-20 Minutes Time
325° F. Average Temperature

VARIATIONS:

Obviously even in the best of systems, there are going to be day-to-day variations in the process.

TYPES OF VARIATIONS:

1. Common Cause: Inherent variation that varies in a constant repetetive manner. (Example - paint usage)

2. Special Cause: Not a part of the normal process. (Equipment failure, abnormalties of incoming material etc.)

The statistical plotting of key variables will control the process. It will also signal special cause variables due to lack of control. In turn immediate corrective action will be required.

Average and Range (X and R) Charting:

This basic type of charting has several advantages important to the processor.

1. Charting will measure key variations in the process in order to evaluate change.

2. Aid in identification of any special causes by recording time and event notations.

3. The sample check represents the total system.

4. Compares to the prior

check, and to what is statistically expected.

5. Allows the establishment of control limits.

6. Establishes relationships regarding averages and systems capabilities.

The Limiting of Variables:

As an example, let's explore another typical paint line.

Pretreatment Section: Five stage zinc phosphate - recirculation spray process.

Premise: Each stage designed for a minimum of one minute contact per stage, and a 30 second buffer zone between stages.

A. Alkaline Cleaner 1-2 oz/gal. 100-125° F.
B. Water rinse - overflowing
C. Phosphate and accelerator phosphate 1-2% by volume accelerator 1/10th of 1% by volume 130-140° F.
D. Water rinse - overflowing
E. Seal - 1% by volume 120-130° F.

Note:

This is just an example of a system. Pretreatment Systems can vary due to size of the equipment and the chemical manufactures recommendations.

Dry Off Section:

The key to this section is to allow the parts to dry prior to painting. Care should be taken not to exceed 325° F. so as not to harm the phosphate crystal.

Paint Section: Key variables

1. Viscosity of material
2. Temperature of material

Electrostatic Operations:

3. Air pressure
4. Conductivity of material
5. KV output (killivolts)
6. Contact Time

Curing Section: Time and temperature per the manufacturer's recommendations:
Example: 15 minutes 325° F.

Time Temperature Concentration:

Time:

Time for the most part can be eliminated in this type of a system. The conveyor line is driven by a mechanism consisting of a motor, reducer, and drive assembly. The conveyor can be set at a constant speed that should not vary unless there is equipment failure. Line speed recalibration can be accomplished very simply with a stopwatch.

Temperature:

With a good total systems approach, temperature can be eliminated, or simplified for SPC control purposes.

Normal heating methods in the pretreatment stage can include direct fire gas, steam heat, or electric immersion heaters. All three systems can be controlled to designated parameters by aquastats. These aquastats should hold a constant heat range and keep the SPC charting to a minimum.

The viscosity of the paint will vary when the temperature of the product does. There are several ways to automatically keep a constant temperature during the winter. The most obvious would be to keep the process area at a specified temperature.

SPC charting of your various formulations will determine variances in film thickness between summer and winter production periods. This charting will allow you to make the proper adjustments before problems occur.

A good oven design, multiple probe chart recorders and periodic recalibration will hold SPC charting of the curing section to a minimum.

Concentration:

This variable concerns the level or concentration of "goodies" in your tank or bath. The commonly accepted method of evaluation is a chemical titration of each stage in the process.

A program must be started to determine how often each bath will be evaluated and by whom. This evaluation is extremely important in job shops where the workload and square footage of parts can vary hour to hour. Chemical consumption and drag out can fluctuate significantly in a normal production day.

The implementation and use of chemo feeds will not minimize your charting, but can greatly reduce fluctuations in the average and range between titrations.

If you "shot feed" your system after every titration, it is recommended that you increase your normal operating percentages by volume. This increase hopefully will insure that your bath does not drop below minimum standards.

Control Chart Interpretation:

A. The control chart will tell you if the process has varied or is still okay.

B. The control chart will point out any common errors in the process.
C. The control charts will graphically point out all normal and unusual patterns.
D. The control charts will allow for rapid evaluation of potential problems and allow for corrective action.

SUMMARY:

The basic concept of SPC controls is quite simple. Once you have established a workable system that allows you to meet the process specification, it is a matter of constantly duplicating the process.

The key variables of an organic finishing system can be narrowed to the three concepts of time, temperature and concentration.

In a total systems approach SPC charting can be greatly minimized by the automation of many systems revolving around the three concepts.

ACKNOWLEDGEMENTS:

Noel Smith, Saran Protective Coatings.
Carl Neimela, Detrex Chemical Industries, Inc.
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All for various input into the total systems approach.

Charles Gates, C. R. Gates and Associates, structuring and training of our in-plant SPC programs.

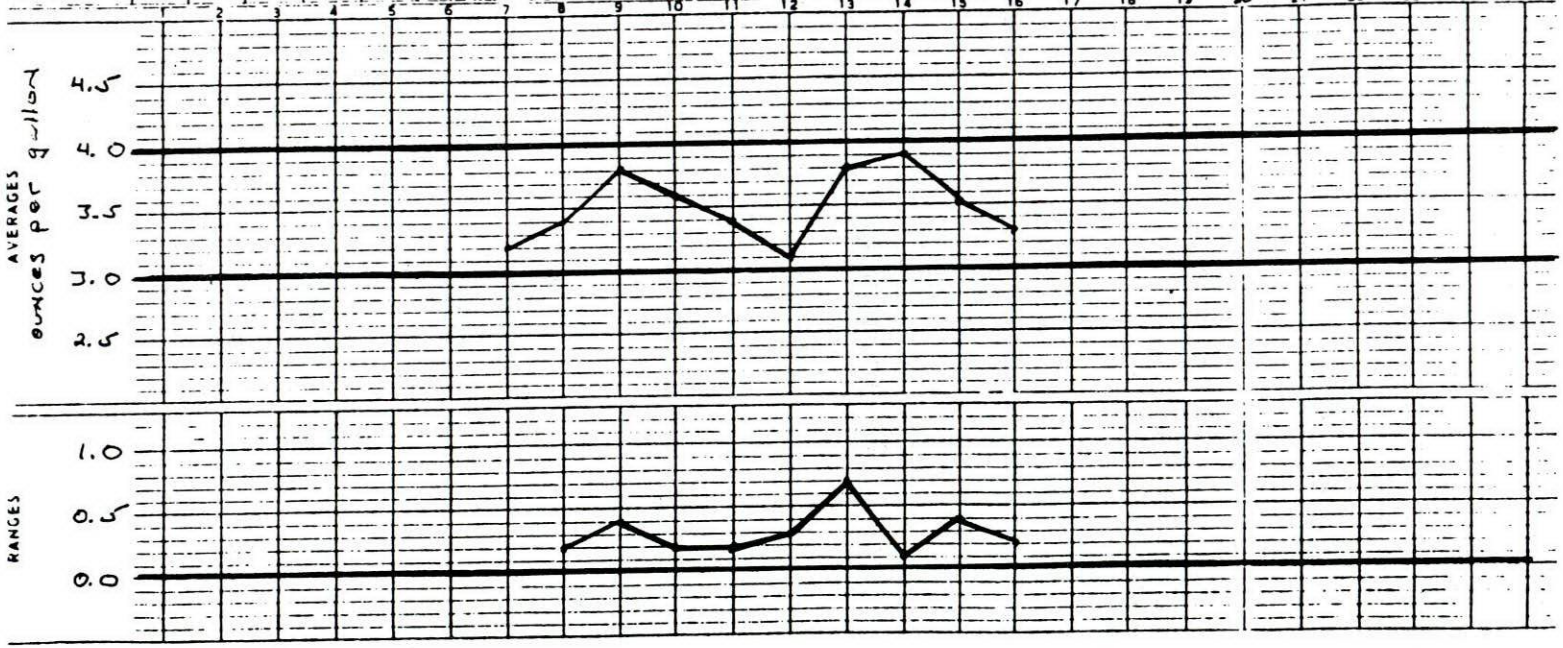
BIBLIOGRAPHY:

1. "Applications Manual for Paint and Protective Coatings"
William F. Gross
Library of Congress
Catalog No. 71-107290
2. "Quality Management System"
General Motors Corporation
Fisher Body Division
3. "Understanding Metal Finishing"
Pamphlet produced by the National Association of Metal Finishers
4. "SPC Training Manual"
C. R. Gates and Associates
5. 1984 Guidebook Directory Issue Metal Finishing Magazine
6. "Guide to Quality Phosphatizing"
Fremont Industries Inc.
7. History of Painting: 75 Years
Dr. George E. F. Brewer

VARIABLES CONT CHART ($\bar{X}$ & R)

PART NAME (PRODUCT): PROPRIETORY PRODUCT	OPERATION (PROCESS): CLEANER	PART NO: ALKALINITY	CHART NO:
OPERATOR	MACHINE: First STAGE	GAGE	UNIT OF MEASURE: TITRATION
		SPECIFICATION LIMITS: 3 to 4 ounces per gallon	ZERO EQUALS

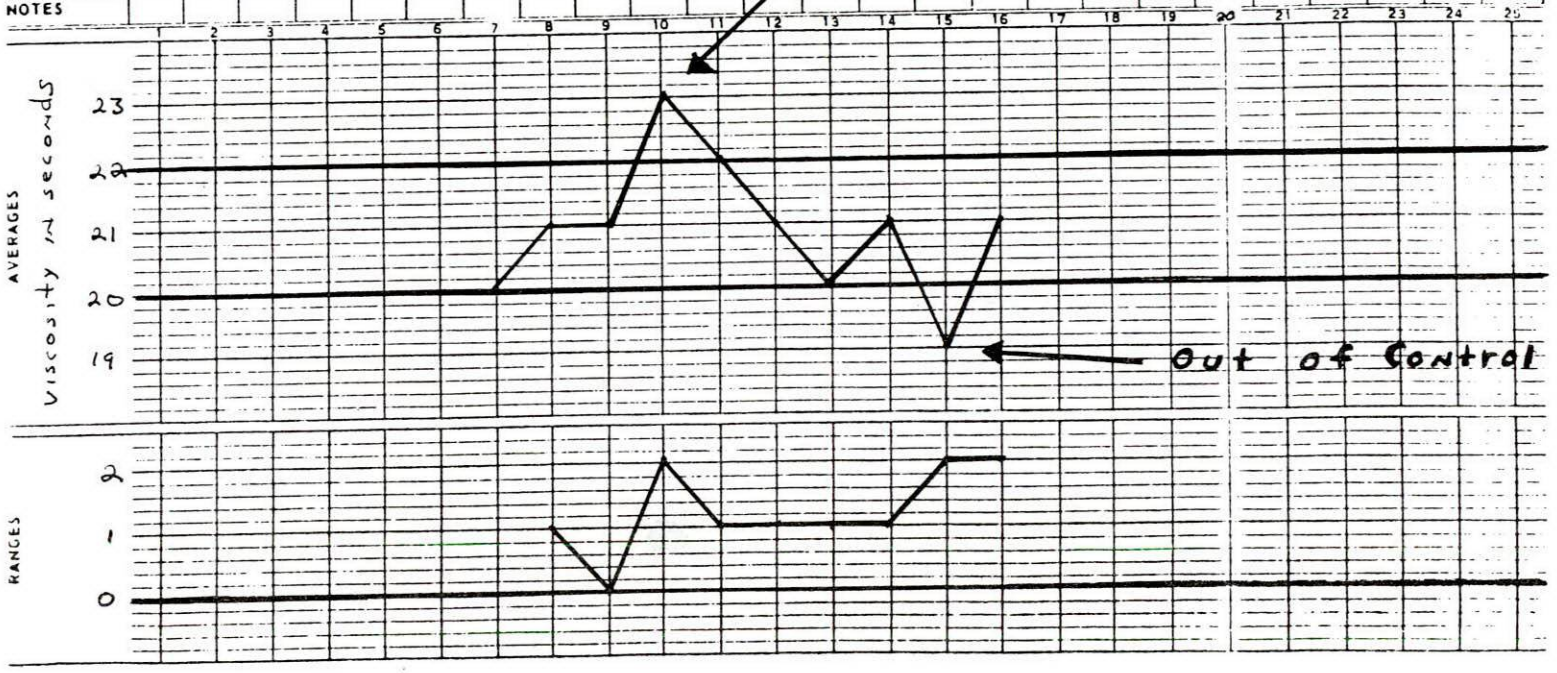
DATE		MON		TUES		WED		THURS		FRI	
TIME		AM	PM	AM	PM	AM	PM	AM	PM	AM	PM
SAMPLE MEASUREMENTS	1	3.2	3.4	3.8	3.6	3.4	3.1	3.8	3.9	3.5	3.3
	2										
	3										
	4										
	5										
SUM											
AVERAGE, $\bar{X}$											
RANGE, R		—	.2	.4	.2	.2	.3	.7	.1	.4	.2
NOTES											



VARIABLES CONT CHART ($\bar{X}$ & R)

PART NAME (PRODUCT): PROPRIETORY PRODUCT	OPERATION (PROCESS): PRIMER	PART NO.: VISCOSITY	CHART NO.
OPERATOR	MACHINE: DIP/DRAIN TANK	GAGE: ZHANN CUP	UNIT OF MEASURE: #2 ZHANN
		SPECIFICATION LIMITS: 20-22 seconds at 70°F	ZERO EQUALS

DATE		MON		TUES		WED		THURS		FRI	
TIME		A.M.	P.M.	A.M.	P.M.	A.M.	P.M.	A.M.	P.M.	A.M.	P.M.
SAMPLE MEASUREMENTS	1	20	21	21	23	22	21	20	21	19	21
	2										
	3										
	4										
	5										
SUM											
AVERAGE, $\bar{X}$											
RANGE, R		—	1	0	2	1	1	1	1	2	2
NOTES											



M-4

Organic Finishing
Session M

Enhancing Bright Surfaces with Powder Coatings

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"ENHANCING BRIGHT SURFACES WITH POWDER COATINGS"

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How many times have you heard this? "You can't paint over chrome!"

Or this? "Stainless simply rejects bonding!"

Perhaps you have had experiences that would give you just cause to make either of these statements yourself. I have!

I have seen many pieces of chrome plated or stainless automotive trim where large shiny spots glared among the ragged portions of low gloss black paint. I was once a design engineer responsible for a similar project in the 1960's. It was, to say the least, a frustrating experience. My boss finally issued the edict - "No more paint over chrome!" That left me without many of the options I had been banking on.

It took me a long time to fully accept that command. And for weeks later I still pleaded with our suppliers asking questions like: "If there is a way to make paint stick to chrome, stainless and other bright surfaces --- I want to know about it."

That was 20 years ago. And since then I would have to say to the finishing industry....."You've come a Long Way Baby!"

Today, there are ways to enhance bright metal surfaces with powder coatings and I thought you might like to know about them.

The founders of our company have worked with powder coatings in some of their earliest days of the 1950's. MetoKote was established to provide powder coating application services to industry in 1969.

I have been a part of that effort and have been assisting finishing engineers of more product applications than I could have imagined for the last eleven years. Many of these applications have effectively enhanced bright surfaces with powder and the purpose of this paper is to share some of our discoveries with you.

Powder Coatings Are Not Paints!

Those of us in the powder coating business often find ourselves explaining to our customers that powder coatings are not paints. This paper assumes the reader knows the difference so time will not be taken to dwell on it. However, it is an important point to emphasize. In short, it is the fusion bonding of plastic to a clean bright metal substrate

that we are talking about as we explore the following successful applications.

Appliance Handles and Trim:

When the self-cleaning ovens first came out there was a serious concern about the heat being transferred to the door handles and trim. One possibility under discussion was the change from metal to a thermosetting plastic. The insulation effect of that was good but strength, durability and heat resistance were obstacles. We were contracted to search out a material and develop a process to apply a clear thermosetting plastic coating to existing metal parts.

The appliance engineers had developed an instrument to measure the "to the touch" heat effects of a hot surface. Metal transmits heat to the skin much faster than plastic. So, plastic can actually be a much higher temperature and still not burn the skin. Also, it gives the nervous reflexes time to reach the brain and allow the skin to be removed from the hot surface before the skin tissue is damaged.

The results of experimentation were that a plastic coating of five mils (or .005 inch) yielded the same "to the touch" heat effect as a totally plastic part.

In the mid seventies it was difficult to find "water clear" materials that could be applied to that thickness without becoming milky, yellowing, or developing a heavy orange peal surface. It also had to pass tests for resistance against chemicals used in oven cleaners and other household cleaners. One company finally developed what was called a "flexible acrylic". That material was used for several years. Coating was even effected over silk screened panels. Later, improvements were made in epoxy resin systems and some products have been converted to them.

Bathroom Fixtures with Fragile Decorative Finishes

Pick up any home decorating magazine or building trade press publication and you will probably find more than one ad displaying decorator bathroom fixtures. These fixtures are beautiful and they add a delicate but elegant effect to many bathroom decorating projects.

Today decorator kits are becoming quite popular with architects, interior designers and "do-it-yourselfers". They are available from building supply houses to discount stores.

The "top of the line" sets are solid brass or zinc castings. They are polished, plated, etched and sometimes buffed out black zinc for shading and antiquing effects. These finishes are truly fragile in their original state. Oxidation and finger printings will take their toll even before operational elements are considered. Early experiments included clear laquers and various liquid urethane resins. There was a 300 hour

running water exposure test to be met. None of these systems could hold up much past 150 hours according to the technician who contacted us.

Clear powder coatings were just coming into commercial acceptance. These applications required a "water clear" coating that was virtually free of "orange peal", or, perfectly smooth to the eye. These were tough specifications and only two powder manufacturers accepted the challenge. But, accept it they did and today, several resin formulation generations later, this is a very cost effective and commercially viable process.

Speaking of cost effectiveness, here is one for the books. One luxury set of bathroom fixtures was being plated with gold. The client's plating manager furnished this analysis of a bathtub water spout. In order to pass the running water exposure tests with gold plating alone, a plating thickness of fifty millionths of an inch is required. He estimated that would be almost one dollar per millionth or fifty dollars for the part. (Admittedly, that was when gold was up around seven hundred dollars per ounce.) However, with the application of three mils of clear epoxy he was able to pass that test with only a flash plating of five millionths of gold. His comment to me was "Replacing forty-five dollars worth of gold with two bits worth of plastic while still getting the luxury effect is what I call a cost effective application." He went on to explain how the selling price was greatly reduced and how this product line then became affordable.

Fishing Equipment - Tinted Clear Epoxy Over Electropolished Stainless Steel

The makers of fishing gear and lures have watched various colors lure various fish to the hook for years. Now, they are using the same technique to lure new customers to their new spinning reels.

At first the attempt was made to use colored annodizing to get the effect they wanted, but the fishing gear takes a lot of abuse so the strength of stainless is required. Various laquer and liquid paint resins were under test when one of the engineers contacted us in the same frustrated state I described at the beginning of this paper. The initial powder tests made this man very happy but we hit one big snag. There were several colors specified by the designer and not one of them was available in powder. Also, some colors were very low volume products as well as small parts. The powder manufacturer can make special orders and they were able to make the specific color tints for the desired bright effect. But the machinery makes that stuff in no less than two thousand pound batches.

The project became a reality when the designers concented to eliminating most of the low volume colors and standardized on a fewer number.

Bicycle Components - Tinted Clear Epoxy over Chrome and Bright Zinc

The yearning for sporty two wheeled vehicles seems just as strong as for the four or eighteen wheelers.

In the late 1970's there was a very popular movie called "Smokie and the Bandit". It is credited with making the C.B. Radio fad come alive. That black and gold sport car also got a lot of attention.

The bicycle designers at one company came out with a "sport bike" design to emulate that car.

To do this they needed a durable gold look for their rims, handlebars, chain sprocket, crank and reflector brackets. Several laquers and liquid paint resins were tried. No need to go into that outcome again. The decision was made to go with a brass plating. However, it was too fragile and wouldn't hold up. We were asked if the brass plating could be overcoated with a clear powder coating to protect it.

The process worked and worked well. Our chief chemist asked around about the cost of brass plating vs. chrome. In this case, it was a low volume project in comparison to the chrome work being done. The cost difference turned out to be substantial. In addition, the powder coating made this an expensive project.

Our chief chemist then prepared a sample of a tinted clear that, when applied over chrome, yielded a close resemblance to brass. With some color matching at the powder manufacturer's lab, this turned into a very cost effective application. The customer liked the idea of being able to use in-house plated inventory to change the color effect.

It didn't take long for the designers to find ways to use other colors like "candy apple red", "candy apple blue" and "burgandy". These models have made a big hit in the marketplace. In fact, I was told that one model using the rims of "candy apple blue" became the largest selling single bike model in the USA.

One important side benefit was discovered when it was learned that these coatings could be bonded to chrome plating. Rims and handlebars with minor plating defects and stains could be salvaged by overcoating the plating with an opaque powder coating. Some models calling for black handlebars and rims can use these components very nicely.

Automotive Trim - Electrocoat and Black Polyester Over Stainless Steel

Yes chrome and stainless steel are very difficult to bond against. Powder directly against chrome does not bond nearly as well as powder against properly prepared cold rolled steel. However, it has been determined to be adequate for the product needs mentioned above. However, performance is not good enough when applied directly over bright stainless used in automotive trim. Cathodic electrocoat is used as a base to beef up the adhesion and then polyester or nylon is applied as a top coat to provide the weatherability or additional wear as in the case of nylon.

This dual process is being used effectively over galvanized substrates too. With the drive toward corrosion protection and the styling trends toward the black trim rather than bright, these coatings are serving a growing need.

Pen and Pencil Sets - Epoxy Over Stainless

Even jewelry type items such as luxury pen and pencil sets made of stainless can be enhanced with powder coatings. You can surely imagine the quality required of this matt black epoxy powder coating material. Performance requirements for this application included a perspiration resistance test and a "purse test" where the product was tumbled for several hours in a container loaded with coins, washers, clips, combs and brushes to simulate life in a ladies' purse.

Appearance and feel are of the utmost importance, but the coating material technology and the application process technology of today has met all these challenges.

Unmet Challenges

There are applications that still need to be met. In a recent project, an effort was made to develop a tinted clear to be applied over chrome to match other components of brass plated furniture items. The volume wasn't there to make the project worthwhile for the powder people or for the customer. A minimum batch of two thousand pounds will go a long way. Perhaps another day...

There are surely other challenges you will come across now that you are aware of these successful applications as you develop projects with your present and future plating customers.

Cautions to Remember

Only plating is plating! These coatings are organic! They are much softer! When coating over plating the surface condition is changed and friction is not the same. The application must be done correctly. The customers must understand what they are getting.

-END-

M-5

Organic Finishing
Session M

Measurement Of Phosphate Coatings By Energy Dispersive Instrumentation

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Paper not received in time for printing

MEASUREMENT OF PHOSPHATE COATINGS BY ENERGY DISPERSIVE INSTRUMENTATION

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Paper not received in time for printing.

M-6

Organic Finishing
Session M

Corrosion Testing of Painted-Phosphated Substrates

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"CORROSION TESTING OF PAINTED-PHOSPHATED SUBSTRATES"

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It is well known within the industry that the corrosion protection of automobiles has significantly improved with the introduction of cathodic electrodeposition paint systems in the 1970's. This improvement also corresponds with the advances in pretreatment technology, specifically phosphophyllite or "iron enriched" zinc phosphate coatings ($Zn_2Fe(PO_4)_2 \cdot 4H_2O$) over the previous hopeite coatings ($Zn_3(PO_4)_2 \cdot 4H_2O$). These phosphophyllite coatings have allowed for an increase in the standards used by the industry in evaluating the performance of the finished product. For example, the exposure time to paint failure in salt spray testing has increased significantly with these improvements in pretreatment and paint technologies. This has made researchers look to alternative test methods to more quickly and accurately predict the performance of the finished product[1].

The test methods used in this study are listed in Appendix 1 and include a cyclic corrosion test procedure. This test has quickly become accepted by the automotive manufacturers as a reliable method for evaluating the quality of the finished vehicle in use[2]. One advantage of this test over salt spray is that it produces the type of paint failure which is actually seen on vehicles. Another is that it clearly shows that galvanized (or zinc-coated) steels provide better corrosion protection than cold rolled steel which correlates to the real world, whereas salt spray testing shows the opposite result; that is, steel giving better corrosion protection than galvanized steel.

These cyclic corrosion tests, however, often must be extended beyond the normal 4 week period to detect differences among various pretreatments on steel and especially galvanized steel under CED paint systems. A major trend in the automotive industry is the increased use of zinc coated steels so that again more severe test methods must be developed or a combination of test procedures developed that can quickly evaluate coating performance for galvanized steels under paint.

One test method being used is a 10 day water immersion followed by crosshatch cutting and taping (see Appendix 1). Another procedure is to measure the ability of the zinc phosphate coating to resist a strong alkaline solution. This test was developed on the theory that since a high pH (>10) occurs at the metal/paint interface during the CED paint process, the

better a coating can resist dissolution, the more coating remains under paint to provide good corrosion protection.

It is known that phosphophyllite coatings provide better resistance to strong alkaline solutions than hopeite coatings and that the paint adhesion and scab corrosion protection is also improved[3]. These phosphophyllite coatings, however, cannot be produced on galvanized steels where no iron is present to form the crystal. The phosphate coatings' resistance to alkaline solutions and paint adhesion on galvanized steel, therefore, has always been inferior to the alkali resistance and paint adhesion on steel. Recent developments in phosphate coating technology for galvanized steels have significantly improved the alkali resistance and paint adhesion and these results are reported in this study.

The main objective of this paper is to present corrosion resistance data of several zinc phosphate coatings under a cathodic electrodeposition (CED) paint system by evaluating results of various accelerated test methods and to determine whether any correlation exists among those tests which measure zinc phosphate coating solubility (see Appendix 1) and those tests which evaluate paint adhesion and scab corrosion.

Experimental

A panel testing program was performed to compare the quality of several zinc phosphate coatings on steel and galvanized steel under a typical automotive CED paint system (Appendix 2) utilizing two methods of coating application (spray and immersion). The phosphate coatings tested included a conventional hopeite type, phosphophyllite type and one recently developed, modified phosphophyllite. These coatings are distinguished by letters as follows: spray application — "A" = hopeite, "B" = phosphophyllite, "C" = modified phosphophyllite; immersion application — "AA" = hopeite, "BB" = phosphophyllite, "CC" = modified phosphophyllite.

A typical automotive processing sequence was used which included a mild alkaline, titanated cleaner and a separate conditioning rinse of colloidal titanium salt prior to the zinc phosphate step to obtain a more dense, fine-grained coating. The phosphate solution was either sprayed on the test panels for 60 seconds or the panels were immersed in the solution for 120 seconds. Spray application is still the predominate method used by automotive manufacturers, however, full immersion application is gaining wide acceptance because of its ability to produce a coating in areas unaccessible to spray application.

The panels were final-rinsed with deionized water only in order to assess the characteristics of the phosphate coating without interference of a chrome final rinse. Further, it

should be noted that for immersion production lines at present, a spray chrome rinse is utilized, thus the interior of the vehicle body does not receive the chrome treatment.

Results and Discussion

The following tables summarize the results of several accelerated test methods on the three types of zinc phosphate coatings that were evaluated.

Table 1

Zinc Phosphate Coating Weight and Appearance

System	Appearance[1]		Coating Weight (g/m^2)[2]	
	Steel	Galvanized Steel	Steel	Galvanized Steel
A	+ -	+ +	2.5	3
B	+ +	+ +	1.5	3
C	+ +	+ +	1.5	2
AA	- -	+ +	2	3
BB	- +	+ +	2.5	3
CC	+ +	+ +	2	3

1 Phosphate coating uniformity and crystal size where "+" = good and "-" = poor (see Appendix 1).
2 Average coating weight of three (3) panels.

Table 1 presents a comparison of the zinc phosphate coating appearance and coating weight. It is widely accepted within the art that a high quality zinc phosphate coating must be uniform in coverage over the entire area to be painted and that the crystal size must be fine (usually <10μ).

The appearance and coating weight of zinc phosphate coatings on steel for spray application was improved with the development of phosphophyllite coatings. This same trend holds for zinc phosphate coatings on steel by immersion application except that the coating weight is often too high for phosphophyllite coatings. This coating weight has been reduced with the modified phosphophyllite coating so that the general appearance has been improved.

Table 2

Comparison of Zinc Phosphate Solubility and Paint Adhesion

System	Alkali Resistance[1]		Paint Adhesion[2]	
	Steel	Galvanized Steel	Steel	Galvanized Steel
A	40	90	100	100
B	10	90	30	100
C	5	20	5	30
AA	10	75	5	50
BB	10	75	5	70
CC	5	20	5	5

1 Results represent the average % of zinc phosphate coating removed in the alkaline solution.

2 Results represent the average % of paint loss in the cross-hatched area.

In Table 2 the results are summarized for zinc phosphate coating solubility and paint adhesion testing. These results demonstrate that if the zinc phosphate coating is more resistant to alkali attack, then the paint adhesion characteristics of that coating are good. The alkali resistance and paint adhesion of galvanized steel has always been a problem unless an additional step is added to the pretreatment sequence. This step involves using chrome final rinsing after the zinc phosphate coating has been formed which seals the pores between the crystals. The modified phosphophyllite zinc phosphate coating evaluated in this study without chrome final rinsing has significantly improved both zinc phosphate coating solubility and paint adhesion. The zinc phosphate coating solubility test appears to be a quick and reliable test method for evaluating paint adhesion.

Table 3(3)

Salt Spray Testing

System	Salt Spray* Galvanized Steel	Salt Spray[2]** Galvanized Steel	Salt Spray*** Steel Only
A	2-3	—	3-4
B	2-3	—	Trace
C	Trace-1	—	Trace
AA	0.5-1	2-3	Trace
BB	Trace-0.5	2-3	Trace
CC	Trace-0.5	1-2	Trace

1 Results reported are the range of paint loss from the scribe in millimeters.
2 Salt spray testing was stopped at 336 hours for System A, B and C.
* 336 hours.
** 672 hours.
***1000 hours.

Salt spray continues to be an accelerated test method used by many automotive companies even though the results of this test do not correlate well to the actual corrosion observed on vehicles in road use. Salt spray test results on galvanized steel, for example, are poor in comparison to steel under cathodic paint systems although the opposite is observed on vehicles in use on road conditions. Chrome final rinsing of the zinc phosphate coating significantly improves the salt spray result on galvanized steel just as it does for the paint adhesion on galvanized steel.

The introduction of phosphophyllite or iron enriched coatings in the 1970's led to significant improvements in both salt spray and paint adhesion results for steel. These same phosphophyllite coatings, however, cannot be produced on galvanized steel since no iron is present so the salt spray and paint adhesion results are poor. The modified phosphophyllite coating has improved these results on galvanized steel without chrome rinsing by introducing to the zinc phosphate formulation an ingredient which modifies the crystalline structure. This new coating on galvanized steel behaves like a phosphophyllite coating on steel.

Table 4

Cyclic Scab Testing

System	Cyclic Scab (4 weeks)[1] Steel	Galvanized Steel	Cyclic Scab (8 weeks)[1] Steel Only
A	1.5-4	0.5-3	2-8
B	1-2	0.5-2	1.5-5
C	1-2	0.5-2	1-4
AA	2-3	1-5	2.5-3.5
BB	1-2	0.5-3	2-3
CC	1-2	0.5-3	1.5-2.5

[1] The results indicate the range of blistering from the scribe in millimeters.

The cyclic scab test procedure has become the most widely used and accepted method for predicting the actual type and extent of corrosion on vehicles in field situations. Although each automotive company has its own unique procedure for determining the scab corrosion protection of the finished product, each procedure usually involves cycles of constant humidity and salt solution exposure over a given period of time.

The results reported in Table 4 show that the phosphophyllite coating is an improvement over the previous hopeite coating and that immersion application of the zinc phosphate coating is generally an improvement over the spray method of application for steel. The modified phosphophyllite coating gives a result slightly better than the phosphophyllite coating on steel for both methods of application.

Table 5[1]

Comparison of Paint Adhesion and Outdoor Exposure

System	Outdoor Exposure (15 weeks)[2] Steel Only	Adhesion (Dry)[3] Steel Only
A	1.5-5.5 mm[4]	90-100
B	0.5-1.5 mm	No loss

1 The results reported are from a previous study where panels were tested for outdoor exposure at various times throughout the year (1983). After removing the panels from the racks, the adhesion was checked to determine if any correlation exists between scab corrosion failure and paint adhesion failure.

2 See Appendix 1 for test procedure. Results reported are the range of scabbing (minimum to maximum) from the scribe.

3 The results reported are the % of paint loss in the cross-hatched area.

4 Filiform and scab corrosion noted along the scribe.

The results in Table 5 demonstrate that a correlation exists between outdoor exposure and paint adhesion testing. More studies are being done to better correlate paint adhesion and alkali resistance to scab corrosion test results for automotive paint finishes since the paint adhesion and alkali resistance test procedures can be completed in a much shorter length of time. A quick test method which can accurately predict the performance of the finished product in use will continue to be an area of intensive research.

Summary

The data indicates that a correlation does exist between alkali resistance and paint adhesion testing, with System C or CC showing the best overall result. This same system also gave the better result in salt spray and cyclic scab testing which are accepted accelerated test methods for the automotive industry. Further, from prior studies it is known that the pH increases at the steel/phosphate/paint interface during the corrosion process (4) (5); therefore, the increased alkaline resistance has a direct bearing on the accelerated test results. Finally, we chose to test alkaline resistance using NH_4OH to more closely simulate field corrosion under an organic paint film.

Appendix 1

Test Methods

- Salt Spray - ASTM B-117
- Paint Adhesion
  - Wet —— 1) Age painted panels a minimum of 72 hours.
    2) Immerse panels in deionized water for 10 days at 50°C.
    3) Remove panels, dry, and within 10 minutes make a crosshatch cut (2 mm and 1 mm spacing) upon the painted surface.
    4) Immediately after crosshatching, apply #610 cellophane tape to the crosshatched area and remove tape quickly.
    5) Measure the % of paint loss in the crosshatched area.
  - Dry —— Conical Mandrel Bend

    Impact
- Zinc Phosphate Coating Solubility (Alkali Resistance)

1) Weigh the phosphated substrate (4 x 6" panel) with an analytical balance to the nearest 0.1 mg (Designate A).

2) Immerse panel into an alkaline solution for 5 minutes at 30°C, where the solution contains 5.83 grams per liter NH_4Cl (using deionized water) and adjusted to a pH of 10 with NH_4OH.

3) Rinse panel with deionized water.

4) Hot air drying or forced air drying of the panel.

5) Second weighing of the panel (Designate B).

6a) Immerse panel in 5% chromic acid solution at 70°C for 5 minutes (use for steel).

6b) Immerse panel in 1% ammonium dichromate solution (using NH_4OH) for 5 minutes (use for galvanized steel).

7) Rinse panel with deionized water and force air dry.

8) Third weighing of panel (Designate C).

$$\text{Coat.Sol.}(\%) = \frac{A(\text{Total panel wt}) - B(\text{Panel wt.after alk.soak})}{A-C\ (\text{Total Coating Wt.})} \times 100$$

- General Motors Cyclic Scab

(1) Prepare panels (age a minimum of 72 hours and scribe)

(2) Test Cycle

a) Salt solution (5% NaCl) immersion (15 minutes, ambient).

b) Room temperature exposure (75 minutes).

c) Humidity Cabinet - 85% RH @ 60°C (22.5 hours).

One cycle = 1 week day.

d) On Monday only, after room temperature exposure.

i) Oven - 60°C 1 hour.
ii) Freezer - minus 13°C 30 minutes.
iii) Humidity Cabinet.

e) On Saturday and Sunday - panels remain in the Humidity Cabinet @ 85% RH.

3) Run 20 cycles (4 weeks)*.

4) Rinse with warm water and scrape along scribe with spatula.

5) Rinse with warm water and clean scribe with a Scotch-Brite pad and a powdered cleanser.

6) Rinse with water and dry.

7) Rate average and maximum paint loss or film eruption from the scribe.

* Note: We also run 40 cycle (8 weeks).

- Outdoor Exposure (Ambler, PA)*

  1) Prepare panel (age a minimum of 72 hours and scribe).

  2) Mount panels on racks facing south and at an angle of 45°.

  3) Spray panels twice per week with 5% NaCl solution.

  4) Exposure period - 15 weeks.

  5) Rate amount of scabbing (and/or filifomr) along the scribe.

* This is a semi-rural, light-industrial area.

- Appearance

  Uniformity of the coating and crystal size.

  Rating —

  \+ = good
  \- = poor

  For example:

  \+ - = good uniformity but poor crystal size.

  \- + = non-uniform coating but good crystal size.

Appendix 2

Paint System

Electropaint — PPG 3002

Cathodic Black Electrocoat
Bath Temperature - 27°C
Voltage and Time - as required to give 0.7 mil.
Bake - 182°C for 30 minutes

Primer Sealer — PPG 80-703

Thermosetting, sandable, high-solids, solvent-bourne
Film Thickness - 0.8 to 1.0 mil.
Bake - 163°C for 30 minutes

Top Coat — DuPont 395-Y-99612

Green 27% Lucite Dispersion Lacquer
Film Thickness - 2 to 3.5 mils DFT
Bake - 163°C for 30 minutes

References

1. E. T. Nowak, L. L. Frank, G. W. Froman, "A Comparison of Corrosion Test Methods for Painted Galvanized Steel", Society of Automotive Engineers, Inc., 1982.

2. G. C. Kent, K. J. Hacias, N. A. Fotinos, "Laboratory Evaluation of Automotive Conversion Coatings", Society of Automotive Engineers, Inc., 1983.

3. J. W. Davis, "The Pretreatment of Steel and Galvanized Steel for Cathodic Electrodeposition Paint Systems", Society of Automotive Engineers, Inc., 1982.

4. A. G. Smith and R. A. Dickie, Ind. Eng. Chem. Prod. Res. Dev., 17, No. 1, 42-44 (1978).

5. R. R. Wiggle, A. G. Smith, and J. V. Petrocelli, Journal of Paint Technology, 40, No. 519, 174-186 (1968).

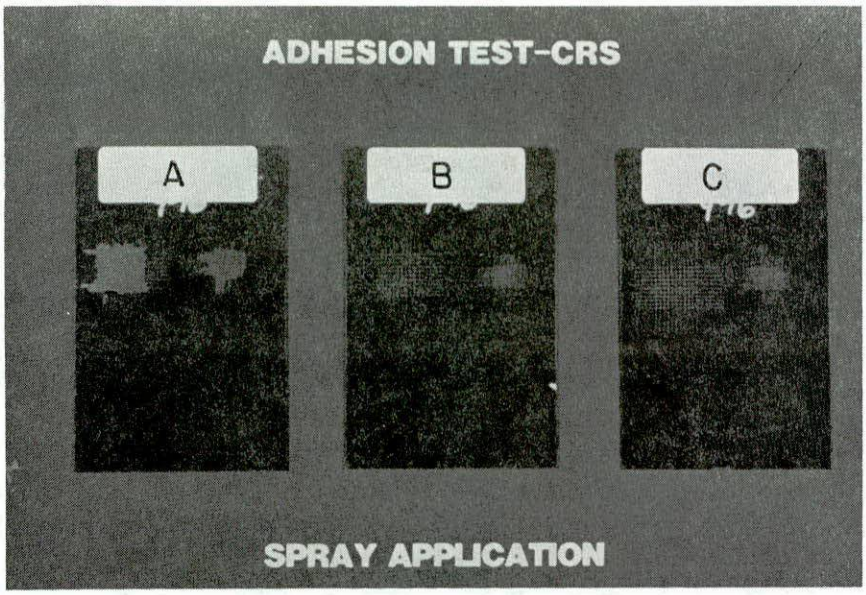

Figure 1 - Paint Adhesion Results for Steel

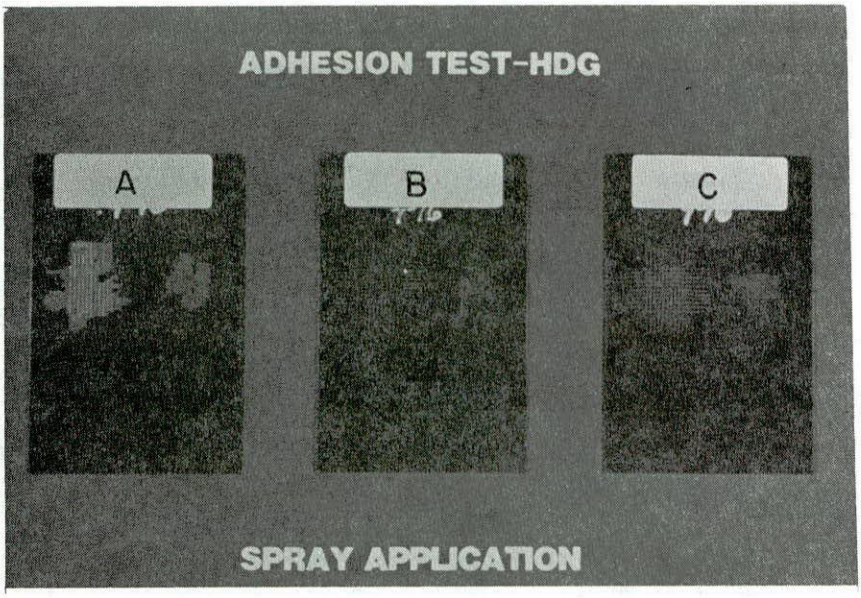

Figure 2 - Paint Adhesion Results for Galvanized Steel

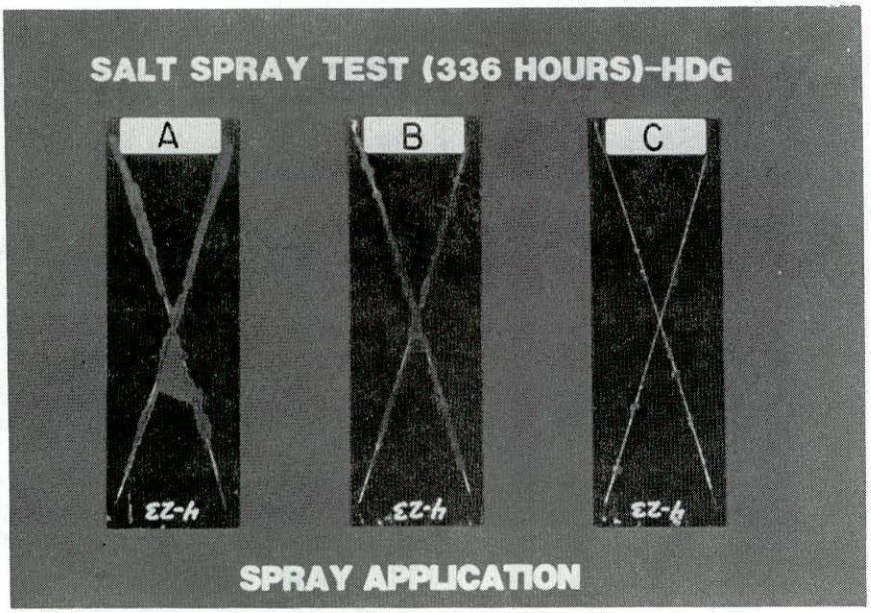

Figure 3 - Salt Spray Test Results for Galvanized Steel

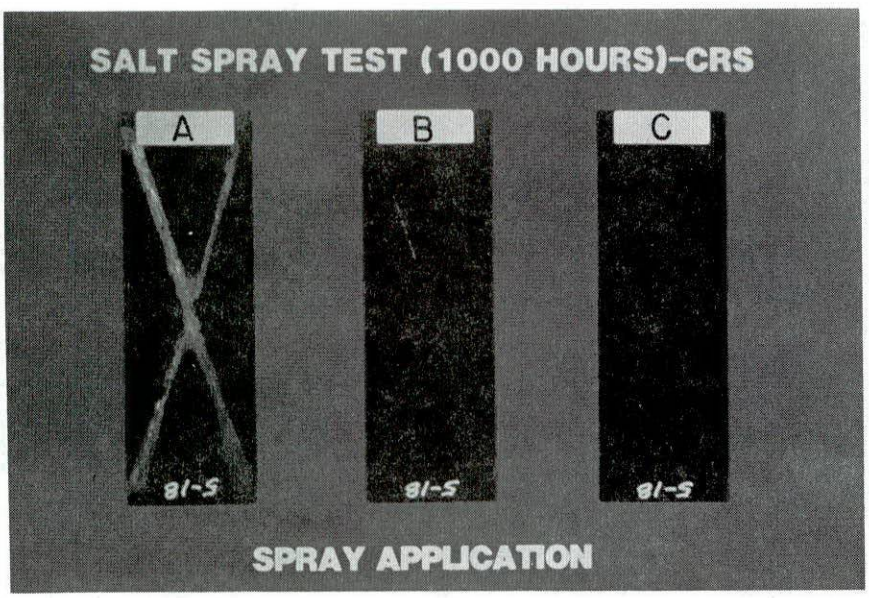

Figure 4 - Salt Spray Test Results for Steel

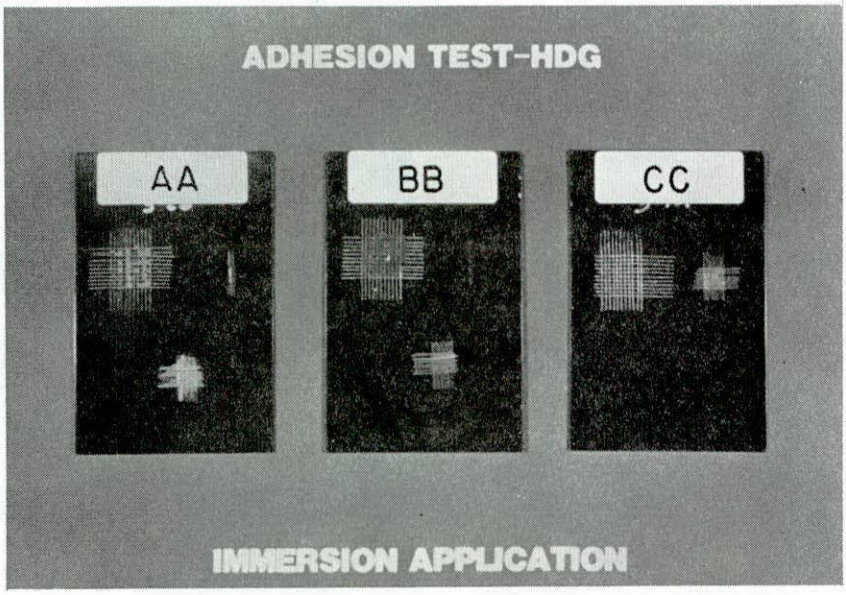

Figure 5 - Paint Adhesion Results for Galvanized Steel

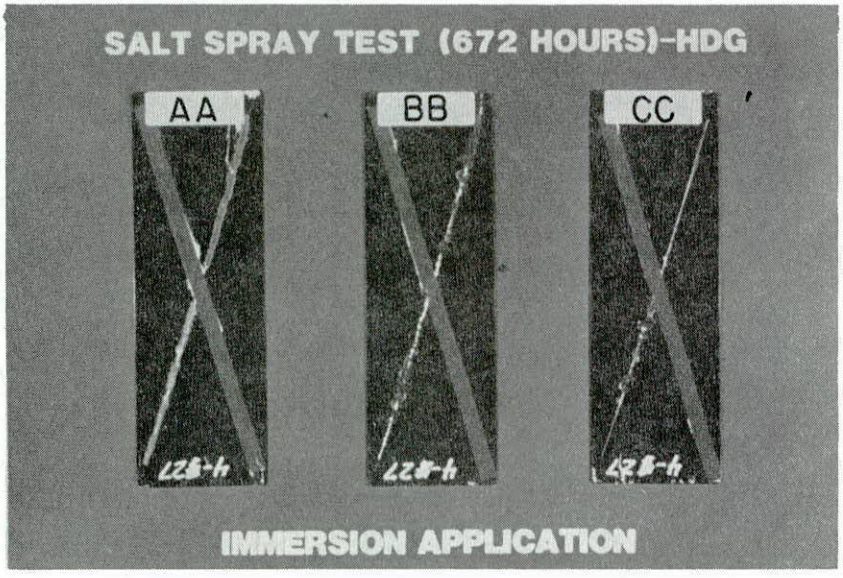

Figure 6 - Salt Spray Test Results for Galvanized Steel

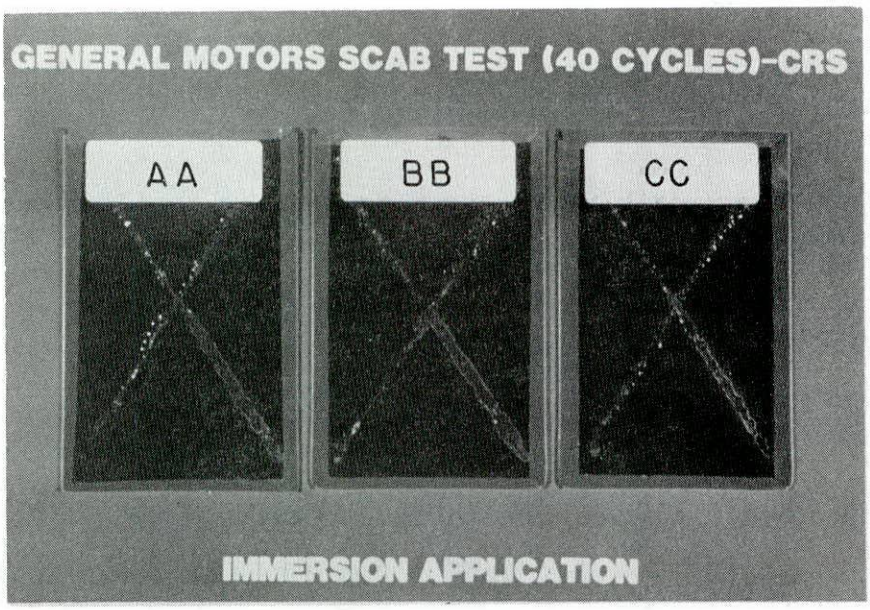

Figure 7 - Cyclic Scab Test Results for Steel

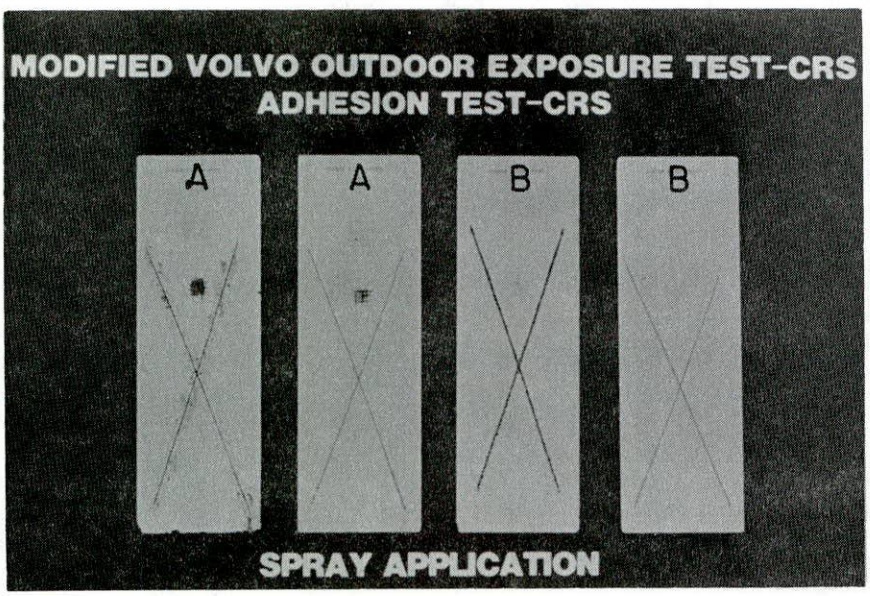

Figure 8 - Outdoor Exposure Test Results for Steel

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Statistical Methods II (A Tutorial, Session N

Introduction To Statistical Methods For Electroplaters— Non Mathematical Techniques

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INTRODUCTION TO STATISTICAL METHODS FOR ELECTROPLATERS - NON MATHEMATICAL TECHNIQUES

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The renaissance of statistical methods in the automotive industry has been precipitated by the realization that certain offshore competition has over the previous three decades successfully utilized the techniques developed by Shewart, Dodge, Romig, Juran and Deming to markedly improve quality of manufactured products. Specific additions and improvements to the body of statistical knowledge have occurred over this same three decade time frame, many developed by the offshore competition, particularly quality circles, and cause and effects analysis (Ishikawa diagrams).

Current thinking within the statistical quality community in the automotive industry is redirecting initial efforts in statistical methods implementation toward advanced planning techniques. These techniques include failure mode and effects analysis, feasibility analysis, process flow diagrams, cause and effects analysis (Ishikawa diagrams), historical quality information analysis (Pareto diagrams), control plans, and process review/signoff. Each of the previously mentioned techniques has a specific function and the individual functions will be described and applications specific to plating and surface finishing provided.

The first topic for discussion will be feasibility analysis. This analysis is normally conducted in a multistage effort beginning at the preliminary or preprogram stage in the design of a vehicle and its component parts. The effort then continues through the successive stages to a final feasibility evaluation. The stages of the effort in their appropriate order are first concept feasibility, second preliminary feasibility-advanced program development phase then production program execution phase, and third final feasibility. Each of these feasibility evaluations is conducted by utilizing historical quality data (i.e. warranty performance, similar part quality history, etc.). Usually the initial feasibility evaluations are performed by in-house manufacturing activities when possible. The final phase feasibility analysis may be performed by an outside manufacturer prior to sourcing.

The second topic for discussion is failure modes and effects analysis. There are in fact two separate categories within this topic design FMEA and Process FMEA. Since plating and surface finishing are processes, we

will focus on the process FMEA and disregard design FMEA. This technique allows for categorization of the potential failure modes, the potential effect(s) of failure, and the potential cause(s) of failure. Included in the FMEA are current controls - those which are intended to prevent cause(s) and those which are intended to detect cause(s), occurrence ranking, severity ranking, and detection ranking and recommended actions and status.

The third topic for discussion is the process flow diagram. The use of a process flow diagram is to provide as much information graphically as possible about the intended manufacturing procedure. The use of process flow diagrams is essential in the appropriate placement of quality inspection stations and the placement of statistical process control charts. Lacking an adequate process flow diagram usually results in the improper and/or ineffective use of quality inspection stations and statistical process control charts. This technique is of course then vital to the continued effective quality evaluation of a plating and surface finishing process.

The fourth topic for discussion is the cause and effects diagram, also known as Ishikawa diagrams or fishbone charts. The use of this technique is particularly simple and gratifying since it provides a relatively straightforward portrait of a specific cause and effect relationship set. There are two principal types, a process classification diagram and a cause enumeration diagram. Each diagram is based on the relationship between specific categories of cause (materials, manpower, method, maintenance, machinery, environment, and the presumed or desired effect). The cause enumeration diagram is used to focus on a specific effect and its probable causes, while a process classification diagram is used to evaluate the cause and effect relationships throughout an entire manufacturing process.

The fifth topic for discussion is the Pareto diagram. Pareto analysis is a convenient method for categorizing historical quality information in an orderly manner. Once the information is categorized and the frequency of occurrence of a specific problem summarized, a graphical presentation of the data is possible. From this graphical data table certain conclusions may be drawn and a problem resolution course determined. The most appealing aspect of this technique is that it allows a focus on the principal problems (usually about twenty percent (20%) of the categories) that are the largest contributors to poor quality (usually about eighty percent (80%) of all instances).

The sixth topic of discussion is the control plan. A control plan in fact is an inspection instruction with specific reaction and reporting procedures in the event a defect or defective is noted in a sample or an out of control situation is signaled on a statistical control chart. This technique is a quality method of long standing and should be a

normal part of the daily quality routine. There are various pro formas for control plans and the relative merits will be compared.

The seventh topic for discussion will be process review and signoff. This technique assures that all the appropriate efforts relating to determination of the quality level of a product. The elements included are process sheets, inspection instructions, gages and test equipment, initial sample evaluation and packaging certification. Each of these elements require an intent statement and verification procedure. When all the elements are verified and signatures obtained, there is consensus agreement that the course established is the most effective of available.

The final topic of discussion is the choice of data collection. Should the data collected be attribute type or variable type? Where should the data be collected? Wherever possible the data collected should be variables data since statistical presentation of variables data is more powerful and effective as a method of decision making. The data should be collected at those points in the process identified on the process flow diagram by Ishikawa, Pareto and FMEA analysis as the crucial points in the process. The data should be presented in the simplest possible form that provides useful information about the process. There are numerous methods of presentation 1) Histograms, 2) Attribute and variables data control charts, 3) Process potential and capability analysis, 4) Checklists, 5) Record sheets, 6) Bar graphs and pie charts, 7) Pareto diagrams.

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Statistical Methods II (A Tutorial, Session N

Introduction To Statistical Sampling Methods For Electroplaters

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Statistical Methods II (A Tutorial, Session N

Experimental Design: How It May Be Used By Electroplaters

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Statistical Methods II (A Tutorial)
Session N

Statistical Process Control Methods For Electroplaters — Methods Other Than X-Bar, R Charts

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Statistical Methods II (A Tutorial) Session N

Statistical Methods For The Laboratory And Non-Manufacturing Process

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Electronics
Session O

The Corrosion Resistance of Tin/Zinc Alloy Coatings and the Development of Passivation Treatments

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INTRODUCTION TO STATISTICAL SAMPLING METHODS FOR ELECTROPLATERS

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Since all sampling can be described by an operating characteristic curve based on the poisson distribution when the sample size N and acceptance number C and the proportion defective P are known, a plater and surface finisher is able to establish a sampling plan that will satisfy a customer's needs when N, P, C are explicitly stated by the customer. The various terms for sampling plans will be described and their significance detailed. However, emphasis will be placed on the use of proper sampling for Statistical Process Control Charts rather than after the fact sampling programs since lot sampling plans are detection methods rather than prevention methods and not in accord with current policy.

The primary emphasis herein will be to describe the need to prevent errors such as sample induced stratification by poor choice of sample size, by poor choice of sample location, by poor choice of sample frequency, by choice of non-consectutive sampling when using control charts so false signals for out of control situations will not occur and correspondingly so control will not be inferred incorrectly when there is an out of control situation existing on the control chart. Sampling is also dependent on the type of control chart chosen attribute charts usually requiring larger sample sizes than variable charts.

EXPERIMENTAL DESIGN:
HOW IT MAY BE USED BY ELECTROPLATERS

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Experimental design is the technique most commonly used to assess the interrelation of several effects in a given process. When properly utilized experimental design will tell the electroplater and surface finisher those process parameters that are significant contributors to process variation and which should be controlled using Statistical Process Control Charts. In addition, experimental design can provide the analytical path to successfully reduce variation. As an aside, the Japanese currently devote about fifty percent (50%) of their statistical efforts to experimental design to reduce variation in processes and the output of those processes.

This presentation will attempt to provide insight into the many methods of experimental design and the analysis of the data derived from the experiments conducted. Cautions will be offered about the improper conduct of experimental design - Failure to randomize, Failure to replicate, Improper correlaton statements, Etcetera. While examples of the various types of designs possible and their analysis will be presented, the principle emphasis will be on a specific category of designs, factorial and fractional factorial designs. The emphasis on factorial type designs is because of their analytic simplicity and the cost time effectiveness. Further, the emphasis will be restricted to the use of 2 level N factor and N-K factor fractional designs since they represent linear approximation models and mathematically and graphically are easiest to convey to the inexperienced statistical practitioner.

Specific instances of designs currently being used to further understanding of plated or coated parts will be provided to demonstrate how this technique is being used in the automotive industry. In addition, some specific comments regarding fruitful areas for application will be discussed.

STATISTICAL PROCESS CONTROL METHODS FOR ELECTROPLATERS - METHODS OTHER THAN X-BAR, R CHARTS

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Statistical Process Control Methods are the use of Shewhart Type Control Charts for variables and attribute data. The purpose of a control chart is to demonstrate the time ordered stability of a manufacturing process. When a process is stable, only a system of chance cause is operating and specific inferences about the process and the output of the process can be drawn. When a process is unstable, some assignable cause is acting on the process thus eliminating the possibility of drawing inferences about the process and the output of the process.

There are in addition to the Shewhart Control Charts for variables and attribute data, a number of non-mathematical techniques for data accumulation and manipulation which allow specific inferences to be drawn. These techniques include checklists, graphs, histograms, Pareto analysis. While essentially non-mathematical, these techniques are sufficiently effective to provide insights about the information collected that are valuable.

As a supplement to the use of the previous methods, a discussion of the use of process potential and process capability studies is in order. These studies provide specific information regarding performance to engineering drawing or specification requirements. The techniques allow the practitioner the opportunity to assess the ability of a machine or process to perform the intended operation(s). While mathematical, the techniques are not extremely sophisticated and require no specialized background.

The emphasis for the discussion in this session will be on three specific control charts - Individuals, Moving Range; Moving Average, Moving Range; U-Charts - Process Potential and Capability Studies, Histograms, Stem and Leaf Diagrams, and Pareto Analysis. Specific examples of each type of procedure will be provided. The examples will be discussed with the intention of providing some insight regarding how the techniques are being used in the automotive industry. Suggestions regarding possible fruitful applications of the techniques will also be provided.

STATISTICAL METHODS FOR THE LABORATORY AND NON-MANUFACTURING PROCESS

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The accuracy and precision of gages and test equipment is fundamental to the to the adequate operation of any manufacturing process. To properly assess the accuracy and precision of gages and test equipment, several methods are available. Gage and test equipment capability studies are one method and Shewhart Control Charts for variables specifically $\bar{x}$, R charts are another method. Discussion of the applicability of these methods is intended as well as provision of examples of the methods as being used in the automotive industry.

Statistics may also be applied to the administrative portion of any business. While applications are certainly less frequent in office surroundings, the techniques of Control Charts, Histograms, Pareto Analysis and Ishikawa Diagrams are apropo and efficient. This section of the session will deal essentially with the use of Ishikawa Diagrams, Pareto Analysis and Control Charts for variables to depict the use of statistical methods in non-manufacturing situations. Specific examples of the methods and possible applications may be provided.

THE CORROSION RESISTANCE OF TIN/ZINC ALLOY COATINGS AND THE DEVELOPMENT OF PASSIVATION TREATMENTS

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ABSTRACT

A short review of previous studies of the corrosion resistance of tin-zinc alloy coatings on steel and the effect of passivation treatments is presented. The results of a current investigation of the corrosion resistance to the salt fog test and the cycled temperature humidity test of different passivation treatments based on the group VIa oxoanions are also described.

INTRODUCTION

The stannate-cyanide electrolyte, capable of producing a good quality tin-zinc coating, was developed during the 1940's, and Angles[1, 2, 3] then studied the alloy deposit's ability to protect steel. He examined a wide range of coating compositions, and compared them to tin, zinc and cadmium deposits, using both accelerated tests and outdoor exposure. He concluded from the accelerated tests that 80%Sn-20%Zn was the best alloy composition for this purpose, finding that it was superior to tin or zinc alone, and was at least the equivalent of cadmium. His outdoor exposure test results were somewhat inconclusive, since only the cadmium coatings had failed in the one year test period, and it was impossible to differentiate between the other coatings in that short a time. Halls[4] compared the 50%Zn and 20%Zn alloys with cadmium and zinc in salt spray, and tropical atmosphere accelerated tests, using coated panels and shaped specimens having both perforations and sharp angular geometry. He found that the 50%Zn alloy produced heavy white rust and that in general, the tin-zinc alloy provided a degree of protection to iron and steel which was broadly similar to that of zinc and cadmium. The alloy was very similar to cadmium for protection in damp conditions and for retention of solderability, and was superior to cadmium, and close to zinc, relative to ease of spot welding the steel.

Angles and Britton[5] carried out a more complete study comparing the same coatings at three outdoor sites for periods of up to 44 months. Their results are summarized in Table 1. They concluded that tin-zinc alloys are not equivalent to zinc as a protective coating against the weather, but do have advantages over zinc, and are comparable to cadmium, in prolonged

high humidity, or where ease of solderability is important. Dettner[6] conducted another large study of zinc, tin, cadmium and 80%tin-20%zinc coatings, in salt spray, humidity, industrial atmosphere accelerated tests, and outdoor urban exposure. He concluded that tin-zinc offered a protection to steel which was generally between that of tin and zinc, but was superior to both in the salt spray test. Compared to cadmium, tin-zinc was generally less protective, except in the industrial atmosphere test, and, for the thinnest coatings in salt spray, where tin-zinc offered greater protection. Lowenheim[7] found, after a series of outdoor exposure tests, that cadmium was superior to both 80%tin-20%zinc, and zinc, in marine environments, with little difference between the zinc and tin-zinc coatings. In the industrial environment, zinc offered superior protection to steel compared to cadmium, and tin-zinc was found to be the least protective of the three.

A large survey of many different coatings on steel was conducted by Longhurst and Clarke[8] in Eastern Africa at coastal, jungle, and town sites, to investigate the effects of tropical atmospheres. The coatings included cadmium, tin-zinc and zinc. In general, cadmium was considered the superior coating at each specific location, but 80%tin 20%zinc was reasonably comparable when the samples from all sites were considered together. Their results are summarized in Table 2. Cooke et al[9] tested a series of duplex cadmium-tin, tin-cadmium, zinc-tin and tin-zinc coatings, together with the pure metal coatings, and different alloy compositions of tin-zinc and tin-cadmium, in an industrial environment, and a salt spray test. They concluded that zinc or laminar tin-zinc gave better protection than tin-zinc alloy coatings in an industrial environment, and that tin-zinc alloy coatings were in turn, better than alloy or laminar coatings containing cadmium. The salt spray test indicated that the presence of cadmium, as part of an alloy or laminar coating, improves corrosion resistance, and is superior to zinc of equivalent thickness. Several other workers investigating these coatings have drawn similar conclusions [10, 11, 12, 13, 14]. to those expressed in the preceding text.

More recently Raub et al[15] appear to have repeated part of the work carried out by Angles[3] and disagree with him on the most protective alloy composition. They compared the resistance of different compositions of tin-zinc, and cadmium, tin and zinc to salt spray and concluded that 55-68% zinc alloys provide the best protection, and were superior to all the pure metal coatings. However, they do not appear to have studied intermediate alloys in the range 10-30% zinc. Another recent investigation by Koeppen and Runge[16], studied a wide range of alloys in terms of their shelf life, resistance to salt spray, the influence of a chromate passivation treatment, and their corrosion potential. They found the tin-zinc alloy to be superior to tin and zinc, but inferior to cadmium. They concluded that for a compromise between a low amount of zinc corrosion product, and the highest possible life-time before rusting, an alloy composition of 8-22% zinc was best. They noted the different conclusions drawn by Raub, and suggested that the use of

different criteria for assessing failure explained the contradictions. Raub's assessment was based on 10% rust coverage, whereas Koeppen and Runge made their assessment on the first sign of rust. The use of differing criteria for assessing failure probably explains many of the other contradictions found in the literature as well.

Finally Phillips and Johnson[17] studied the contact resistance behaviour of a number of tin alloy coatings after different aging treatments. Contact resistance can be very sensitive to corrosion product, so this investigation essentially assessed the ability of a coating to resist the formation of surface corrosion products. Tin alloys with lead, cadmium, antimony and zinc were studied, but only the tin-cadmium and tin-zinc coatings remained essentially free from rust, and maintained a low contact resistance. Different coating thicknesses were also investigated, and for the thinnest coatings, tin-zinc was superior to tin-cadmium.

While steel is the main substrate covered by this review, several workers have looked at other substrates[10, 18], such as aluminium and magnesium for aircraft applications. Lowenheim[19] considered 80%Sn-20%Zn as a coating for copper wire in preference to tin. Britton and de ver Stacpoole[20] considered the effect of different coatings on steel in contact with aluminium panels, and concluded that tin-zinc provided better protection to the overall system then did cadmium or zinc.

Passivation Treatments.

Although the initial work by Angles[3] considered passivation treatments for tin-zinc, no further development of these treatments has occurred since then. He concluded that of the seven treatments he tried, all based on the chromium VI ion, 2% chromic acid (either as a short dip hot or a longer dip cold) was the best all-round treatment. Actually, the best protection was offered by a 5% chromic acid, 2% chrome-alum hot treatment, but this adversely affected the solderability of the coating. All other investigators since have used the 2% chromic acid treatment.

Britton[5] concluded that passivation treatments did not have a marked effect on the corrosion resistance of coatings in his outdoor exposure tests. Lowenheim[21] concluded much the same, although earlier he had stated they were efficacious. Unpublished work at the International Tin Research Institute, and that of Koeppen and Runge[16], indicates there can be a substantial improvement in corrosion resistance resulting from passivation treatments in accelerated tests such as salt fog and cycled temperature humidity, but that the improvement can also be inconsistant. The present authors feel that the whole area of passivation treatments on tin-zinc coatings requires further study, and the initial part of such an investigation is

presented here.

Experimental Study

Electrodeposition of samples of the tin-zinc alloy were produced from a standard stannate-cyanide electrolyte[22], using 1 dm^2 mild steel panels and tin-zinc anodes. The alloy coating had a thickness of $10 \pm 1 \mu m$, and a composition of approximately 75%Sn-25%Zn; these values being determined by gravimetric analysis. The four passivation treatments utilized have been described in the literature[3, 23, 24, 25, 26], but relative to other applications. They have been modified in this study to facilitate comparison between them. The treatments were based on chromic acid, sodium dichromate, sodium tungstate and sodium molybdate. Experimental details of the treatments are given in Table 3, together with the individual variations of treatment for each panel, i.e. the different temperatures at which the chromic acid solution was used and the different parameters for the electrolytic treatments. It was not possible to standardize the electrolytic treatments for each solution because of their different effects on the tin-zinc coating. The intent of the investigation was to provide information concerning the corrosion resistance of four films as a preliminary step to studying variants of the best surface treatment. This part of the study assesses the corrosion resistance in a salt fog test, according to B.S. 3900, pt. F4, but at ambient temperature, and a cyclic temperature humidity test according to B.S. 3900, pt. F2 (high, constant humidity with a cycled temperature range).

Results.

The passivation film was judged to have broken down when the first sign of zinc corrosion product was observed, although this was sometimes quite localized. In some cases, the film gradually darkened as it became less protective, making the onset of zinc corrosion difficult to detect. The coating was judged to have broken down with the first definite sign of substrate corrosion. The subsequent spread of rusting was also recorded, since, in some cases, early rusting at a single spot was not followed by further deterioration.

Table 3 shows the differences between passivation treatments for the test panels. Tables 4 and 5 summarize the information obtained from the salt fog, and cycled temperature humidity tests, respectively. They show the number of days to the appearance of visible corrosion product on the panels: the left-hand and right-hand columns indicating onset of zinc corrosion and iron corrosion respectively. The salt fog test ran for 150 days; the cycled temperature humidity test was last observed after 300 days.

Discussion.

The salt fog test was considerably more corrosive than the cycled temperature humidity test. The coatings tended to corrode in the descending order of chromic acid-tungstate-molybdate-dichromate, for both tests. There were slight differences between the variants within each treatment, and the results indicate that, in general, more protection was provided by the cathodic-anodic cycle than by the cathodic cycle alone, for the dichromate and tungstate treatments.

The dichromate treatment provided outstandingly good protection delaying both zinc and iron corrosion for the longest times. The molybdate treatment provided second best protection and, although the film did not prevent the onset of zinc corrosion for long, it helped to considerably delay the onset of iron corrosion, especially for the cycled temperature humidity test, where the protection it provided was much closer to that of the dichromate treatment.

The tungstate treatment appears to offer a similar degree of protection as did the molybdate treatment with respect to the onset of zinc corrosion, but does not have such a retarding effect on coating breakdown. Previous observations of untreated tin-zinc alloy deposits suggest they would be expected to survive at least 10 days in the salt fog test. This suggests that the chromic acid treatment actually reduces the protection of a tin-zinc alloy coating. Not only was there rapid initial substrate corrosion, but it also spread and penetrated as if the coating was providing very little, if any, sacrificial protection.

There is some indication that a correlation exists between the applied current density used for the treatments and the degree of protection offered by them.

Conclusions.

The treatment based on sodium dichromate was superior to all others. The molybdate treatment imparted reasonable protection in the salt fog test and good protection in the cycled temperature humidity test, but it was inferior and less consistant than the dichromate treatment. The tungstate treatment provided a lesser degree of protection than the molybdate in most cases for both tests. The chromic acid treatment appeared to be detrimental to the normal properties of a tin-zinc coating.

Unexpectedly large differences in protection occurred for the closely related species of sodium dichromate and chromic acid, and this may explain in part, earlier reports of great variability in the protection offered by

passivated tin-zinc coatings.

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References.

1. R. M. Angles, J. Electrodeposition Tech. Soc., 21, 45 (1946).

2. R. M. Angles and J. W. Cuthbertson, J. Electrochem. Soc. 94, 2 (1948).

3. R. M. Angles and R. Kerr, Engineering, 29, March (1946).

4. E. E. Halls, Metal Finishing, 54-58, April (1950).

5. R. M. Angles and S. C. Britton, Metallurgia, 44, No. 185, Oct. (1951).

6. H. W. Dettner, Plating, 469-480, May (1959).

7. F. A. Lowenheim, M. & T. Corp. Report No. 218 (1955).

8. S. G. Clarke and E. E. Longhurst, First Int. Congr. on Metallic Corrosion, Butterworths, London, 1961, p70.

9. F. Cooke, J. K. Cosslett, R. W. Scott, C. E. A. Shanahan, Br. Corros. J., 1, 283 (1966).

10. B. Cohen, Plating, 44, 963-968 (1957).

11. Anon, Automobile Engineer, 75, Feb., (1955).

12. H. Heinemann, Metalloberflache, 6B, 33 (1954).

13. A. B. Trippler, G. Fuller, C. L. Faust, Air Force Tech. Rept. 5692, Suppl. 4 (1953).

14. R. T. Gore, Corrosion, 15 (3), 113 (1959).

15. C. J. Raub, W. Pfeiffer, M. Vetter, Galvanotechnik, 70, 7 (1979).

16. H. J. Koeppen and E. Runge, Galvanotechnik, 73, 11, 1217-1221 (1982).

17. S. L. Phillips and C. E. Johnson, J. Electrochem. Soc., 117, 827, (1970).

18. S. V. Lashko-Avakyan and N. F. Lashko, Svarochnoe Proizrodstro, 5, 13 (1961).

19. F. A. Lowenheim and R. T. Gore, Wire and Wire Products, 30, 1219 (1955).

20. S. C. Britton and R. W. de ver Stacpoole, Metallurgia, 52, 64 (1955).

21. F. A. Lowenheim, Trans. Inst. Metal Finish, 31, 386-397 (1954).

22. Anon, Tin-Zinc Alloy Plating, Intl. Tin Research Institute, Pub. No. 202, London, 1961.

23. S. C. Britton and K. Bright, Metallurgia, 56, No. 336, 163-168 (1957).

24. R. E. van de Leest G. Krijl. Thin film solids, 72, 237-246 (1980).

25. R. E. van de Leest et al., Dutch Patent 7906441, (1979).

26. D. R. Gabe & K. K. Chew, Corr, Prev. and Control, 7-10, Aug. (1979).

Table 1.

Performance of Tin-Zinc, Zinc and Cadmium Coatings 13μm Thick on Steel in Outdoor Environments

Atmosphere	Coating	Time to first appearance of rust (months)	Time for test panel to become rust covered (months)
Industrial	Zinc	24	80% covered at 44
	Tin-Zinc	4	100% covered at 18
	Cadmium	4	100% covered at 11
Suburban	Zinc	37	10% covered at 44
	Tin-Zinc	14	100% covered at 28
	Cadmium	8	100% covered at 19
Marine	Zinc	33	10% covered at 45
	Tin-Zinc	18	100% covered at 38
	Cadmium	21	70% covered at 45

Results from Reference (5)

Table 2.

Performance of 13μm Coatings on Steel After Two Years Tropical Exposure in Eastern Africa

Coating	Jungle	Town	Coast
Cadmium	Slight rusting	Slight rusting	Unaffected
Zinc	Slight rusting	Unaffected	0.5-50% rust coverage
Tin-Zinc	Slight rusting	50-99% rust coverage	Unaffected

Results from Reference (8)

Table 3.

Treatment	Individual Variants of the Passivation Treatment.			
	Sample Numbers			
	1	2-5	6-7	8-10
Chromic Acid: 0.1M, pH 0.2-0.4, 30 sec.	30°C	50°C	50°C	60°C
Sodium Dichromate: 0.1M, pH 4, 30-40 mA/cm^2	-60/+15 sec.	-20/+5 sec.	-30 sec.	-30 sec.
Sodium Molybdate: 0.1M, pH 7, 10-15 mA/cm^2	(All cathodic for 30 sec.)			
Sodium Tungstate: 0.1M, pH 9 (buffered), 5mA/cm^2	-60 sec.	-60 sec.	(5mA/cm^2 cycles, 10 sec cathodic followed by 10 sec anodic repeated 10 times.)	

- Indicates cathodic current

+ Indicates anodic current

Table 4.

Breakdown of Coating in Salt Fog

Treatment	Time taken to produce visible corrosion product, (days).									
	Sample Numbers									
	1		3		5		7		9	
	zinc	iron	zinc	iron	zinc	iron	zinc	iron	zinc	iron
A (Chromic acid)	< 2	2	< 2	15	< 1	15	< 1	1	< 2	5
B (Dichromate ion)	21	>150	25	150	25	>150	12	102*	12	>150
C (Molybdate ion)	5	40	5	50	5	53	5	53	5	53
D (Tungstate ion)	5	18	5	18	5	25	5	25	5	32

* The single rust spot denoting failure did not become worse during the remaining 48 days of the test.

The test was finished at 150 days.

Table 5.

Breakdown of Coating in Cycled Temperature Humidity Test

Treatment	Time taken to produce visible corrosion product (days).									
	Sample Numbers									
	2		4		6		8		10	
	zinc	iron	zinc	iron	zinc	iron	zinc	iron	zinc	iron
A (Chromic acid)	< 18	63	< 1	1	< 1	1	< 1	1	< 1	1
B (Dichromate ion)	157	258#	152	188#	63	185*	63	108*	63	163*
C (Molybdate ion)	12	185	21	159	21	166	21	142	21	175
D (Tungstate ion)	12	50	12	50	18	50	18	50	18	50

* Red rust spotting occurred at the mounting points on the lower edge, no further rust spots appeared until 216 days

\# Red rust spotting was similar to above but passivation film was still protecting the majority of the surface at 300 days.

O-2

Electronics
Session O

Laser-Induced Direct Metal Deposition On Semiconductor and Polymeric Substrates From Electroplating Solutions

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LASER-INDUCED DIRECT METAL DEPOSITION ON SEMICONDUCTOR AND POLYMERIC SUBSTRATES FROM ELECTROPLATING SOLUTIONS

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ABSTRACT

This work is aimed at studying the feasibility of laser-induced high speed, high selective direct plating of metals and alloys on semiconductor and polymeric substrates immersed in plating solutions without external electric current and masking procedures.

A Q-Switch Nd/YAG pulse laser was used together with a commercial gold plating solution to obtain gold deposition at laser irradiated zones on the surfaces of silicon and GaAs semiconductors and on polyimide polymeric substrates.

Gold deposit morphology, structure, composition and electrical properties were examined by surface analytical techniques such as SEM, TEM, X-RAY, AES, ESCA and R.B.S.

Deposits were found to be elemental gold ranging from a few hundred angstroms to a few micrometers depending primarily on laser irradiation energy density. Increase in laser energy density resulted in an increase of the amount of gold deposited both on the semiconductor and polymeric substrates. Gold deposits exhibited Schottky barrier contacts on N-type silicon and gallium arsenide.

The mode of laser induced gold plating together with the possible associated mechanism and processes is discussed both for the semiconductor and polymeric substrates.

INTRODUCTION

Background

Recently, laser-induced chemical and electrochemical reactions intended to give either deposition or etching processes on metallic, semiconductor and polymeric substrates immersed in aqueous electroplating solutions - have received much attention with a view to possible use in fabrication of microelectronic devices [1-8].

- Metallic substrates. Laser-enhanced electroplating and electroless deposition processes on metallic substrates for applications such as micron-sized circuit personalization and repair was reported [1]. In that study, use was made of a continuous (c.w.) argon laser beam (10^5 watt/cm^2) with a commercial plating solution and an external electric current source, yielding a higher electrodeposition rate compared to conventional electroplating not involving a laser. The authors of the study attributed their results to local temperature increase at the laser irradiated zones on the cathode surface, but this may not have been the only major cause of the improvement.

- Semiconductor substrates. Pulse Q-Switch Nd/YAG laser irradiation operating at peak energy density in the range of 10^7-10^9 watt/cm^2 (pulse duration from 7×10^{-9} sec. to 150×10^{-9} sec.) was used to induce metal or alloy deposition on semiconductor substrates immersed in aqueous electroplating solutions with a view to potential formation of conductive lines, as well as of silicides serving as ohmic or Schottky barrier contacts [2-6]. These investigations demonstrated that semiconductor substrates such as InP [2], Si [3-5], and GaAs [6] can be selectively plated with metals such as Pt, Au, Pd-Ni from commercial electroplating aqueous solutions, making use of laser pulse irradiation without external electric current and without masking procedures. Photoelectrochemical methods for metallic film deposition on GaAs and Si immersed in aqueous solutions were carried out with external current making use of a 100 watt tungsten-halogen lamp [9]. Furthermore, photoelectrochemical etching processes of GaAs immersed in aqueous electrolytic solution was carried out [10], making use of He-Ne laser beam irradiation of 0.57 watt/cm^2.

- Polymeric substrates. So far, only limited attempts have been made to apply laser beam technology in inducing and enhancing direct maskless plating on polymeric substrates either from electroless solutions [7] or electroplating solutions [8]. Recently, the feasibility of obtaining direct high-speed high-selective gold deposition on polyimide substrate immersed in electroplating solution via pulse laser irradiation without external electric current and without masking procedure - was demonstrated by Zahavi et al [8].

In this work, we present results of such deposition of gold and palladium-nickel on semiconductor substrates (GaAs and Si) and on a polymeric substrate (polyimide) using commercial aqueous electroplating solutions. The possible mechanisms and processes involved are discussed.

MECHANISM

Semiconductor Substrates

Following the work reported earlier by the authors [3-6] together with the results produced by other investigators [9,10], the mechanism involved in the case of a semiconductor substrate could be characterized by three main simultaneous stages, as shown schematically in Fig. 1.

A. Deposition of metal atoms from the electroplating solution on the substrate at laser irradiated zones; at this stage the following processes take place (Fig. 1A):

(a) Photogeneration of electron-hole pairs at laser irradiated zones of the semiconductor surface.

(b) Chemical reduction of metal ions from the electroplating solution by the photogenerated electrons, followed by deposition of metal atoms at the irradiated zones.

B. Surface heating and possibly melting, followed by diffusion of deposited atoms into the substrate surface. (The duration of the heating or melting process considerably exceeded the actual laser pulse interaction time in order of magnitude [11,12]. Rapid diffusion of the deposited atoms took place, advancing deeply into the substrate surface through its heated or melted layer [3,12] (Fig. 1B)).

C. Solidification and regrowth of the liquid phase, forming alloys or compounds with the substrate [3,11,12] (At this stage termination of the irradiation was followed by rapid cooling [13] to form silicides [3] or other compounds between the semiconductor material and the deposited metal atoms (Fig. 1C).)

Polymeric Substrates

The detailed mechanism and processes involved in this case were not completely understood [7,8]. Recently, results obtained by electron spectroscopy for chemical analysis (ESCA) and infrared examination of laser-irradiated zones on a polyimide surface indicated transformation of imide into amide groups [8], but no such transformations or changes were observed upon annealing of the material up to 360°C in ultra high vacuum [14]. Accordingly, three main simultaneous stages were again hypothesized:

A. Generation of electrons through the above transformation of imide into amide groups.

B. Chemical reduction of metal ions from the electroplating solution by the generated electrons, followed by deposition of metal atoms at the irradiated zones.

C. Surface heating followed by diffusion of the deposited atoms into the substrate surface, making for better adhesion.

The present study was undertaken with a view to better understanding and evaluation of the above processes and parameters. The semiconductor substrates used were Si and GaAs, and the polymeric substrate - again polyimide; the metals in the electroplating solutions - gold and palladium-nickel.

EXPERIMENTAL

Experimental Set Up

The experimental set up, shown schematically in Fig. 2, consisted of a pulse laser system equipped with a computerized x-y table, and a plating cell containing the electroplating solution and the specimen material to be treated.

- Laser Systems. The laser systems used in this work were (A) a Q-switched frequency doubled Nd/YAG laser (Quntronix Co.) operating at wave length 1060 nm and 530 nm, pulse width in the range of 50 ns to 150 ns, and repetition rate 1 KHz to 5 KHz, or in single pulses; the beam diameter used was up to 150 microns. (B) Q-switched Nd/YAG lasers (Quantel Co., Quanta-ray Co.) at wave length 1060 nm and 530 nm, pulse width 5 ns to 15 ns and repetition rate 1 Hz to 10 Hz. The beam diameter ranged up to 5 mm. In both systems, the laser peak energy densities were controlled by a set of calibrated neutral density filters and ranged from 10^6 watt/cm^2 to 10^9 watt/cm^2, overlapping of irradiated spots ranged from 50% to 95%.

- Specimen Materials. Rectangular 10×5×1 mm semiconductor specimens were prepared from GaAs and Si wafers. The GaAs was (a) N-type tellurium-doped; (b) intrinsic; (c) P-type zinc-doped, - all three with (100) orientation. The Si was N-type and P-type, also with (100) orientation. The polyimide was Kapton H-500 (Dupont Co.).

- Electroplating Electrolytes. The gold plating solutions were: (A) potassium gold cyanide (Lea-Ronal Co., N.Y.) marketed under the name of Arospeed C.V.D.; (B) acid gold chloride. The palladium-nickel solution was based on an 60/40 atomic % alloy (Lea-Ronal Co., N.Y.) marketed under the name Pallamet 75.

- Examination of Deposits. The deposits were examined by scanning and transmission electron microscopy (SEM, TEM), and by surface analysis techniques such as Auger electron spectroscopy (AES), electron spectroscopy for chemical analysis (ESCA), Rutherford back-scattering (R.B.S.) and x-ray diffraction. They were also characterized with regard to their electrical properties, especially their behavior as ohmic or Schottky barrier contacts with the semiconductor substrates.

RESULTS AND DISCUSSION

Scanning Electron Microscopy

- Silicon Substrates. The surface morphology and structure of the gold and palladium-nickel deposits obtained are shown in Figs 3-4 and 5, respectively. The first figure shows typical single deposition spots obtained for different pulse energy densities and interaction times at a constant repetition rate of 2 KHz. These spots exhibited a circular morphology reminiscent of the lunar craters. Increase of interaction time (i.e. of the number of pulses) yielded a rougher surface (Fig. 3A, 3B) and probably caused surface heating which in turn resulted in the melting effect mentioned as the second stage of the proposed mechanism (Fig. 1). Increase of the pulse energy density at the same interaction time (same number of 25 pulses) also resulted

in possible recrystallization, as is indicated by comparing Fig. 3C with Fig. 3B.

Lines of deposited gold were obtained by 50% to 90% overlapping of the irradiated spots. A typical Fig. 4 shows the surface and cross section morphologies and their x-ray images for the deposit lines. The surface morphology is seen to be coarse (Fig. 4A) and the continuous deposits have a thickness of the order of 10 micrometers (Fig. 4B). Fig. 5 shows a typical surface morphology of the palladium-nickel deposits at different laser peak energy densities; lower energy densities are seen to yield a smooth undamaged deposit surface.

-Gallium-Arsenide Substrates. Figure 6 shows a typical surface morphology gold deposition from potassium-gold cyanide solution on undoped GaAs. The severe surface damage (characterized by craters and possibly voids) observed at high energy densities (Fig. 6A, 6B) is probably the consequence of surface melting and fast cooling, as suggested in the proposed mechanism. Reduction of the energy to the 0.1 joule/cm^2 level resulted in deposition with minimum surface damage (Fig. 6C). The cross-sections (example in Fig. 7) showed that the thickness was of the order of several micrometers. Similar results were also observed for the doped substrate variants.

-Polyimide Substrate. The general surface morphology, structure and cross sections of the deposits obtained from potassium gold cyanide and acid gold chloride are shown in Figs. 8-9 and 10-11, respectively . Irradiated zones were characterized by clusters of bubble-shaped craters about 10 μm in diameter with localized high concentrations of gold deposit (Figs. 8, 10).

The density of these clusters increased with the energy density, as did the general roughness of the irradiated surface (Fig. 8). At lower energy densities the clusters thinned out considerably (Figs. 8C and 10C). Deposit thickness was again of the order of several micrometers (Figs. 9, 11). It should be noted that in the case of acid gold chloride some of the deposit was revealed immediately below the substrate surface (Fig. 11).

As regards the palladium-nickel variant, a typical irradiated area is shown in Fig. 12, with the deposit clearly visible in the bright zones of the photomicrograph (Figs. 12B).

AES AND ESCA

- Si and GaAs Substrates. For the silicon substrate, AES surface analysis and depth profiles established continuous presence of pure elemental gold throughout the deposit thickness at the irradiated zones, together with silicon and oxygen (Fig. 13) indicating intermixing of the deposit with silicon and silicon oxide.

For the GaAs substrate, Fig.14A shows uniformly distributed pure elemental gold. Fig. 14B shows the AES depth profile at the interface between deposit and substrate; here gold concentration was found to decrease continuously, while those of gallium and arsenic increased, and the gold was also found to diffuse into the substrate.

A typical ESCA profile (Fig. 15) confirms the presence of pure elemental gold.

These findings support the proposed mechanism of Fig. 1. They indicate cathodic reactions, in which electrons photogenerated at the irradiated zones were taken up by gold complex ions to give a pure elemental gold deposit.

- Polyimide Substrate. Typical ESCA examinations are shown in Figs. 16 and 17 for potassium gold cyanide and for acid gold chloride respectively, and again indicate presence of pure elemental gold (the spectrum in Fig. 16 was obtained from the irradiated zones shown in Fig. 8B). These findings support the proposed mechanism described earlier for the polymeric substrate, namely uptake of photogenerated electrons by gold complex ions to give gold metal deposits.

ESCA plots of an as-received polyimide substrate and of a laser-treated one in deionized water are shown in Fig. 18. The effect of the treatment is seen to consist in disappearance of the imide carbonyl group (carbon spectrum, Fig. 18A) and appearance of an amide group (nitrogen spectrum, Fig. 18B), while the oxygen spectrum remained unchanged (Fig. 18C). This transformation of the imide into amide groups yielded free electrons which were subsequently taken up by complex metal ions, as suggested in the proposed mechanism.

TRANSMISSION ELECTRON MICROSCOPY

- Laser Gold Deposition , N-Type Silicon Substrate. Typical TEM photomicrographs of gold deposited on N-type silicon from potassium gold cyanide are shown in Fig. 19. The deposit structure was characterized by small grains around 250 Å in size as seen in the bright field image (Fig. 19A). The dark field image of the same deposit (Fig. 19B) revealed presence of polycrystalline gold ranging from less than 100 Å to several hundreds of angstroms in size. Furthermore, the deposit was again found to consist of pure elemental gold as indicated by the electron diffraction image (Fig. 19C) and its interpretation in Table 1, the latter showing that the pure gold deposit was probably intermixed with silicon.

TABLE 1: Electron Diffraction of Gold Laser Plating on N-Type Silicon

D[Å] Measured and calculated	D[Å] ASTM 4-0784	Identification compound ASTM	HKL	Intensity
3.139	3.138	Si (polycrystal)	(111)	Strong
2.377	2.355	Au	(111)	Very strong
2.045	2.039	Au	(200)	Medium
1.927	1.920	Si (polycrystal)	(220)	Weak
1.468	1.442	Au	(220)	Medium
1.248	1.230	Au	(311)	Medium

- Palladium-Nickel Deposition on P-Type Silicon Substrate

Conventional TEM specimens were prepared from the Pd-Ni deposit by chemical thinning from the backside of the samples. Typical selected area electron diffraction patterns taken from various zones of the Pd-Ni deposit are shown in Fig. 20. These images consisted of spots (corresponding to silicon single crystals) and rings (corresponding to polycrystallites such as oxides and silicides).

Tables 2 and 3 show the different possibilities for indexing the diffraction rings shown in Fig. 20 A and B (representing two deposit zones) and for possible identification of the various compounds. Figure 20 A indicates formation of nickel silicides together with silicon oxide or possibly with silicon polycrystals (Table 2). Figure 20 B indicates primarily presence of palladium silicides, possibly with some silicon oxide (Table 3). These findings provide further important evidence for the suggested mechanism.

Formation of the silicides is associated with surface melting followed by liquid phase solidification according to the second and third stages of the proposed mechanism (Figs. 1 B and C).

TABLE 2: Electron Diffraction of Palladium-Nickel Laser Plating on Silicon. Zone A.

D[Å] Measured	D [Å] ASTM	Compound ASTM	HKL	I/I_1 (Bulk)
	3.138	Si (polycrystal)	111	100
	3.138	SiO_2 [4.0379]	111	12
3.132	3.13	$NiSi_2$ (Zeta)	220,204	80
	3.121	$NiSi_2$** (FCC)	111	-
	1.920	Si (polycrystal)	220	60
	1.932	SiO_2 [4-0379]	113	4
	1.9217	NiSi*	202	-
1.9201	1.918	PdSi [7-127]	310	60
	1.911	$NiSi_2$** (FCC)	220	-
	1.900	$NiSi_2$ (Zeta)	512,504	100
1.8026	1.80	Pd_2Si (Palladium Silicon [6-0559])	121	30
Not sharp	1.815	Pd_2Si (Palladium Silicide [19-8921])	248	50
Defined	1.8118	Ni_2Si***	201	-

TABLE 2 (Cont'd)

D [Å] Measured	D [Å]	Compound ASTM	HKL	I/I_1 (Bulk)
1.6431	1.638	Si (polycrystal)	311	35
	1.642	SiO_2 [4-0379]	104	1
	1.64	$NiSi_2$ (Zeta)	327	50
	1.63	$NiSi_2$** (FCC)	311	-
1.2528	1.246	Si (polycrystal)	331	13
	1.246	Ni (polycrystal)	220	21
	1.25	$NiSi_2$ (Zeta)	641	60
	1.25	Ni_2Si***	040	-
	1.2582	NiSi*		-

* NiSi orthorhombic A = 5.238 A° B = 3.24 A° C = 5.657 A° H. Foll - Phil. Mag. 45, No.1, 1982.

** $NiSi_2$ cubic A = 5.406 A F. Mohammadi - Solid State Technol., January 1981, p. 65.

*** Ni_2Si orthorhombic H. Foll - Phil. Mag. 45, No.1, 1982.

TABLE 3: Electron Diffraction of Palladium-Nickel Laser Plating on Silicon. Zone B.

D[Å] Measured	D [Å] ASTM	Compound ASTM	HKL	I/I_1 (Bulk)
2.0790	2.07	SiO_2 [4-0359]	222	30
	2.067	PdSi Palladium Silicon	220	60
	2.082	Pd_2Si Palladium Silicide	3011	20
1.479	1.460	SiO_2 [4-0359]	422	50
	1.474	Pd_2Si Palladium Silicide	443	40
1.214	1.21	[4-0359]	531	30
	1.213	Pd_2Si Palladium Silicide	648	90
	1.20	PdSi Palladium Silicon	510	30

- Gold Deposition on GaAs Substrate

The typical structure of gold deposition shown in Fig. 21 was characterized by small crystalline grains around 250 Å in size (Fig. 21 A). The dark-field picture of the same zone again revealed the presence of polycrystalline gold (bright spots in Fig. 21 B) ranging from less than 100 Å to several hundreds of angstroms. A typical selected area electron diffraction pattern (Fig. 21 C) consisted of single spots (indicative of GaAs single crystals) as well as of complete rings (indicating presence of pure polycrystalline elemental gold in the substrate). The electron diffraction was identified as corresponding to metallic gold according to ASTM card No. 4-0784 (Table 4): very good agreement was found between the measured and calculated D values and those characterizing pure standard gold.

TABLE 4: Electron Diffraction of Gold Laser Plating on Undoped GaAs

D[Å] Measured and calculated	D[Å] ASTM 4-0784 Gold	HKL
2.04	2.039	200
1.44	1.442	222
1.22	1.230	311
1.17	1.177	222
1.02	1.019	400
0.93	0.935	331
0.91	0.912	420

X-RAY DIFFRACTION

A typical x-ray diffraction spectrum of gold deposition on GaAs is shown in Fig. 22. Intensity peaks characteristic of Au (111) and Au (200) indicate pure elemental crystalline gold in the deposit rather than gold compounds or gold salts. For the polymeric substrate, XRD showed presence of elemental gold within the deposit zones (picture not shown). This presence of pure elemental gold on both types of substrate further supports the first stage of proposed mechanism.

RUTHERFORD BACK-SCATTERING

The RBS analyses were carried out with a 3.05 MeV He beam, the energy level being chosen so as to enhance the detection limit for oxygen to about 10^{15} atom/cm^2.

Typical RBS spectra taken from gold deposits on GaAs substrate are shown in Fig. 23. Only gold was detected within the deposit zone (Fig. 23 A), confirming the TEM and x-ray diffraction findings.

The depth profile of gold relative to the GaAs surface is given in Fig. 23 B, the peak representing the deposit/substrate interface. Depth of penetration of the gold was calculated at around 1.0 micrometer, on the basis of a 2.82 MeV level at the interface and a 2.58 MeV at the limit of penetration, the conversion factor being 4.29 nm per KeV.

These findings are in good agreement with the AES depth profile, which indicated a substantial concentration of gold at the substrate GaAs surface and in its matrix below the interface (Fig. 14 B).

The RBS depth profile yielded the diffusion coefficient, D, of gold into the substrate, using Fick's second law. The value thus obtained, of the order of 10^{-5} cm^2/sec (detailed calculation not shown), is in agreement with the diffusion coefficient values of gold, nickel, and palladium in melted or liquid phases of silicon or GaAs substrate. In other words, it could again be deduced (albeit indirectly) that surface heating and possibly melting was associated with the deposition processes, as suggested in the second stage of the proposed mechanism.

ELECTRICAL PROPERTIES OF DEPOSIT

Current-voltage curves for the deposits on the semiconductor substrates were obtained by two-point probe measurements and the calculated linear slopes of these curves yielded the ohmic resistance. Typical I-V curves obtained at the same deposit line for and the dependence of the ohmic resistance of the gold deposit on GaAs on laser energy density are given in Fig. 24. The resistance decreased with increasing energy density, namely with increasing gold deposition.

In order to determine the mode of contact resistance between deposit and substrate, the probes were applied [5] so that one touched the deposition area and the other unirradiated part of the substrate surface. Figures 25 and 26 show current-voltage curves characteristic of Schottky-contact behavior of the gold deposit on n-type silicon and n-type GaAs, respectively. The same behavior was also observed in Pd-Ni deposition on silicon.

CONCLUDING REMARKS

A. It was demonstrated that a metal (gold) and a metal alloy (Pd-Ni) can be deposited on semiconductor and polymeric substrates directly from commercial electroplating solutions via pulsed laser irradiation.

B. High-rate high-selective gold and palladium-nickel deposition was carried out in a single step without masking, without recourse to an external electric current and without any surface pre-treatment of either of the

substrate types.

C. The process consisted in photoelectrochemical deposition followed by diffusion of metal atoms into the substrate, possibly through a molten surface layer which subsequently solidified to give intermix compounds such as silicides.

D. Gold and Pd-Ni deposits showed Schottky contact behavior on N-type silicon and N-type GaAs substrates.

REFERENCES

1. J.C. Puippe, R.E. Acosta and R.J. von Gutfeld, Investigation of Laser-Enhanced Electroplating Mechanisms, J. Electrochem. Soc. 128, 12, pp. 2539-2545.
2. R.F. Karlicek and V.M. Donnelly, Laser Induced Metal Deposition on InP, J. Appl. Phys. 53 (2), pp. 1084-1090 (1982).
3. Y.C. Kiang, J.R. Moulic and J. Zahavi, Metal Silicide Formed by Laser Irradiation of Silicon Chip in Plating Solution, IBM Technical Disclosure Bulletin, Vol. 26, No. 1, p. 327 (June 1983).
4. J. Zahavi and S. Tamir, Laser Induced Deposits on Non-Metallic Substrate - Gold Deposit on Silicon, Annual Technical Report No. 504533, Israel Institute of Metals, Technion, Haifa, Israel (October 1984).
5. J. Zahavi and S. Tamir, Laser Induced Gold Plating on Non-Metallic Silicon Substrate, Proceedings of Noble Metals Fabrication and Technology International Seminar, Jerusalem, Israel, April 27 - May 5, 1985. The Seminar was organized by the IPMI, International Precious Metal Institute, Government Building, ABE Airport, Allentown, Pennsylvania 18103, U.S.A.
6. J. Zahavi and M. Halliwell, Laser Beam Inducing Selective Plating Process on GaAs Semiconductor Substrates, in Proceedings of Interfinish 1984, 11th World Congress on Metal Finishing, Jerusalem, Israel, p.p. 173-177, October 21-26 (1984). Published by International Ltd. 10 Rothschild Blvd. 65121, Tel-Aviv, Israel.
7. J. Zahavi and S. Tamir, Laser Beam Technology Promoting High Speed and Selective Plating Processes, AFWAL-TR-83-4113 Wright Patterson Air Force Base, Ohio 45431, U.S.A. (Sept. 1983).
8. J. Zahavi, S. Tamir and M. Halliwell, Laser Gold Deposition on Polyimide, Abstract in Proceedings of Interfinish 84 , 11th World Congress on Metal Finishing, Jerusalem, Israel, p. 497 (October 21-26, 1984). Published by International Ltd. 10 Rothschild Blvd. 65121, Tel-Aviv, Israel. Also J. Zahavi and S. Tamir, unpublished work.
9. R.H. Micheels, A.D. Darrow and R.D. Rauh, Photoelectrochemical Deposition of Microscopic Metal Film Patterns of Si and GaAs, Appl. Phys. Lett. Vol. 39, No. 5, pp. 418-420 (Sept. 1981).
10. F.W. Ostermayer, Jr. and P.A. Kohl, Photoelectrochemical Etching of p-GaAs, Appl. Phys. Lett. Vol. 39, No. 1, pp. 76-78 (1981).
11. O. Aina, S.W. Chiang, Y.S. Liu and F. Bacon, Microstructure and Resistivity of Laser-Annealed Au-Ge Ohmic Contacts on GaAs, J. Electrochem. Society, Vol. 128, No. 10, pp. 2183-2187 (1981).
12. M. von Allmen, Dynamics of Laser-Induced Formation of Palladium Silicide, Appl. Phys. Lett. 34, 1, pp. 68-70 (1979).

13. N. Bloembergen, Fundamentals of Laser-Solid Interactions, in "Laser-Solid Interactions and Laser Proceedings - 1978", Editors S.D. Ferris, H.J. Leamy and S.M. Poate, American Institute of Physics, N.Y. (1979).
14. P.O. Hahn, G.W. Rubloff and P.S. Ho, J. Vac. Sci. Technol. A 2 (2), April-June (1984), pp. 756-760.

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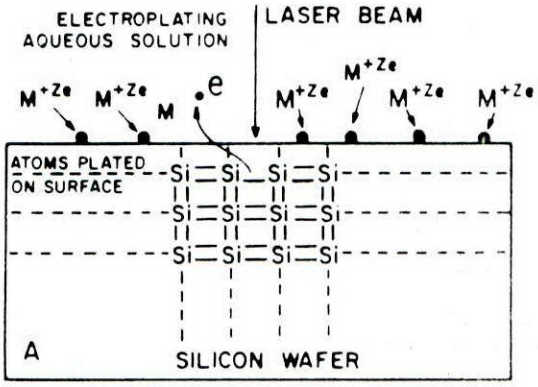
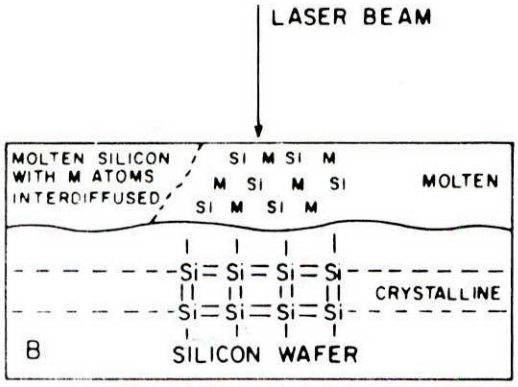
Thanks are due to Dr. R. Brener, Solid State Institute, Technion for conducting ESCA and AES examinations. Also thanks are due to Dr. Z. Bart Dept. of Material Eng. Technion for conducting the TEM examination analyses.

PLATING MECHANISM



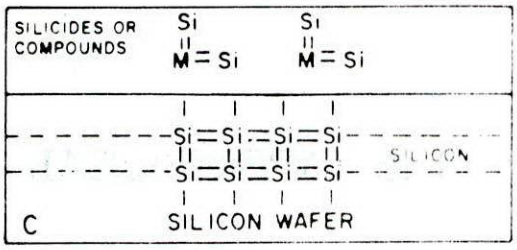
SUPPLYING OF FREE ELECTRONS FROM SILICON THRU PHOTON ABSORPTION

DIFFUSION MECHANISM



SURFACE MELTING AND INTERMIXING OF METAL ATOMS AND SILICON

SILICIDE OR COMPOUND FORMATION



LIQUID PHASE EPITAXIAL REGROWTH

FIG. 1: SCHEMATIC DESCRIPTION OF THREE STAGES PROPOSED MECHANISM FOR LASER INDUCED GOLD PLATING ON SILICON SEMICONDUCTORS

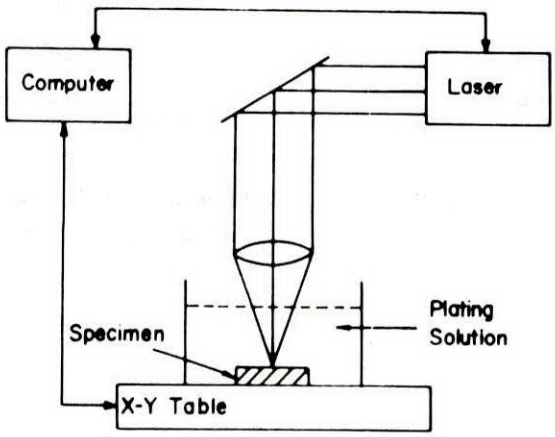


FIG. 2: SCHEMATIC VIEW OF THE EXPERIMENTAL SET-UP

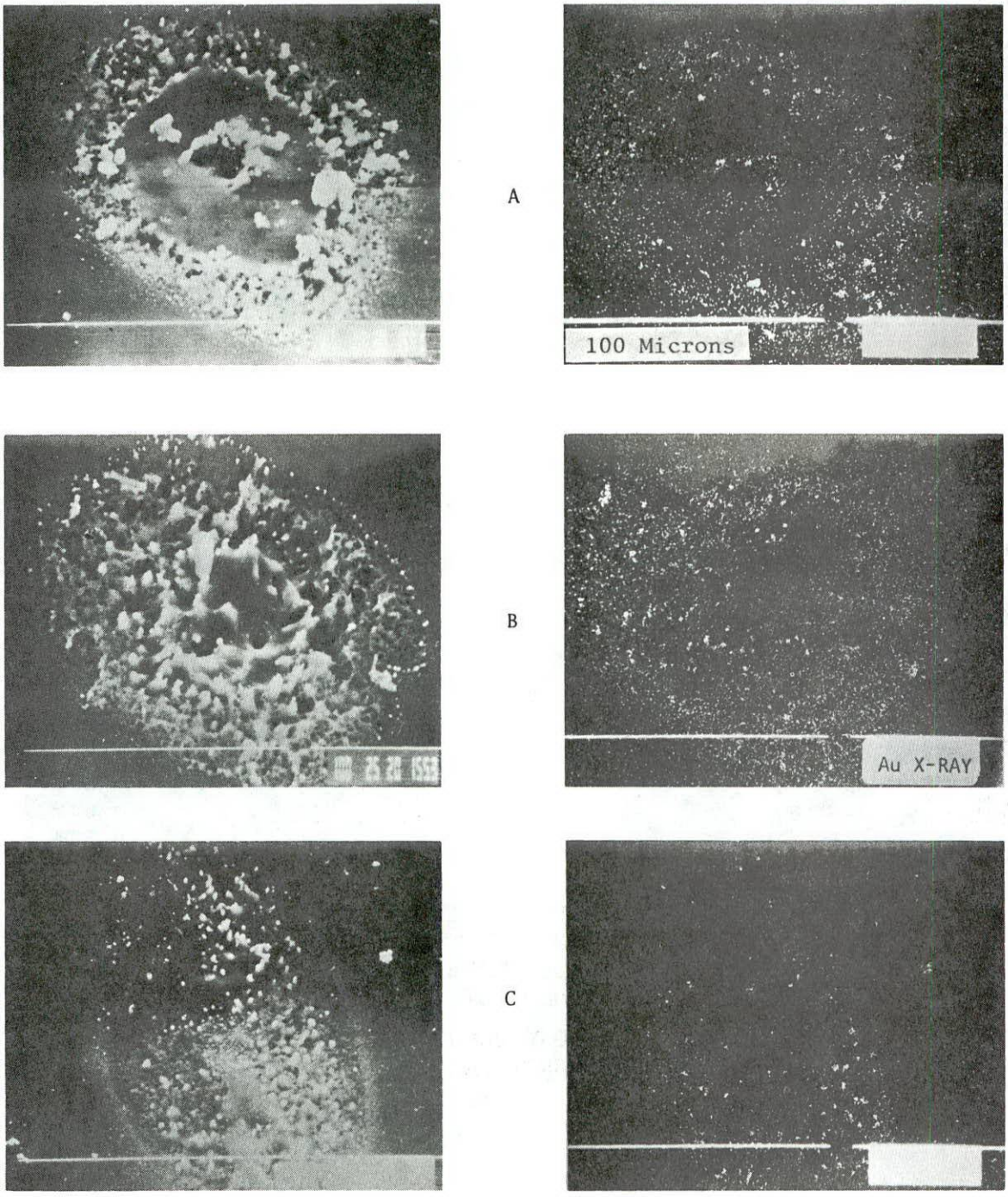
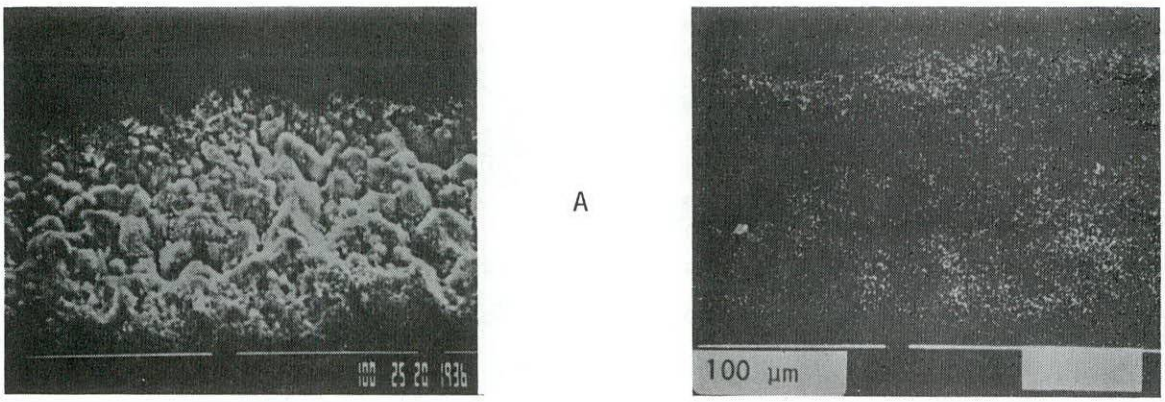


FIG. 3: SEM OBSERVATIONS OF SURFACE MORPHOLOGY AND GOLD X-RAY IMAGES OF LASER IRRADIATED ZONES AT REPETITION RATE OF 2 KH_Z AND VARIOUS TIMES AND PEAK ENERGY DESITIES.

A) 7.04 x 10^6 WATT/CM^2, 10 SEC.
B) 7.04 x 10^6 WATT/CM^2, 20 SEC.
C) 3.4 x 10^6 WATT/CM^2, 20 SEC.



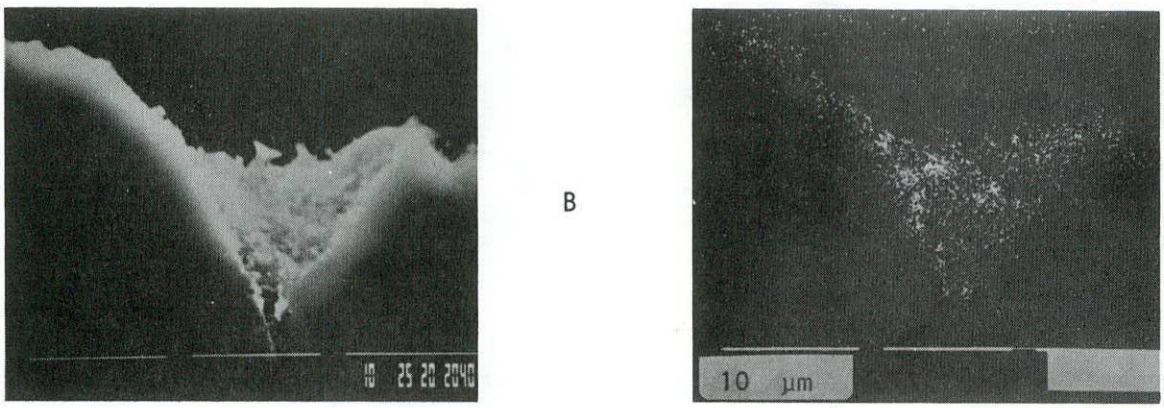


FIG. 4: SEM OBSERVATIONS OF SURFACE MORPHOLOGY AND CROSS SECTIONS OF GOLD DEPOSIT LINE PRODUCED AT LASER IRRADIATED ZONES. LASER PEAK ENERGY DENSITY WAS 6×10^6 WATT/CM^2 AT 1 KH$_Z$ AND INTERACTION TIME OF 20 SEC.

A) SURFACE MORPHOLOGY AND ITS GOLD X-RAY IMAGE.
B) CROSS SECTION MORPHOLOGY AND ITS GOLD X-RAY IMAGE.



A

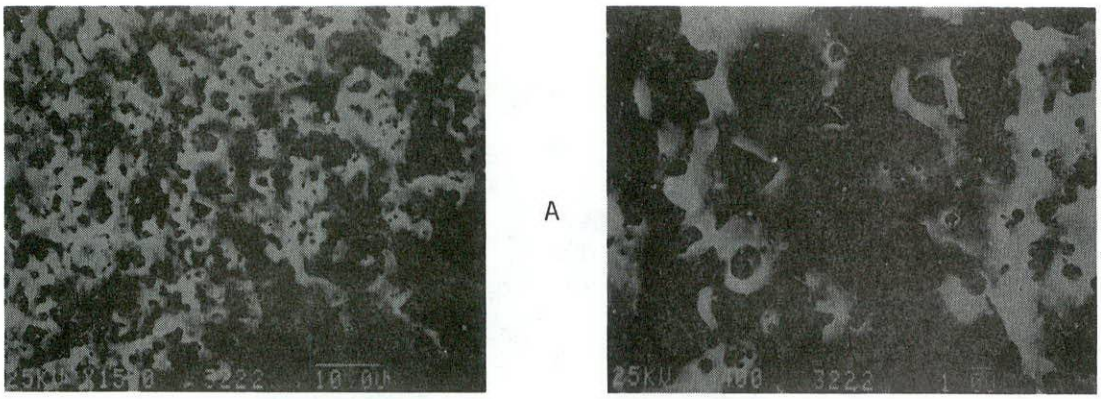


B



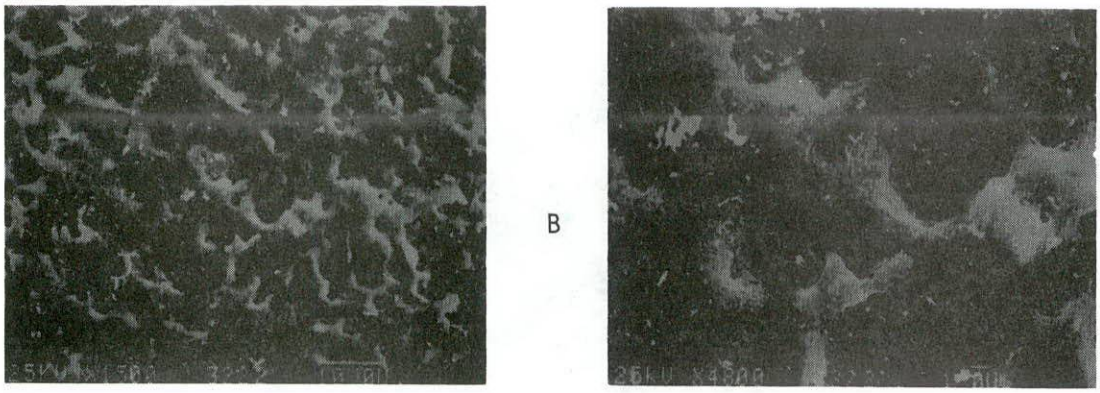
C

Fig. 5: Typical SEM observations of surface morphology of Pd-Ni deposit produced at laser irradiated zones on N-type silicon substrate. Laser beam diameter was 56μm, repetition rate 1Hz, pulse duration 100ms and laser beam wavelength 0.53μm. Laser peak energy densities were: (A) 9.45×10^7 watt/cm^2; (B) 7.65×10^7 watt/cm^2; (C) 5.90×10^7 watt/cm^2.



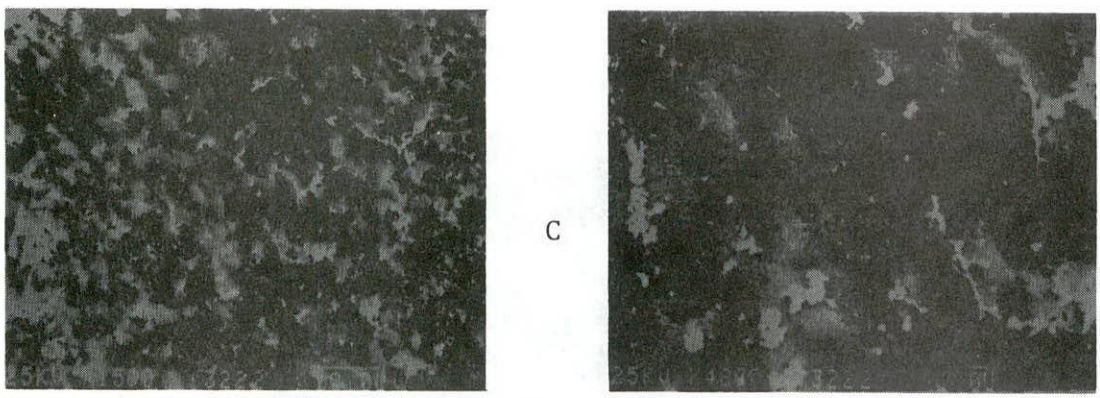
A

0.27 JOULE/cm^2



B

0.16 JOULE/cm^2



C

0.10 JOULE/cm^2

< Fig. 6: Typical SEM observations of surface morphology of gold deposit produced at laser irradiated zones on undoped GaAs (100) substrate immersed in potassium gold cyanide electroplating solution. Laser wave length was 1.06μm, pulse width 15ms, repetition rate 1Hz. Laser peak energy densities were: (A) 0.27 joule/cm^2; (B) 0.16 joule/cm^2; (C) 0.1 joule/cm^2.

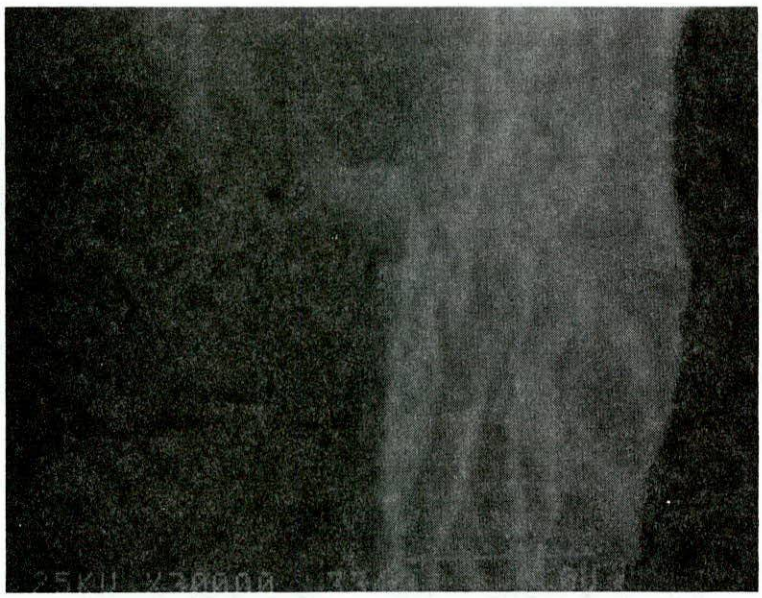


Fig. 7: Typical cross section SEM observation of gold deposit produced via pulse laser irradiation on intrinsic GaAs substrate from potassium gold cyanide electroplating solution. Laser wave length was 1.06μm, repetition rate 1Hz, pulse width 15ms and laser peak energy density 0.15 joule/cm^2.

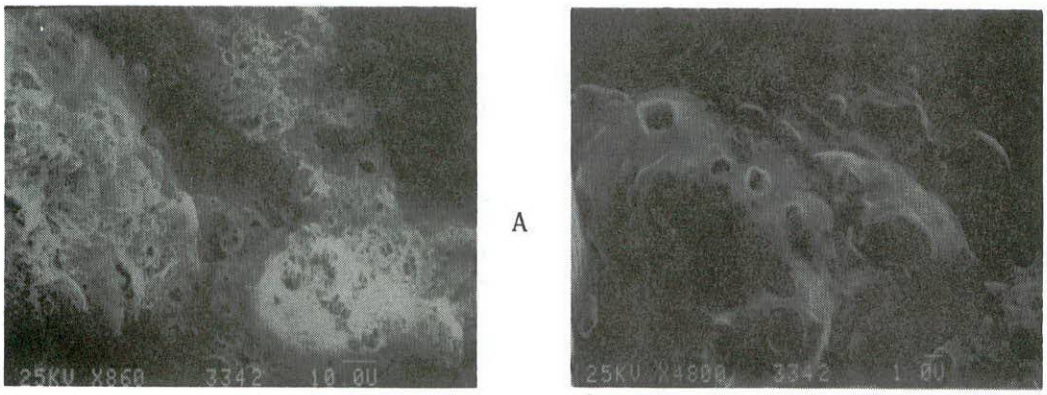


Fig. 8: Typical SEM observations of gold deposit produced via pulse laser irradiation on polyimide substrate from potassium gold cyanide electroplating solution. Laser beam diameter was 0.5mm, wave length 0.53μm, repetition rate 1Hz, at laser peak energy densities 0.39 joule/cm^2, 0.23 joule/cm^2 and 0.15 joule/cm^2 with overlap of 95%.

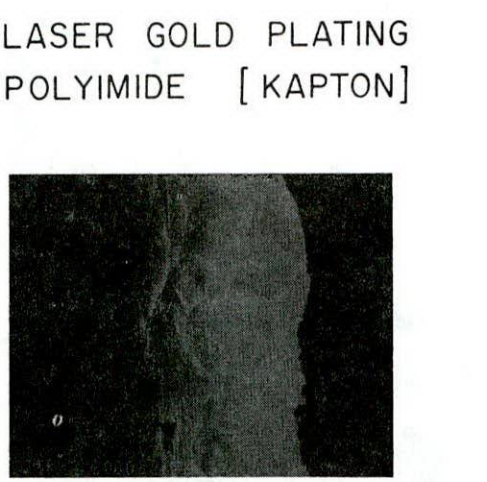
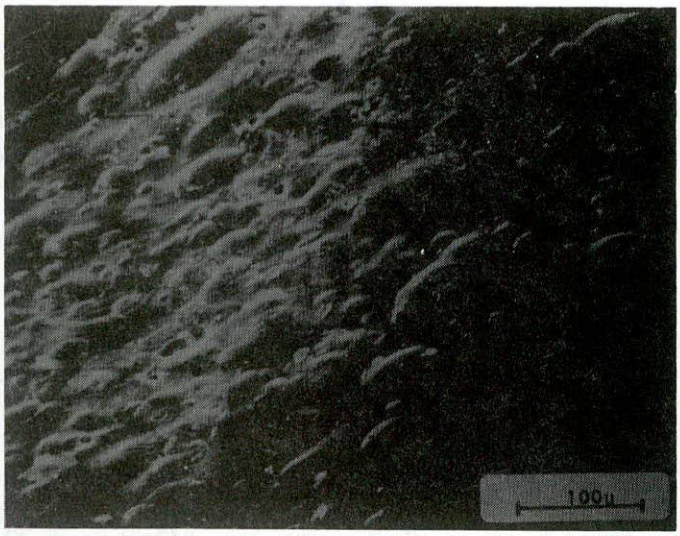


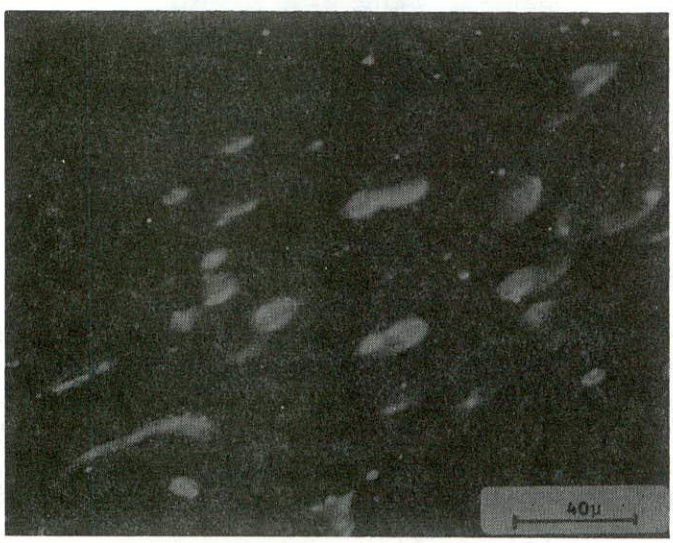
Fig. 9: Typical cross section SEM observation of gold deposit produced via pulse laser irradiation on polyimide substrate from potassium gold cyanide electroplating solution. Laser beam diameter was 0.5mm, wave length 0.53μm, repetition rate 1Hz at laser peak energy density of 0.23 joule/cm^2 with overlap of 95%.



A



B



C

Fig. 10: Typical SEM observations of gold deposit produced on polyimide substrate via pulse laser irradiation from acid gold chloride electroplating solution (20 g/ℓ). Laser repetition rate was 5Hz, interaction time 20 sec, wave length 0.53µm, laser peak energy intensity 2.86×10^8 watt/cm^2.

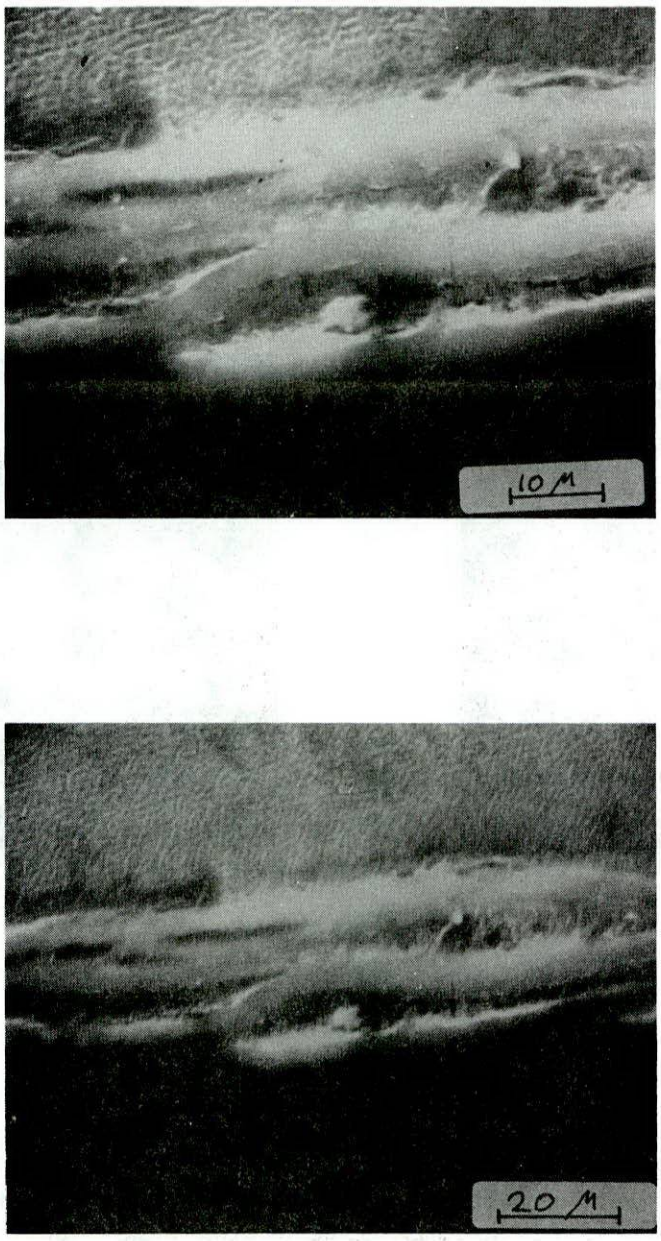
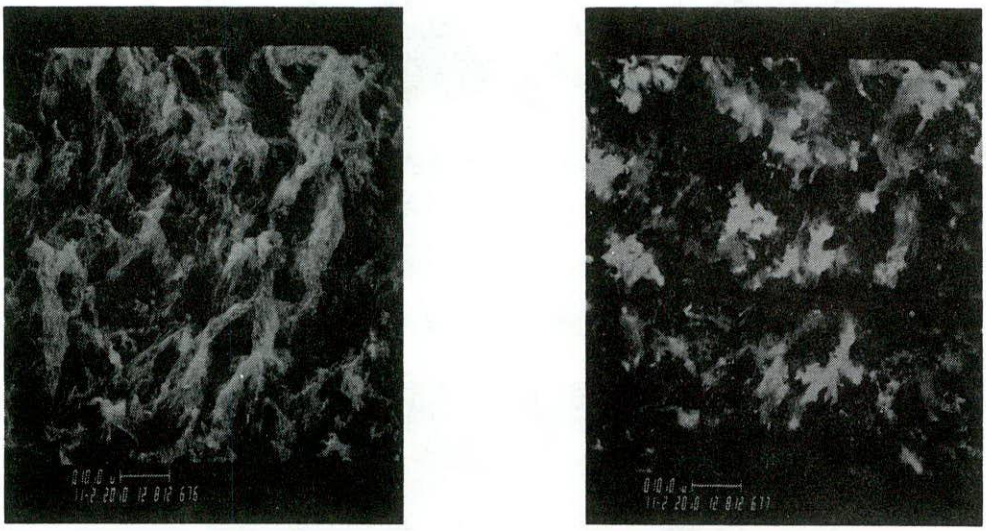


Fig. 11: Typical cross section SEM observations of gold deposit produced via pulse laser irradiation on polyimide substrate from acid gold chloride electroplating solution (20 g/ℓ). Laser repetition rate was 5Hz, interaction time 20 sec, wave length 0.53μm, laser peak energy intensity 2.86×10^8 watt/cm^2



A B

Fig. 12: Typical SEM observation of surface morphology of Pd-Ni deposit produced at laser irradiated zones on polyimide substrate from Pd-Ni alloy electroplating solution. Laser repetition rate was 1Hz, pulse width 15ms, interaction time 5 sec, laser peak energy density 0.27 joule/cm^2.
(A) SEM secondary electron image;
(B) SEM back-scattered image showing presence of Pd-Ni deposit at bright areas.

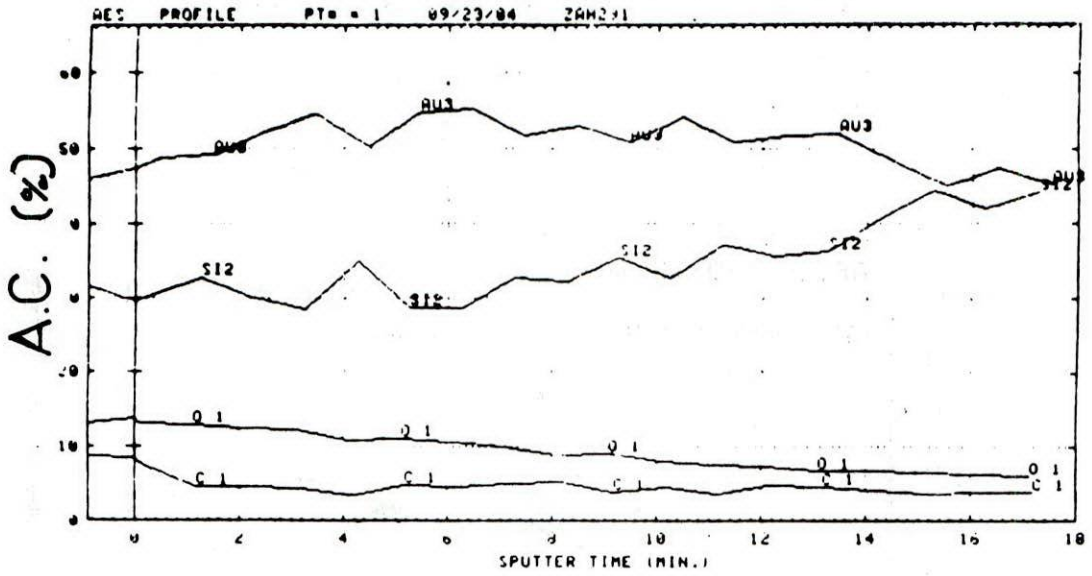
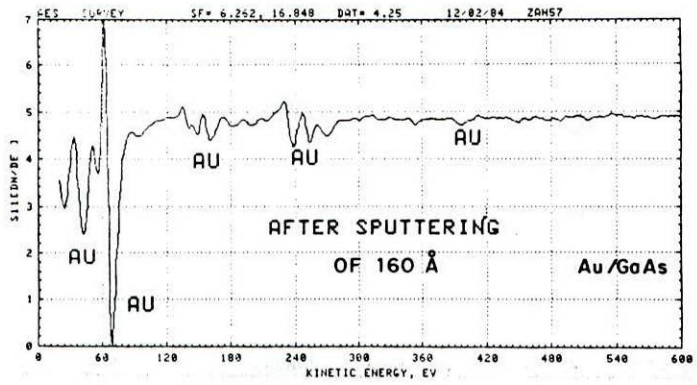
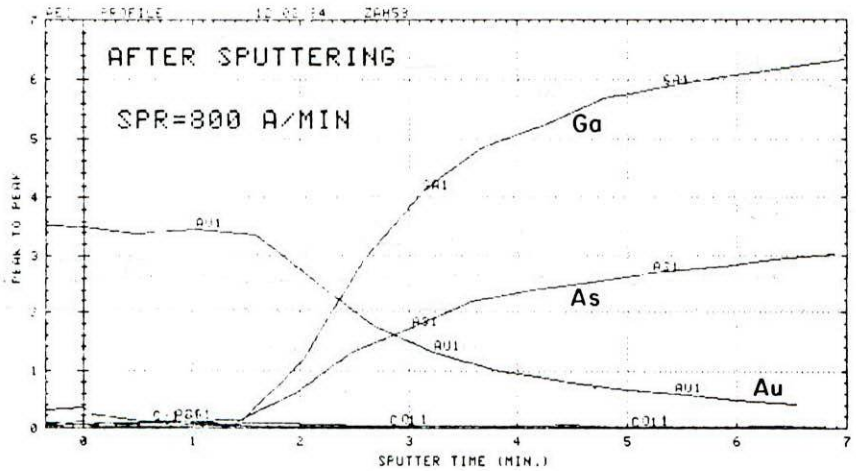


Fig. 13: Typical AES depth profile for distribution of gold, silicon and oxygen at laser gold deposition on silicon substrate from acid gold chloride electroplating solution. Laser repetition rate was 1KHz, interaction time 20 sec, laser peak energy density 3×10^6 watt/cm^2.



A



B

Fig. 14: Typical AES profiles of gold deposit produced via pulse laser irradiation on undoped GaAs from potassium gold cyanide electroplating solution.
(A) Surface profile showing presence of gold after removal of 160A from the as-received surface.
(B) Depth profile at gold/GaAs interface

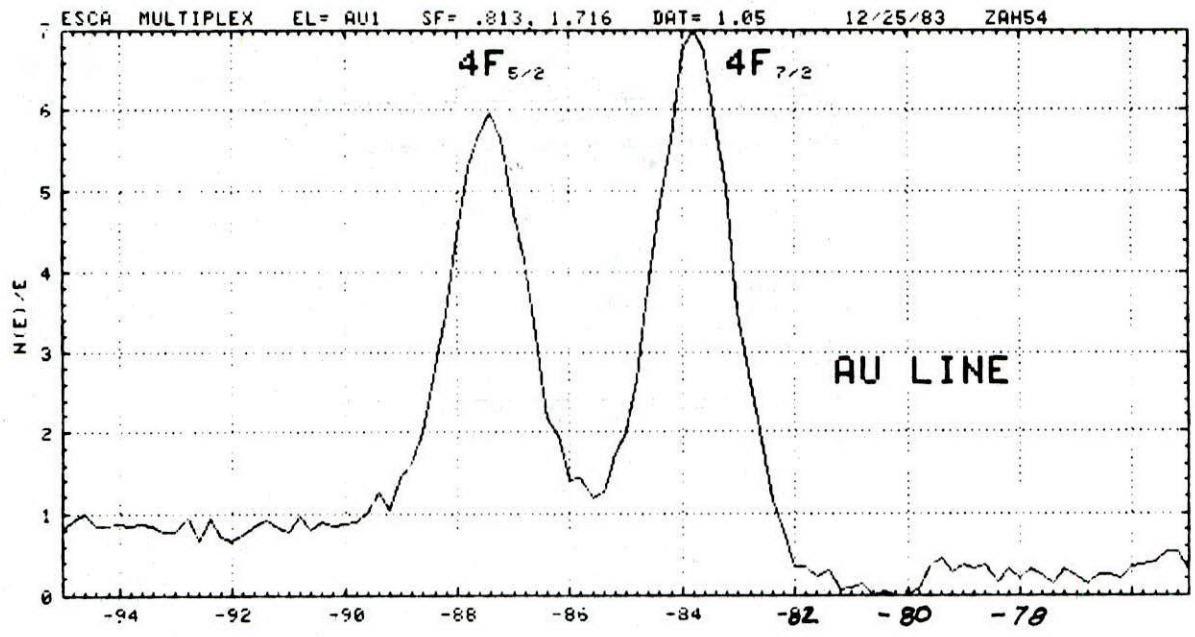


Fig. 15: Typical ESCA profile showing presence of elemental gold in laser-induced deposition from potassium gold cyanide electroplating solution on intrinsic GaAs substrate.

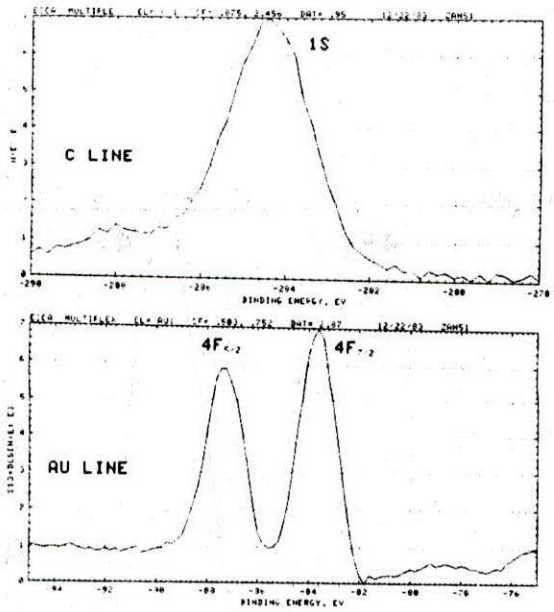


Fig. 16: Typical ESCA profile showing presence of pure elemental gold within gold deposit on polyimide substrate shown in Fig. 8. Deposition was carried out from potassium gold cyanide electroplating solution at repetition rate 1Hz, beam diameter 0.5mm, overlap 95%, wave length of 0.53μm, laser peak energy density 0.23 joule/cm^2.

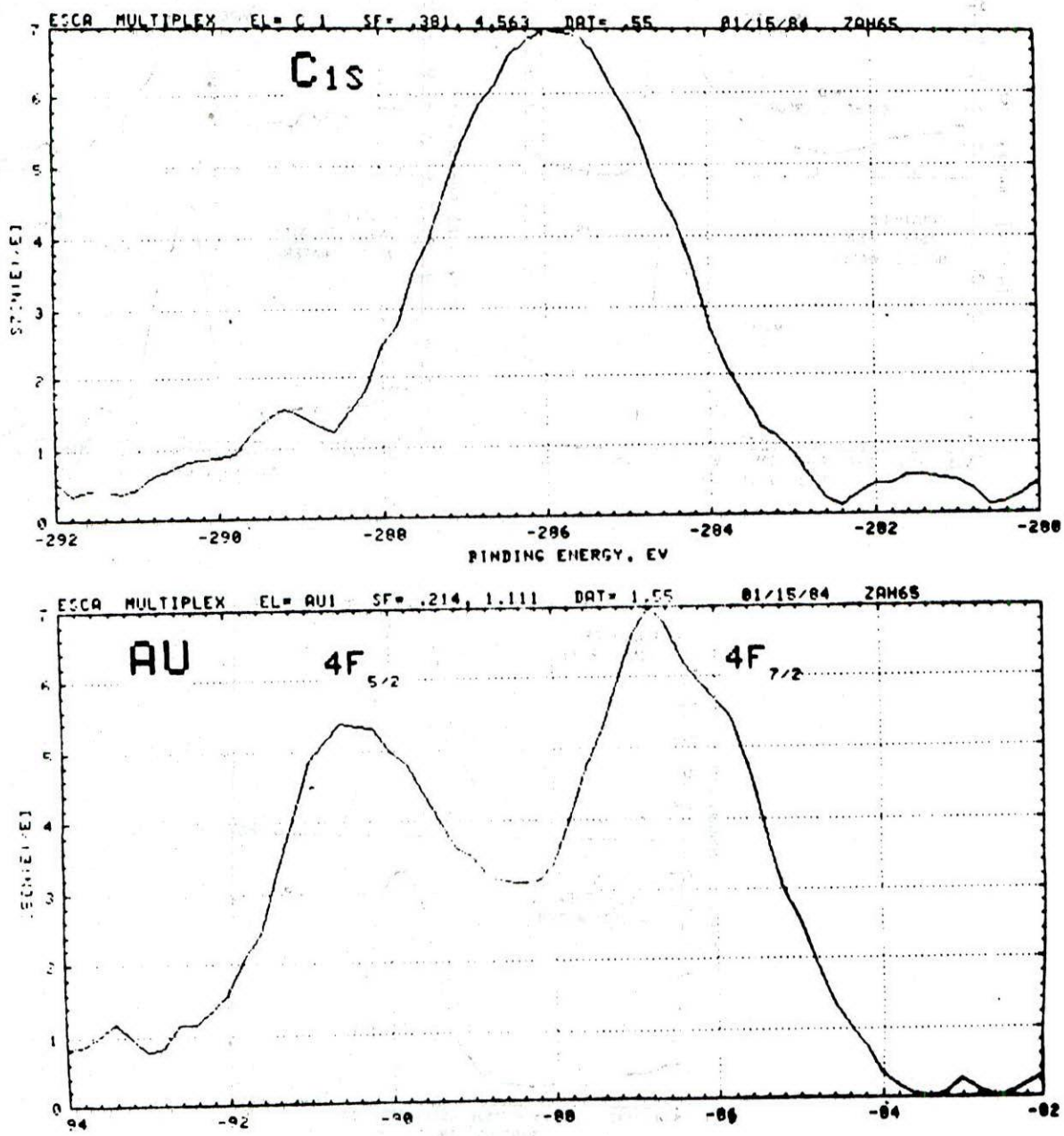


Fig. 17: Typical ESCA profile showing presence of elemental gold within gold deposit on polyimide substrate from acid gold chloride electroplating solution. Laser repetition rate was 2Hz, interaction time 20 sec, peak energy density 3.18×10^8 watt/cm^2.

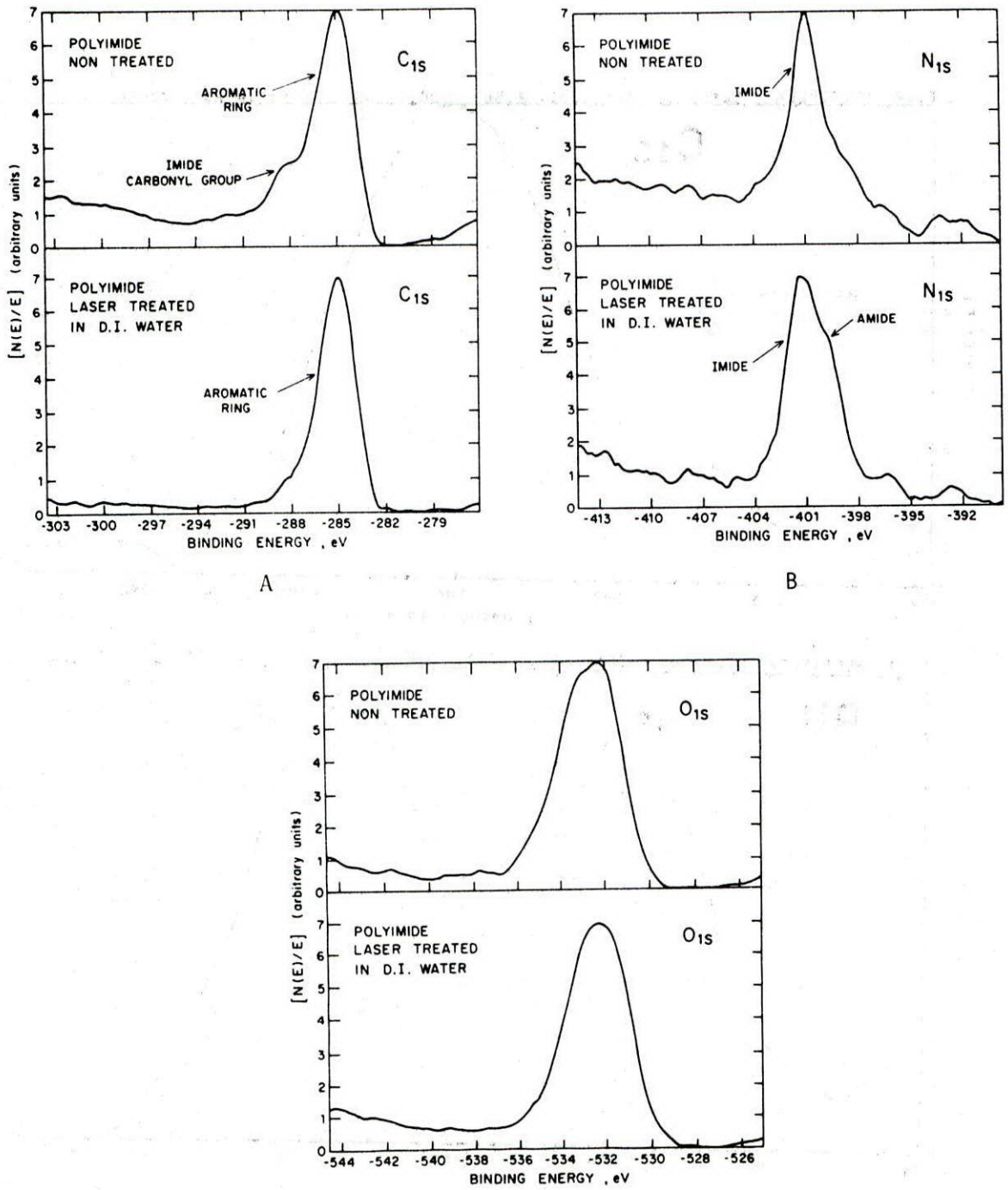
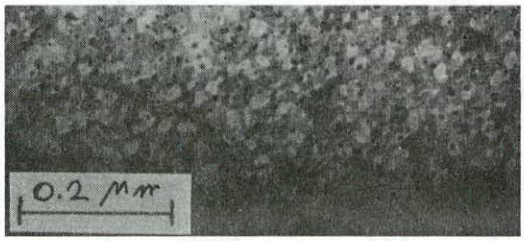


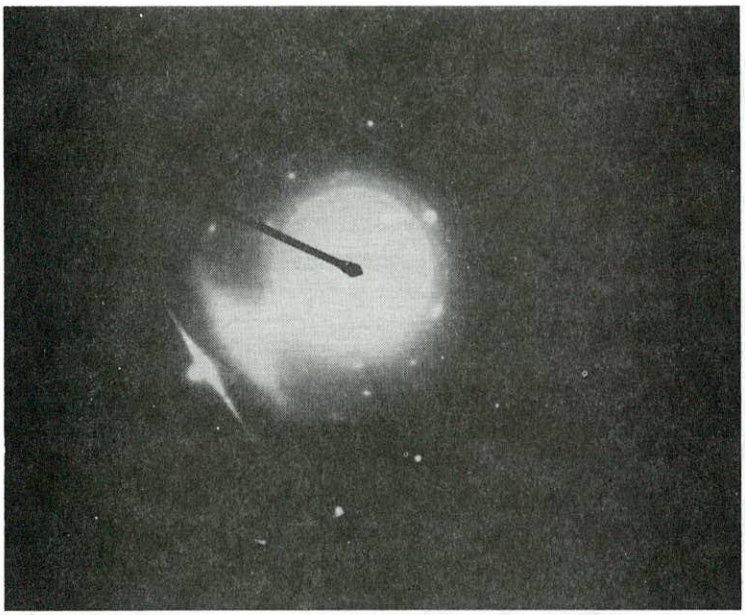
Fig. 18: Typical ESCA profiles of laser irradiated and unirradiated zone on polyimide substrate immersed in deionized water (D.I.).
Laser repetition rate was 5Hz, interaction time 20 sec, peak energy density 2.86×10^8 watt/cm^2
(A) ESCA profile for carbon.
(B) ESCA profile for nitrogen.
(C) ESCA profile for oxygen.



A

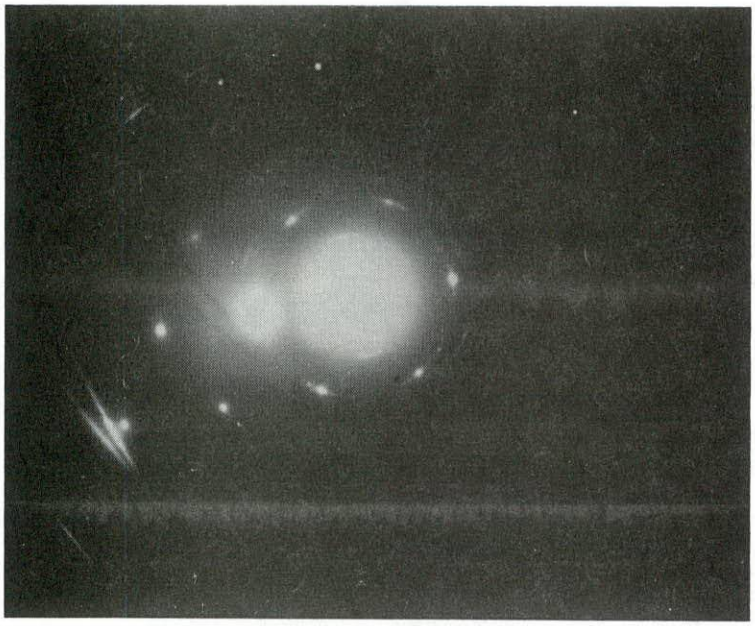


B

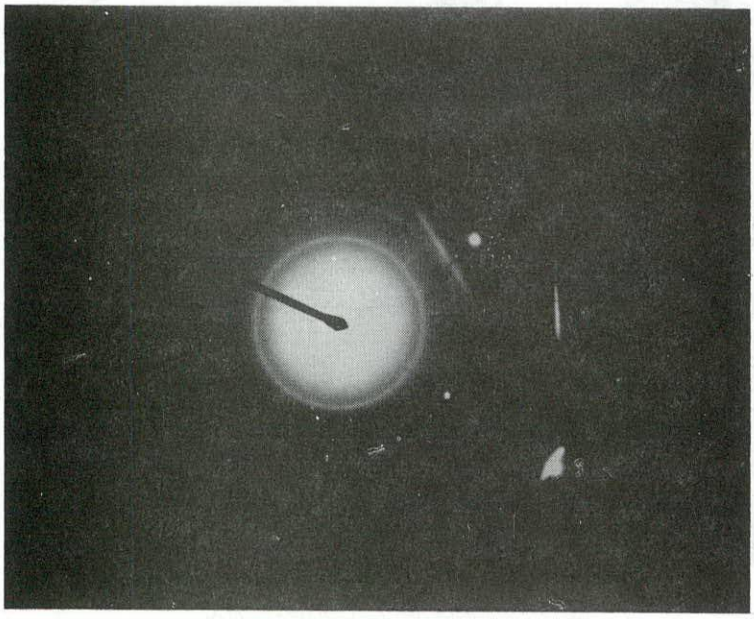


C

Fig. 19: Typical TEM observations of gold deposit produced via pulse laser irradiation on N-type silicon substrate from potassium gold cyanide electroplating solution. Laser wave length was 0.53μm, beam diameter 56μm with overlap of 50%, laser peak energy density 1.0×10^8 watt/cm^2.
(A) Bright field image
(B) Dark field image
(C) Selected area diffraction

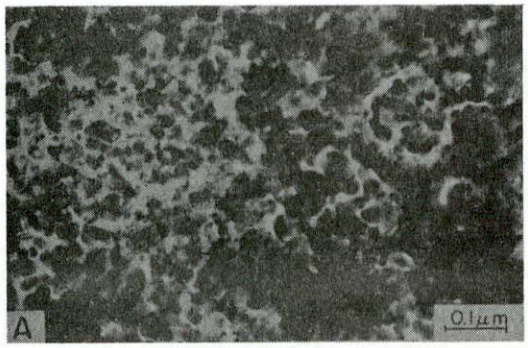


A

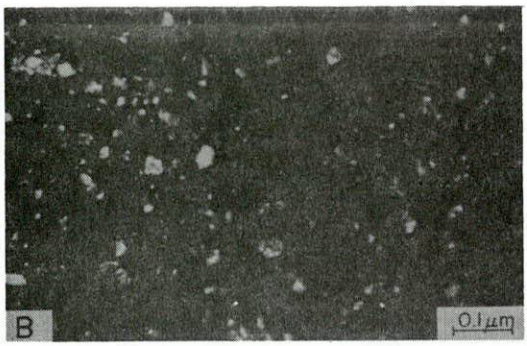


B

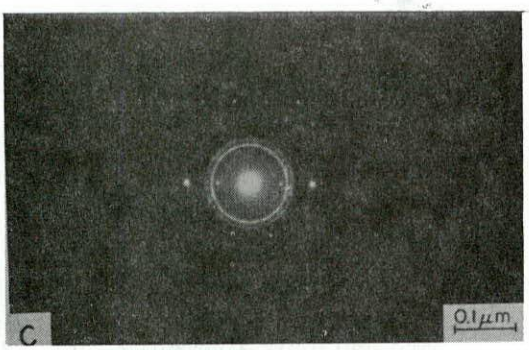
Fig. 20: Typical TEM examination of Pd-Ni deposit produced via pulse laser irradiation on p-type silicon substrate from Pd-Ni alloy electroplating solution. (A) Typical selected area diffraction of zone A. (B) Typical selected area diffraction of zone B.



B.F.



D.F.



E.D.

Fig. 21: Typical TEM observation of gold deposited on undoped GaAs via pulsed laser at 0.53μm and laser energy density of 0.23 joule/cm^2 at pulse width of 15ms.
(A) Bright field.
(B) Dark field.
(C) Selected area diffraction.

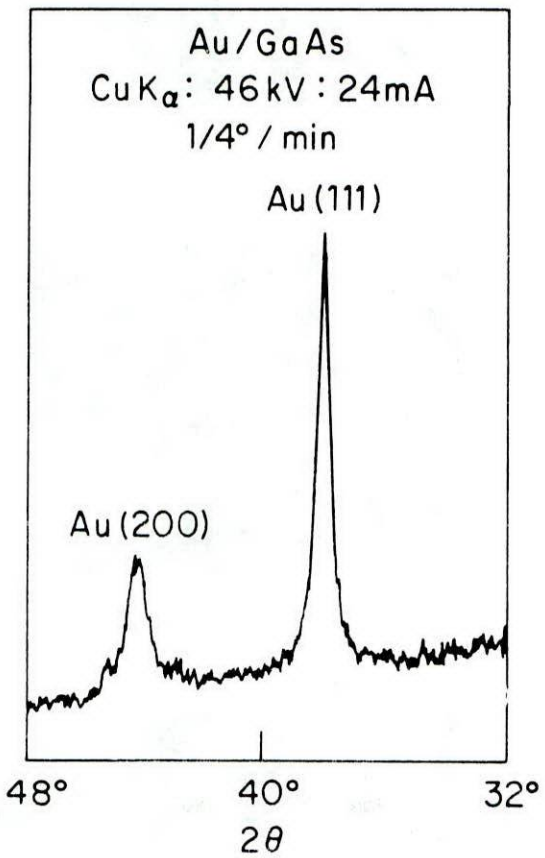


Fig. 22: Typical x-ray diffraction profile showing the presence of elemental gold within gold deposit produced via pulse laser on GaAs from potassium gold cyanide electroplating solution.

O-3

Electronics
Session O

Qualification of Palladium-Nickel Deposits On European Connectors

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Abstract

This paper describes qualification tests and results for three types of connectors; the Eurocard two-part connector (IEC 130-1 and DIN 41612), a male header pin (Philips F095) and a D-Sub rack and panel connector (performance to IEC 512; dimensionally equivalent to MIL C-24308). Hydrogen absorption of palladium-nickel deposits was measured by anodic stripping technique as an incidental to the main work and this is reported also.

Introduction

Many papers published in the last five years have reported favorable results for palladium and palladium-nickel deposits in connector applications. (1,2,3,4)

In summary, these papers have indicated that certain palladium-nickel electrodeposits, particularly when gold overflashed, are equivalent, or better, in meeting service requirements than hard gold deposits. When electrolyte chemistry is such that lamellar deposits (figure 1) are obtained, corrosion resistance (figure 2) and wear resistance (5) are much enhanced. Contact resistance, both as deposited and after ageing, is dependent on alloy composition (figure 3). Deposits containing over 78% of palladium satisfy requirements after ageing

and a reliable elelctrolyte system must be employed to ensure consistent deposit character (6).

Engineers and scientist evaluating this palladium-nickel system have been surprised at the excellent ductility of the deposit and relatively high elongation without cracking which is possible. Pure palladium systems are frequently troubled by hydrogen inclusion in the deposit which leads to stress cracking. This difference in behavior between palladium and palladium-nickel prompted the following experimental work.

Hydrogen Absorption

At 20°C the solubility of hydrogen in palladium is 67 atomic percent. The phases of palladium hydride are well documented. The alpha phase occurs with up to 3 atomic percent hydrogen present and the beta phase exists at between 3 and 67 atomic percent hydrogen. Since there is a 4 percent difference in the lattice constant (the beta phase having the larger lattice constant), an increase in internal stress and crack formation occurs when the beta phase reverts to the alpha phase on standing. Pure palladium, both palladium hydrides and palladium-nickel are all face-center cubic structures.

The hydrogen contents of these palladium-nickel deposits were measured by the anodic stripping method described by Raub. Palladium-nickel was deposited on a glassy carbon electrode at various current densities. The probe was washed and transferred quickly to a IM NaOH solution, polarised to 0.0V versus Ag/AgCl and the anodic current for the oxidation:

$$H_2 \longrightarrow 2H^+ + 2e$$

was recorded with time. The current was integrated graphically and the amount of hydrogen calculated from Faraday's law. Since hydrogen seems to be lost fairly quickly after the deposition, the time delay

Conclusions

Once again palladium-nickel electrodeposits produced from a controlled electrolyte system, when overflashed with gold have proved to be "as good as gold".

- Evidence has been provided which explains the remarkable ductility of these deposits. The absence of the threat of beta phase palladium hydride formation removes a major processing difficulty experienced with many pure palladium processes.

References

1. M.J. Pike - Biegunski, R. Bazzone; Proc. of AES symposium on Economic Use of and Substitution for Gold, Danvers 1980.

2. I.S. Wright; Proc. of Connectors "81", I.M.F., Leicester, England

3. A. Graham, S. Updegraff, M.J. Pike - Biegunski; Proc. of AES 2nd Symposium on Economic Use of and Substitution for Gold, Danvers 1982.

4. J.A. Abys, Ibid

5. P. Wilkinson, Proc. of Connectors "81", I.M.F., Leicester, England

6. A. Blair, Proc. of IPMI Tech. Conf., Newport Beach, 1982.

7. Hedwich H.D., Raub Ch. J., Metalloberflache 31, 1977, II.

8. Bowden F.P., Tabor D., "The Friction and Lubrication of Solids" Part I, pp 111-117, Oxford Univ. Press.

TABLE 2

Some Requirements for Professional Connectors

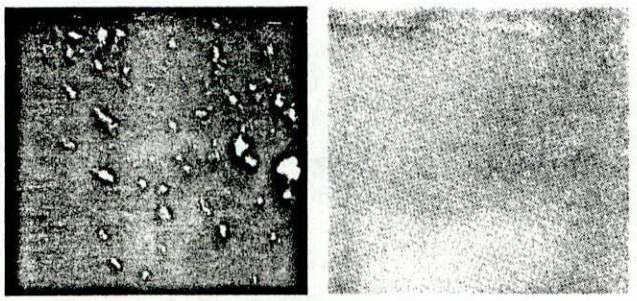
Connector Type		Insertions	Vibration	Damp Heat	Dry Heat	Corrosion
Eurocard F068	K12	400	5g 6h	40°C 90-95% RH 56 days	1000 hrs 125°C	damp-heat 2 cycles 10ppm SO_2 10ppm H_2S
	K11	500	20g 6h			
Male Headers F095		300	10g 6h	40°C 90-95% RH 21 days	500 hrs 125°C	5% NaCl 96 hrs
D-Sub F161		500	10g 6h	40°C 90-95% RH 21 days		damp-heat 2 cycles

TABLE 1

Anodic Stripping of H_2 from Electrodeposited Palladium - Nickel

Run No.	Pd deposition current Electrode: 0,2 cm^2 glassy carbon Charge passed: 600 mA	Average of Integrated anodic H_2 oxidation currents at 0V (Ag/Ag Cl)	Atomic % H_2 in Pd
1 - 2	10 mA	1,16 mQ	0,19
3 - 7	20 mA	3,53 mQ	0,59
7 - 9	40 mA	6,73 mQ	1,12
10 - 11	5 mA	0,33 mQ	0,055

FIGURE 2



Pd-Ni (80/20) deposits after immersion in 50 percent nitric acid for 30 sec at 20° C. Photo at left shows results of traditional brightener system; photo at right shows results of modified brightener system.

FIGURE 3

The Effect of Palladium Content of the Deposit on the Contact Resistance Before and After Ageing

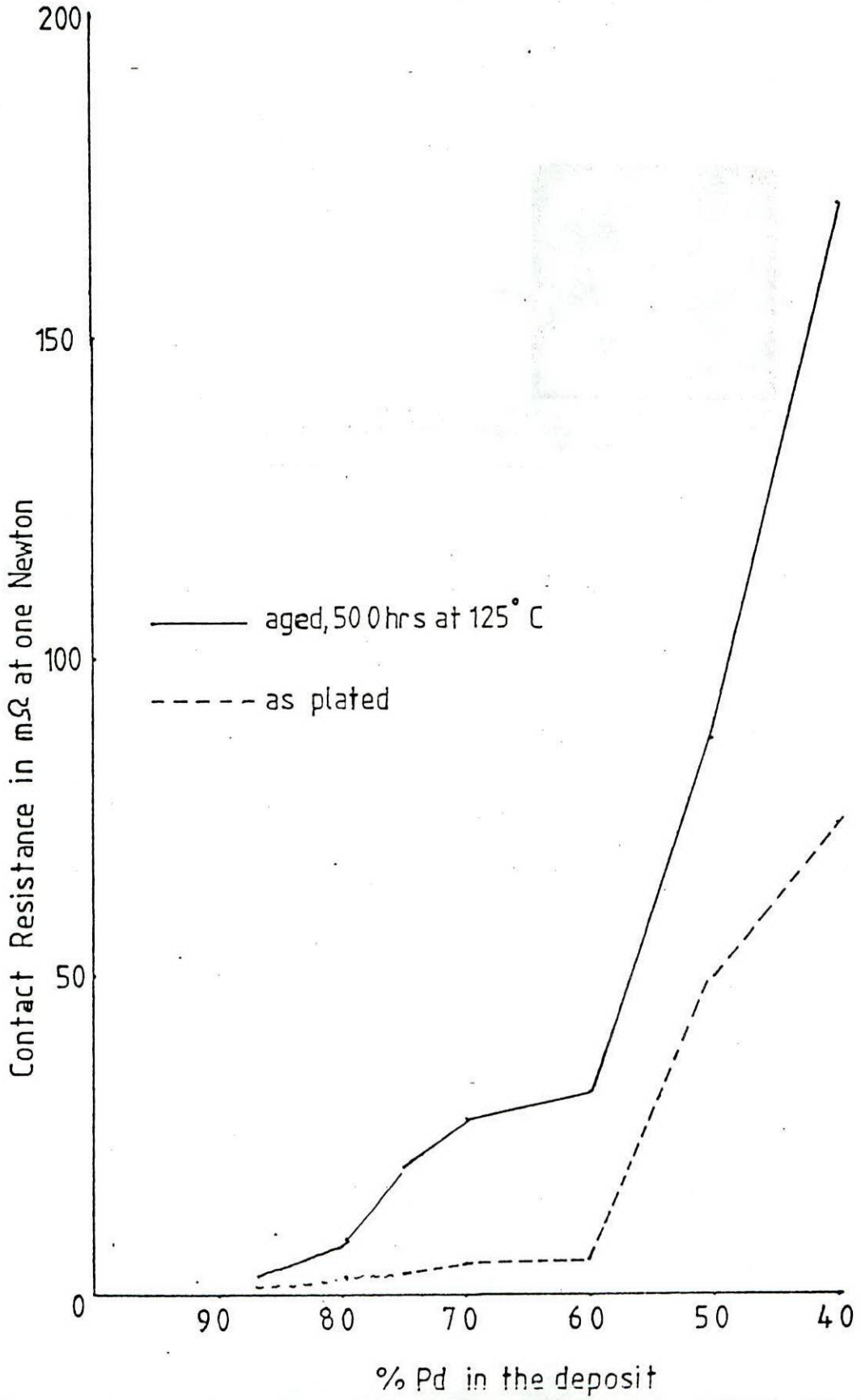
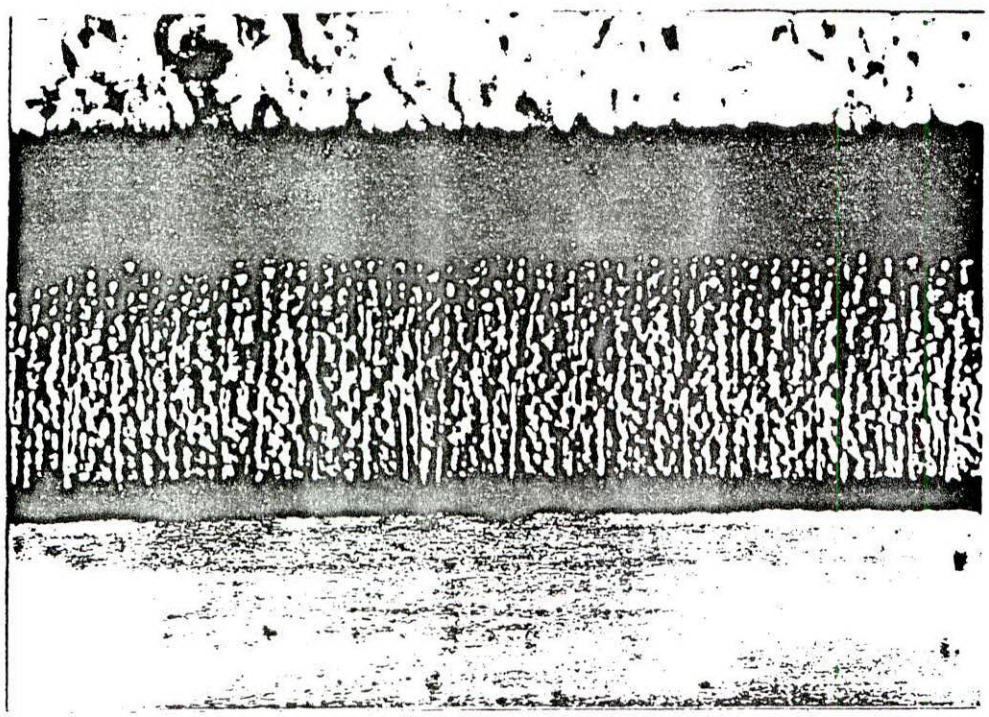
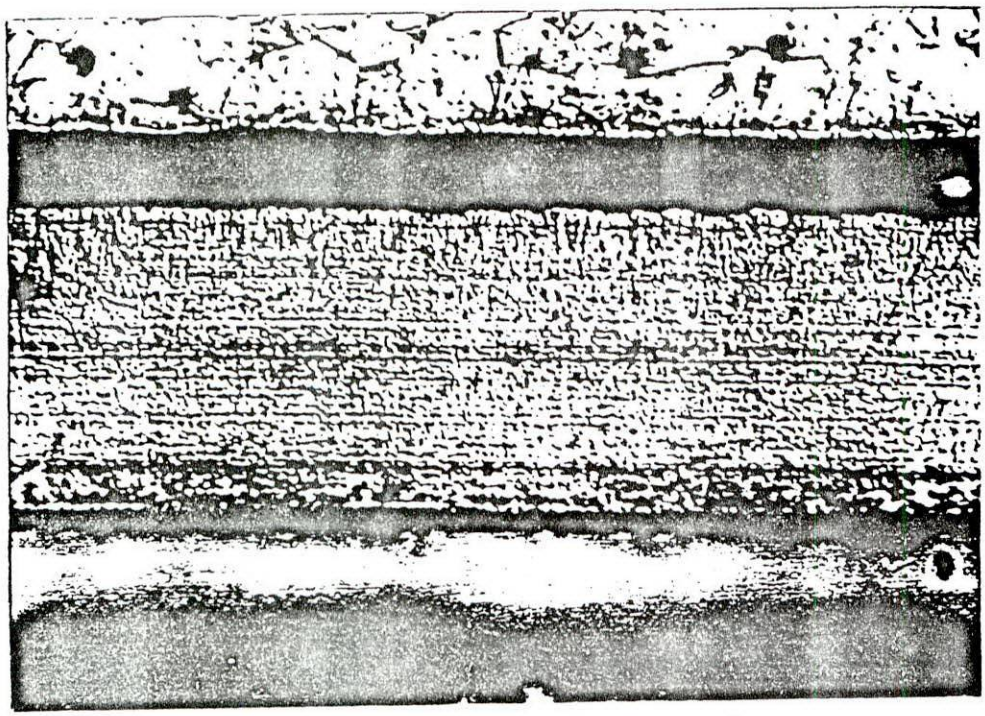


FIGURE 1

Palladium-Nickel Electrodeposit Structures



Columnar



Lamellar

TABLE 5

Solderability Testing of F095 Headers, Lot AP

Solderability of square pins using non-activated flux: % of surface wetted. (95% coverage required)

Test and Soldering Conditions	State of Pins: New	State of Pins: After Ageing in steam at 100°C for 16 hours
Wetting 235°C, 2 sec.	100%	95%
Dewetting 260°C, 5 sec.	100%	100%

TABLE 4

Results on IEC 512 Testing

Conditioning Steps and measurements	IEC 512 Test Program	Male Header: Requirements/ Test method	Male Header: Result Obtained	Eurocard Connector: Requirements/ Test Method	Eurocard Connector: Result Obtained
Contact resistance x	2.2a	≤ 15mΩ	$\bar{x}$ 10.00mΩ xmax 11.80mΩ	≤ 20mΩ	$\bar{x}$ 7.43mΩ xmax 8.10mΩ
Insertion Fi /Withdrawal Force Fw	7.13b	≤ 96 N (64 way-connec) ≥ 6.4N	46-63N 40-67N	≤ 90N (96 way-connec)	≤ 78.5N ≤ 60N
Vibration	4.6d	Sine wave 10 - 2000 Hz acceleration 10g duration: 2 hours on each of the 3 axes Change of contact resistance ≤ 5mΩ (IEC 512 - 2.2c) No loss of contact for more than 1, µsec (IEC 512-2.2c)	ok ok	Sine wave 10 - 500 Hz acceleration 5g duration: 2 hours on each of the 3 axes ≤ 40mΩ No loss of contact for more than 1, µsec	
Contact resistance x	2.2a	≤ 15mΩ	$\bar{x}$ 10.00mΩ xmax 11.30mΩ	20mΩ	$\bar{x}$ 7.63mΩ xmax 8.9mΩ
Rapid temperature changes	6.11d	-55°C/125°C 10 cycles 2x30min each 1/2 connectors paired		as for male header	
Dry Heat	6.11i	16 hours 125°C		as for male header	
Cycled high humidity	x5	upper temperature 55°C		as for male header	
Coldness	6.11j	2 hours -55°C		as for male header	
Cycled high humidity	x5	upper temperature 55°C 5 cycles		as for male header	
Contact resistance x	2.2a	≤ 20mΩ	$\bar{x}$ 10.30mΩ xmax 11.50mΩ	≤ 20mΩ	$\bar{x}$ 7.84mΩ xmax 9.3mΩ
Insertion Fi /Withdrawal force Fw	7.13b	≤ 96N (64way-connec) ≥ 6.4N	29-36N 23-25N	≤ 90N	≤ 59.5N ≤ 58.0N

TABLE 3

Standard Potentials for Common Contact Metals

Gold	:	Au^{+}	+ e → Au	1,68V
Palladium	:	Pd^{2+}	+ 2e → Pd	0,83V
Silver	:	Ag^{+}	+ e → Ag	0,80V
Copper	:	Cu^{2}	+ 2e → Cu	0,34V

Eurocard Connectors F068 - 1/80

A stamped band of these connectors (figure 7) was plated by reel-to-reel technique. Assembled samples were subjected to similar climates as for the F095 headers. There were some differences, the salt spray test followed 200 insertions and withdrawals and encompassed three combinations of mating contacts. These were palladium-nickel on both male and female, gold males with palladium-nickel females and palladium-nickel males with gold females. There was no difference in the results in that they all met specification. Testing was comprehensive, in this test alone 24 assemblies of 94 way connectors were employed. Results are illustrated in figure 8.

F161 (D-Sub) Connectors

These connectors (figure 9) were plated in a Vibrobot with 0.4 micrometers (16 microinches) of copper, 1.0 micrometers (40 microinches) of nickel, 0.4 micrometers (16 microinches) of palladium-nickel and 0.1 micrometers (4 microinches) of gold. All thicknesses referring to the contact zone.

Testing conditions were more demanding than for previously described components. Conditions were:

Lot BP: 500 insertions and withdrawals 2 cycles high humidity, 55°C; 16 hours dry heat, 125°C

Lot CP: 21 days high humidity.

Lot CP: 250 insertions and withdrawals 500 hours dry heat, 125°C

Maximum resistance prior to climate 3mΩ;
after climate 5mΩ

Results are shown in Figures 10 and 11. In no case were any failures identified.

Headers F095

Male headers (figure 4) are examples of components traditionally barrel plated. Normal procedure had been the plate 1 micrometer (40 microinches) of gold over a nickel plated layer and it was decided to substitute a similar thickness of palladium-nickel plus a gold flash. The equipment used was a Vibrobot.

Actual thickness obtained on the test parts was 1.1 micrometers (44 microinches) of palladium-nickel on the contact area and 0.1 micrometers (4 microinches) of gold. Measurement was by X-ray technique.

The square pins were assembled in plastic blocks and tested against gold plated female parts in accordance with IEC 512. Conditioning steps and summarized results are given in Table 4.

Solderability testing was performed on lot AP and the results are shown in Table 5.

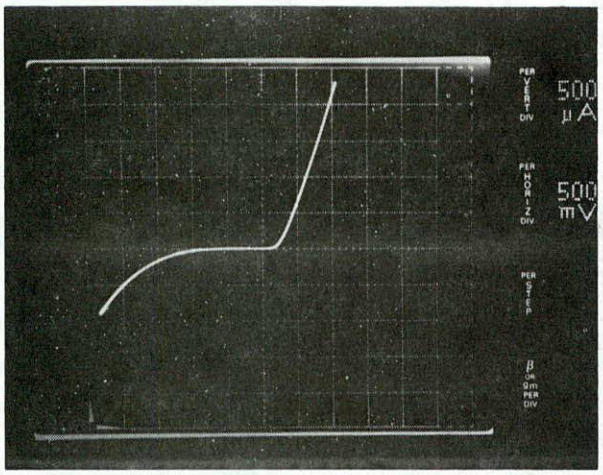
Other tests included contact resistance measured before and after the following:

Lot BP: 150 insertions and withdrawals followed by a salt spray test (5% salt solution for 96 hours)

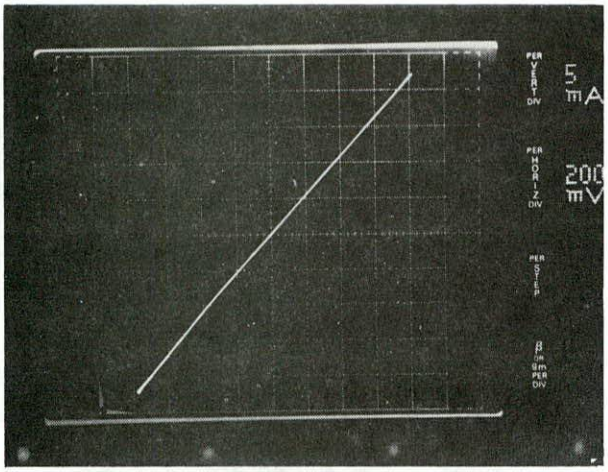
Lot CP: 150 insertions and withdrawals followed by 21 days constant high humidity.

Lot DP: 150 insertions and withdrawals followed by 500 hours at 125°C in air.

The results of these tests are illustrated in figures 5 and 6. Specified maximum tolerable resistance after testing is 20 milli ohms.

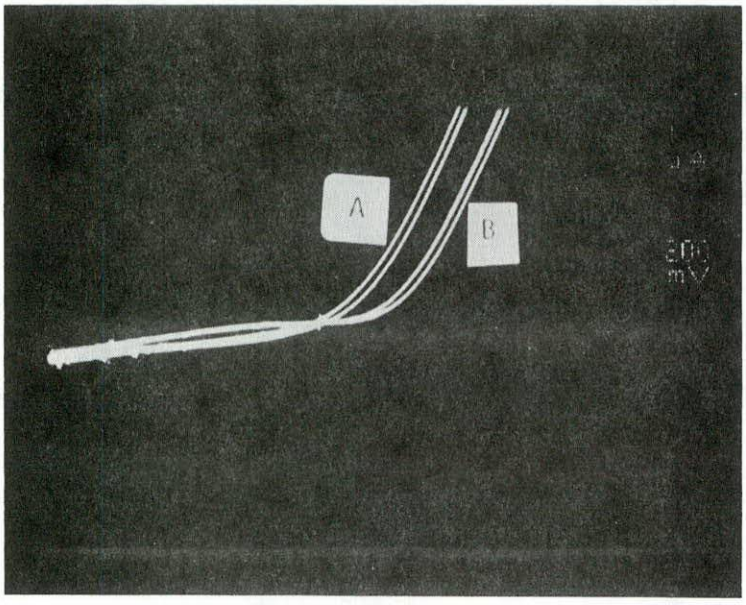


A TYPICAL SCHOTTKY BARRIER CONTACT. TWO POINTS PROBE MEASUREMENT.



B TYPICAL OHMIC RESISTANCE DETERMINED FROM I-V CURVE MEASURED ON THE SAME LINE.

Fig. 26: Typical I-V curves of gold deposit formed on N-type GaAs substrate via pulsed laser irradiation from potassium gold cyanide electroplating solution. Laser peak energy density was 0.28 joule/cm^2.



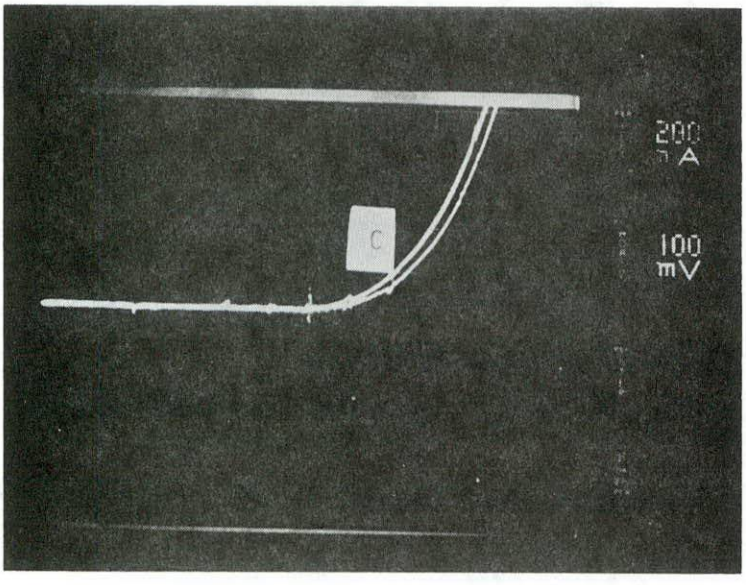


Fig. 25: Typical current voltage curves showing Schottky contact behavior. Deposits were formed on N-type silicon at various laser peak energies.
(A) 6×10^6 watt/cm^2, 1KHz
(B) 3×10^6 watt/cm^2, 2KHz
(C) 3.1×10^7 watt/cm^2, 1KHz

stringent professional applications belong to the gold and platinum groups. Up to now, gold has been the most widely used for low signal levels.

Some of the requirements of professional connectors are given in table 2.

Suitability of Palladium-Nickel for Electrical Connectors

The standard potentials of some commonly used metals in contact applications are given in table 3.

Palladium is thermodynamically considerably less noble than gold (since its standard potential is about 0.8 lower) and slightly more noble than silver. However, a consideration of the rates of reactions of palladium and a comparison with silver reveals that better corrosion resistance than silver is to be expected. Indeed, the corrosion resistance of palladium to the common test environments for connectors such as H_2S, SO_2, NaCl, H_2O appears to be completely satisfactory. Thus the slow kinetics of palladium in comparison to the generally very fast kinetics of silver result in palladium-nickel (especially when having a lamellar structure) being fairly resistant to attack by nitric acid and resistant to attack of H_2S. On the contrary silver is rapidly attacked by these two reagents. The corrosion properties of palladium are therefore comparable to those of gold for the normal test and environments encountered for connectors. It is therefore, legitimate to quote the often used phrase that palladium-nickel is "as good as gold".

Performance of Palladium-Nickel on Professional Connectors

In line with previously established practice, all connectors plated in palladium-nickel were finished by overflashing with 0.1 micrometers (4 microinches) of pure gold. It is generally accepted that there is no discernible difference between hard and soft gold in this application. The mechanism of providing surface lubricity can be explained by the theory of Bowden and Tabor (8).

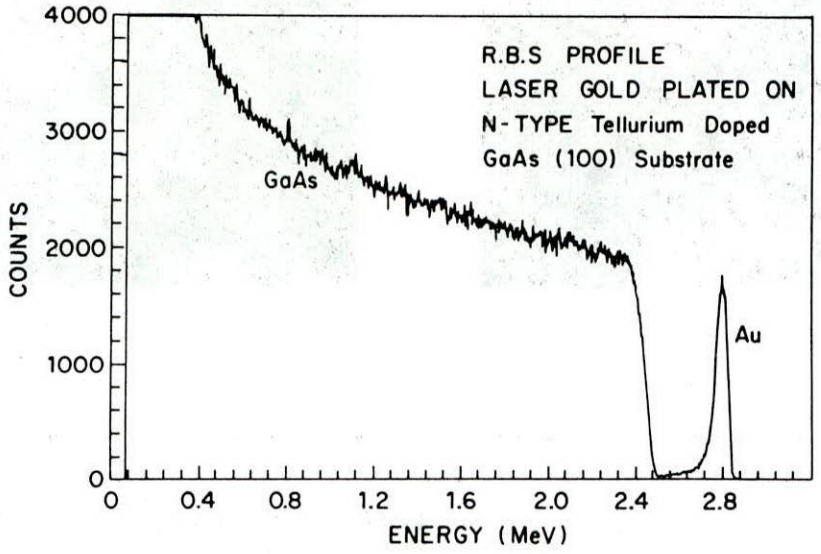
between the deposition and the anodic stripping was kept as short as possible. All runs were carried out with a 10 second delay in which the electrode was washed and transferred to the anodic stripping cell. Runs with 5 and 15 seconds delay did not show great differences in the H_2 content. It was therefore assumed that for the 10 seconds delay a negligible error arose. The measured amount of hydrogen together with the atomic ratios H_2:Pd (assuming 100% current efficiency for the deposition of this palladium-nickel) and the deposition conditions are given in table 1. The highest current density here employed was above the limiting current density since rough matt deposits were obtained, nevertheless, the hydrogen content was less than 2.2 atomic percent. At the typical current densities employed with this bath (20-40 A/dm^2 the initial hydrogen content in the sample was less than 0.3 atomic percent.

These values are very much lower than those found for pure palladium where from a similar electrolyte as much as a 1000 times higher H:Pd ratio was measured. They are of the same order of magnitude as those reported by Raub (7) for deposits from a different Pd-Ni ammoniacal bath. Obviously, the problems previously noted with palladium are non-existent with an appropriately formulated Pd-Ni, since the H:Pd ratio never comes close to the maximum of the Pd Hx phase of 3%.

Requirements for Contact Materials

The material chosen must provide a low contact resistance under all working or test conditions. Since tarnished or corrosion product covered surfaces would not meet the criteria, the contact material must be noble enough to withstand chemical attack and also provide, through a negligible pore-count, protection of the normally non-noble base material.

The metal and its thickness must also be correctly chosen such that the required performance is also maintained after a prescribed number of insertion/withdrawal cycles. The metals that are most suitable for



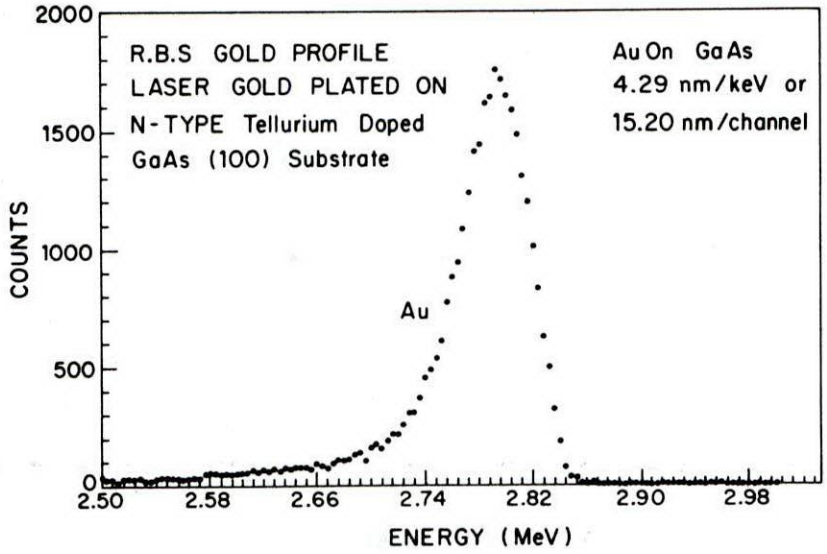


Fig. 23: Typical RBS profile of gold deposit obtained via pulse laser irradiation on GaAs substrate from potassium gold cyanide electroplating solution.
(A) RBS profile showing presence of pure gold together with GaAs.
(B) RBS profile showing distribution of gold within GaAs substrate.



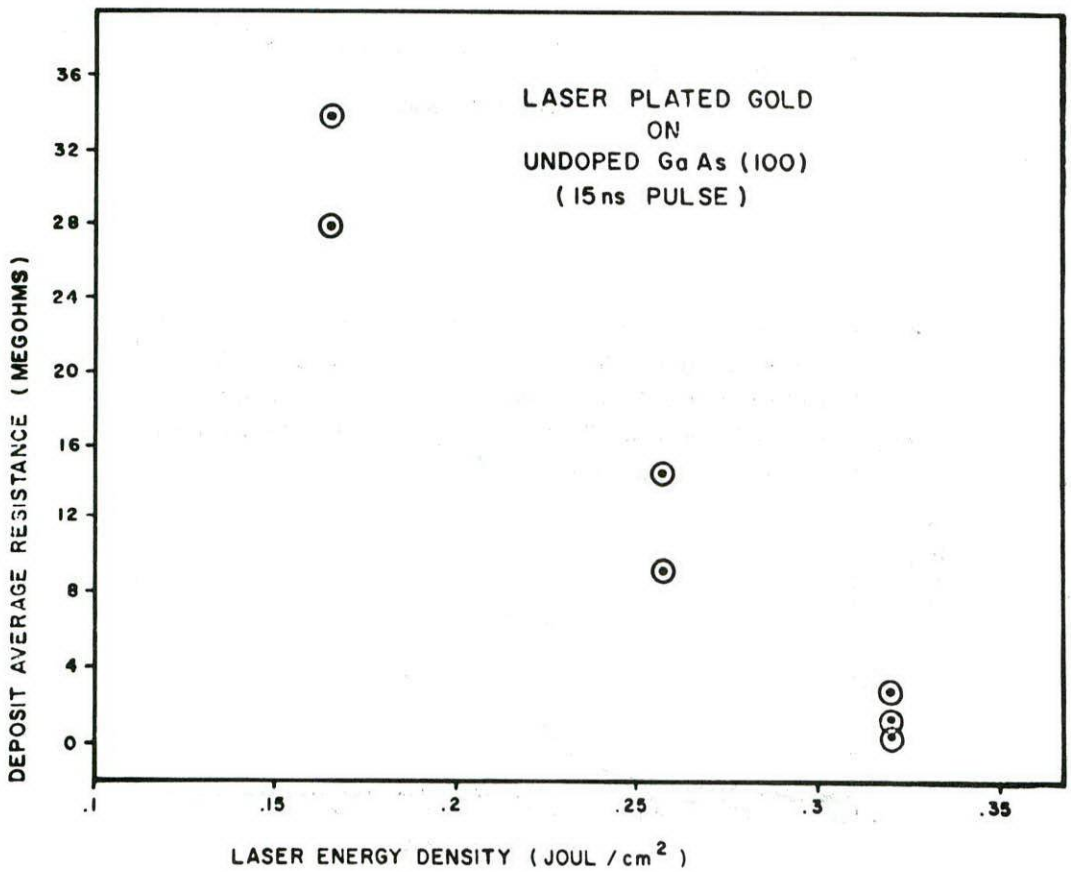


Fig. 24: Typical I-V curves and ohmic resistance of gold deposit on undoped GaAs. Average resistance values were measured from slopes of I-V curves to give a correlation with laser energy density.

FIGURE 4

F095 CONTACT PINS IN MOUNTING BLOCKS

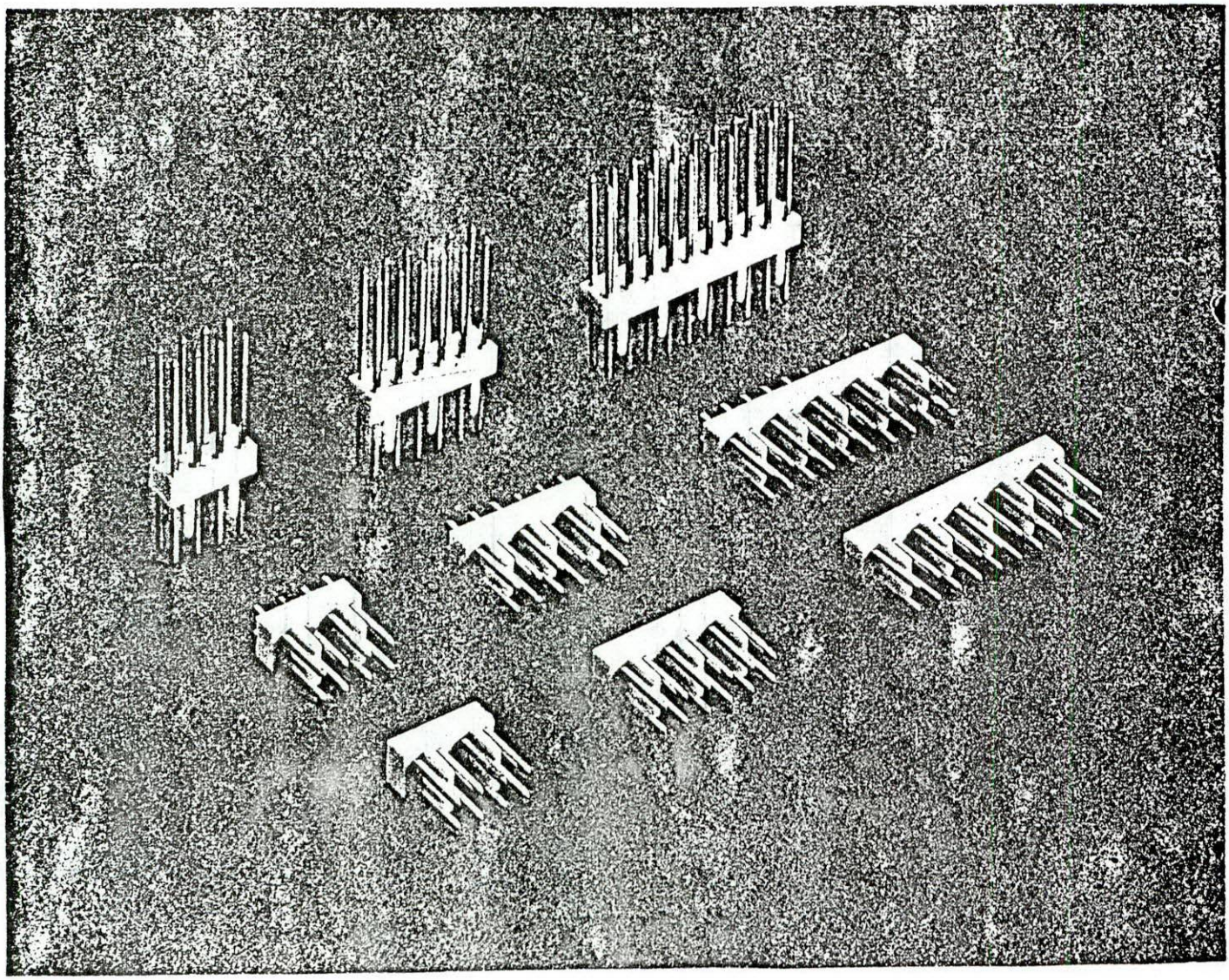


FIGURE 5

LOT BP, F095 HEADERS

Climate: Salt spray (5% solution, 96 hours)

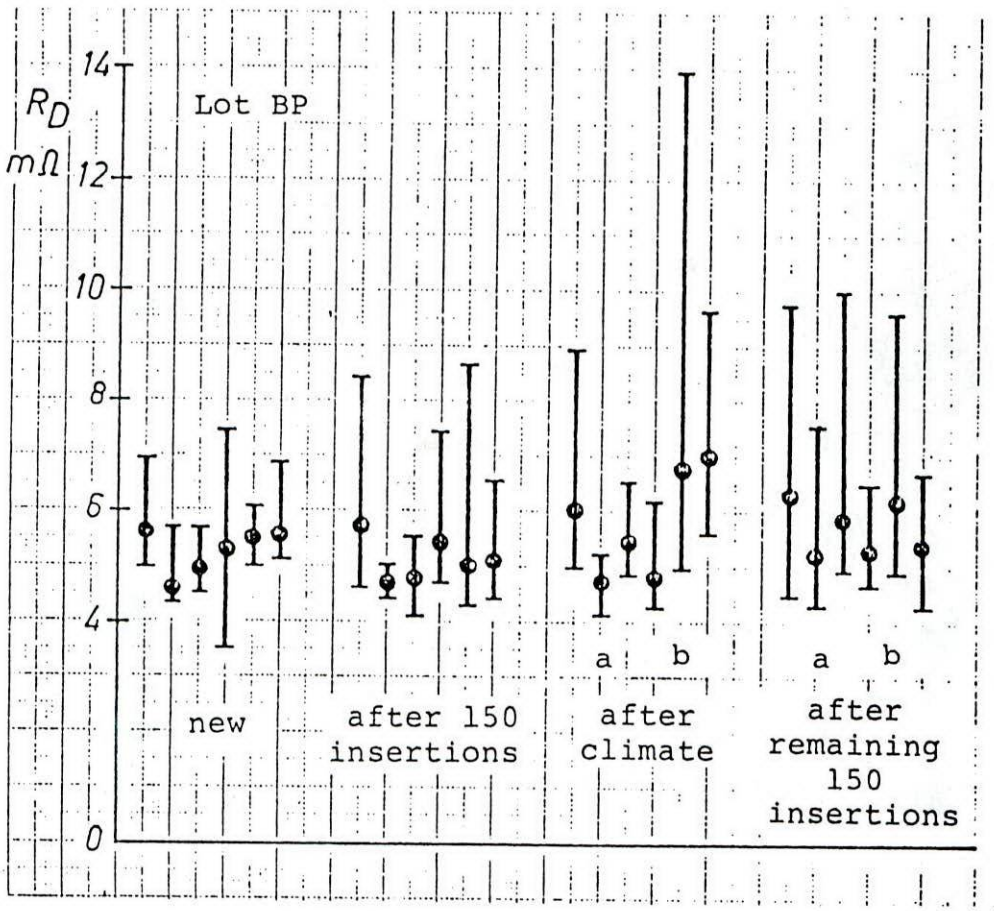


FIGURE 6

LOT CP, F095 HEADERS

Climate: Constant High Humidity, 21 Days

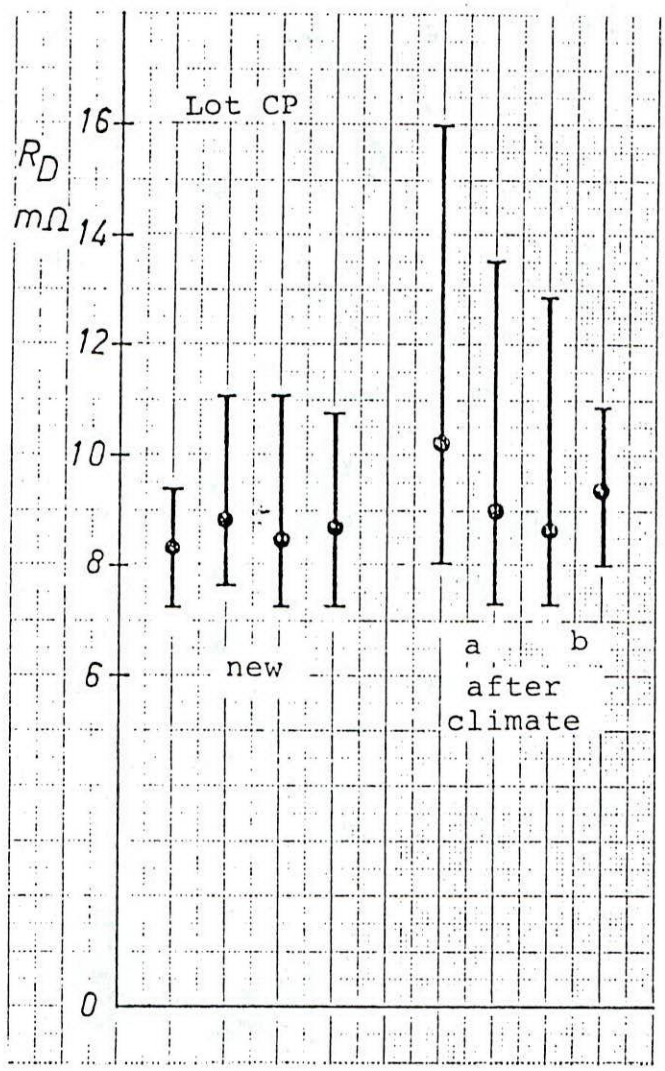


FIGURE 7

CONNECTORS F068

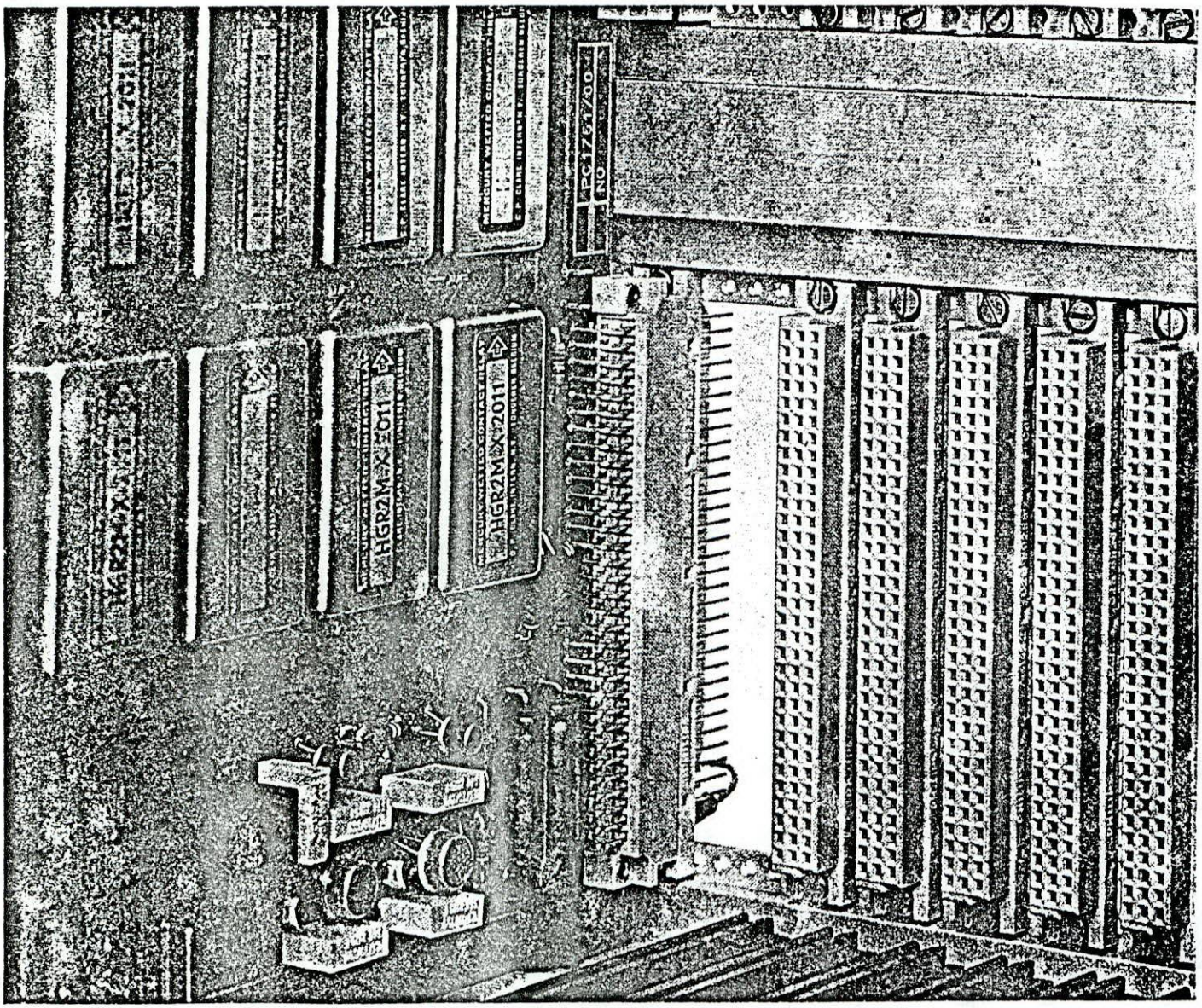


FIGURE 8

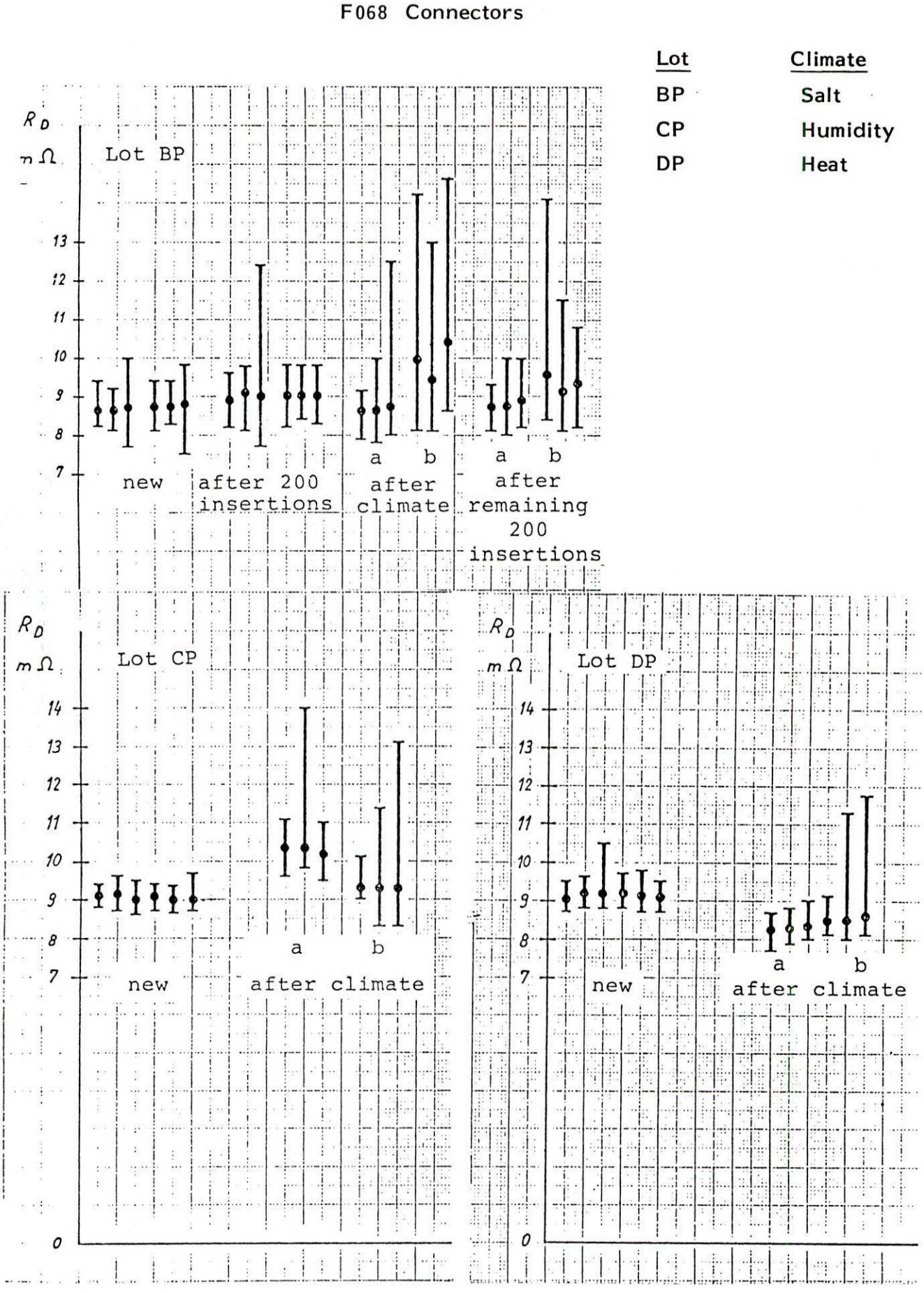

F068 Connectors
Lot
BP
CP
DP
Climate
Salt
Humidity
Heat
R_D
mΩ
Lot BP
13
12
11
10
9
8
7
new
after 200 insertions
a
b
after climate
a
b
after remaining 200 insertions
R_D
mΩ
Lot CP
14
13
12
11
10
9
8
7
0
new
a
b
after climate
R_D
mΩ
Lot DP
14
13
12
11
10
9
8
7
0
new
a
b
after climate

FIGURE 9

F161 (D-Sub) Connectors

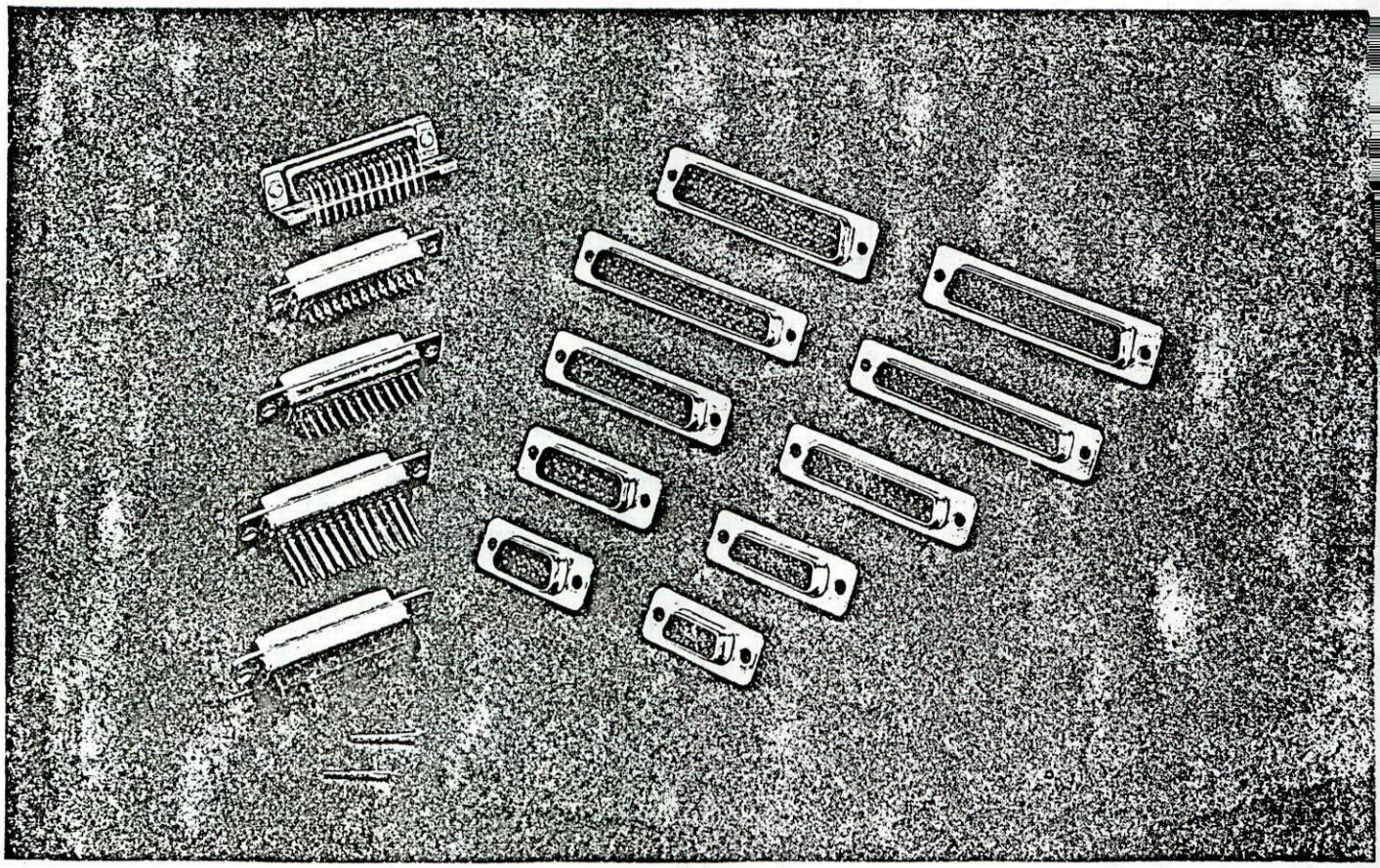


FIGURE 10

LOT BP, F161 (D-Sub)

Climate: 2 cycles high humidity, 55°C
16 hours dry heat, 125°C

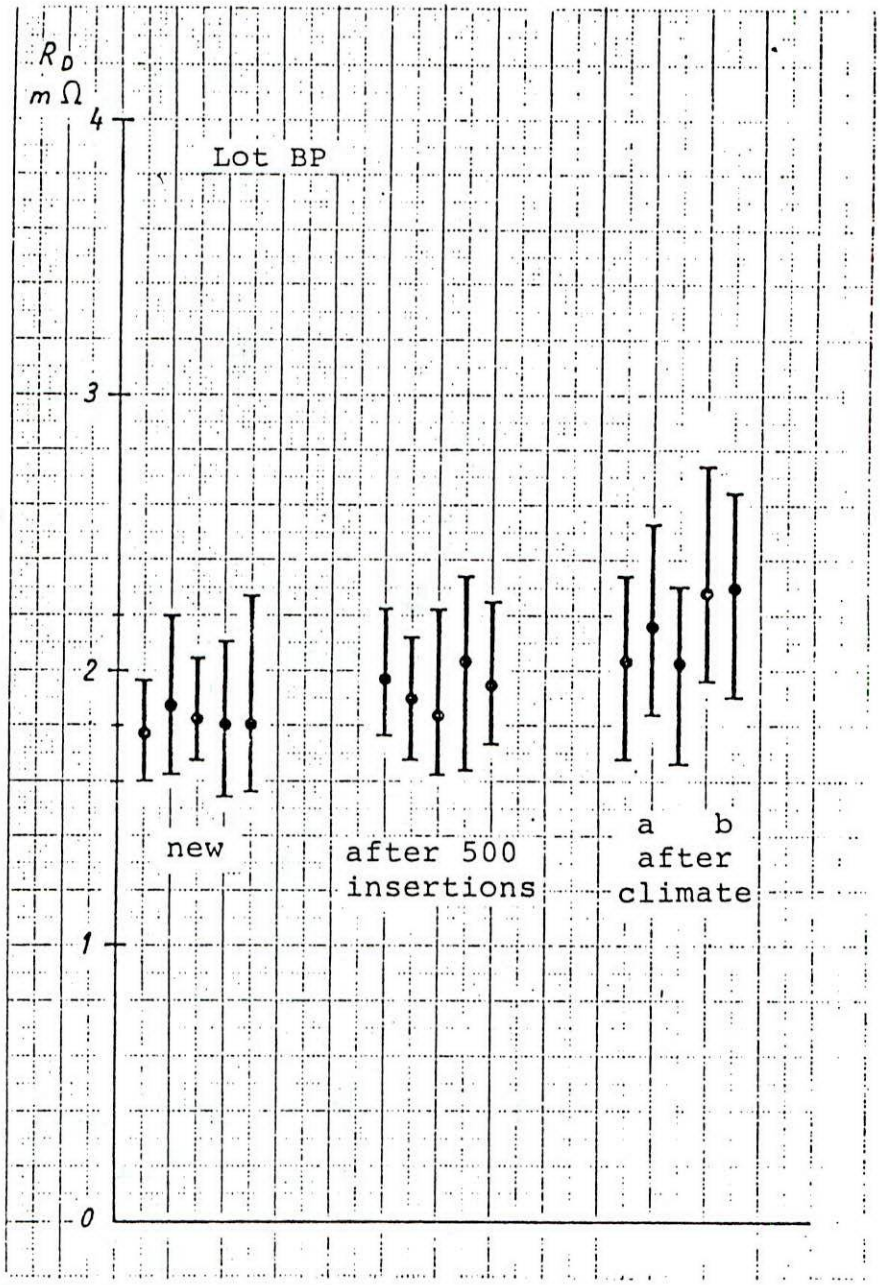
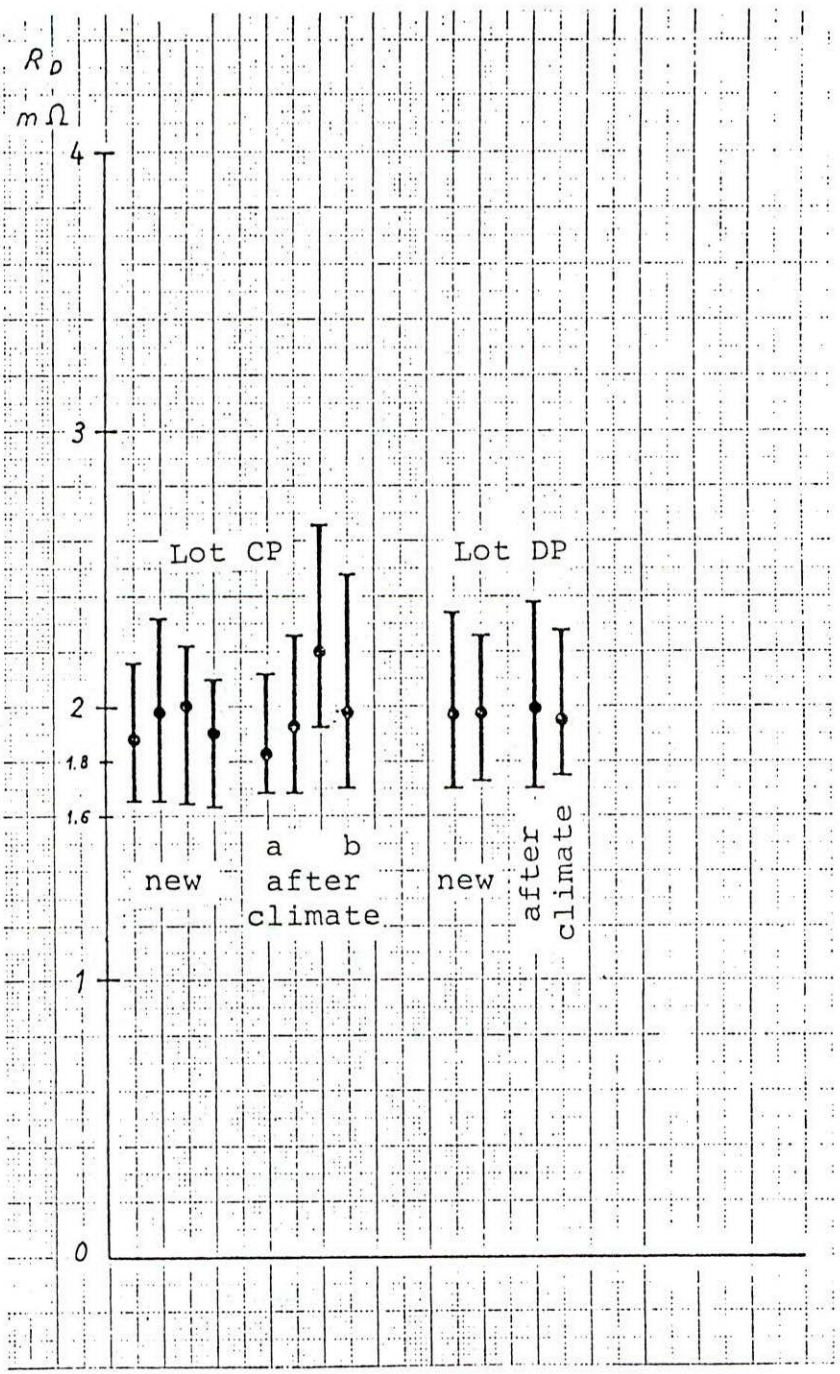


FIGURE 11

LOTS CP AND DP F161 (D-SUB)



O-4

Electronics
Session O

Thin Film Electroless Technology for Shielding of Electronic Devices

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THIN FILM ELECTROLESS TECHNOLOGY FOR SHIELDING OF ELECTRONIC DEVICES

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ABSTRACT

Essential features of electromagnetic theory are discussed from the standpoint of attentuation of low and high impedance electromagnetic radiation under near and far field conditions. It is demonstrated that highly conductive electroless copper deposits offer a high performance solution to the EMI/RFI shielding of electronic devices, both in the factory/office environment and in automotive applications.

INTRODUCTION

The growing presence of electronic devices in the home, industry and in the automobile has created a demand to reduce the electromagnetic noise level in the environment. Many of the electronic devices cannot function in an electromagnetically polluted environment. To better understand this noise and the methods available to control it, a brief review of the basic principles of electromagnetic radiation theory will be undertaken and specific applications of their principles will be shown.

Electromagnetic interference is of concern within a very narrow region of the total electromagnetic spectrum. Figure 1 shows that the region of interest is the band between 10^6 and 10^9 Hz. This band encompasses FM, AM and TV broadcast frequencies.[1]

The operation of electronic equipment can be affected by radiation emitted within this region of the spectrum. The interference results in static noise in radios and video interference, and can also cause malfunctions in computers and other electronic equipment. Several agencies have started to regulate the maximum amount of electromagnetic radiation that can be emitted by different electronic devices. FCC Regulations affect most equipment sold in the U.S. The regulations are listed for equipment in Class 15 under FCC Docket 20780[2]. The German Society of Electronic Engineers (VDE) has established emission limits[3], and there are also a series of military standards in existence. These rules and regulations apply to different regions of the electromagnetic spectrum; however, the FCC Regulations of primary interest cover the region from 30 MHz to 1000 MHz for emitted radiation.

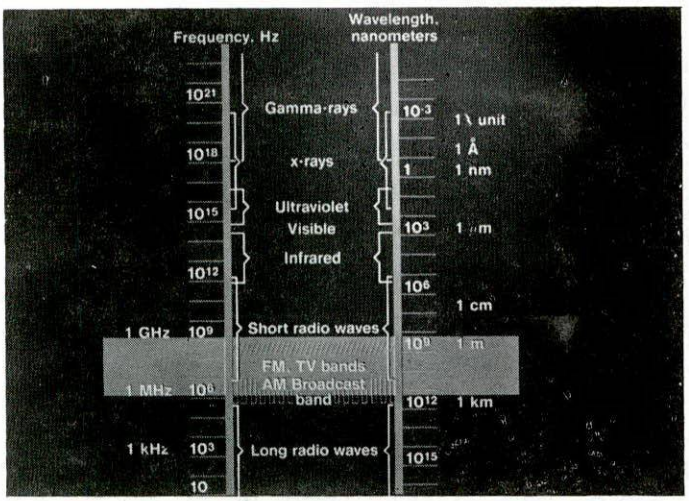

FIGURE 1. Electromagnetic Spectrum showing region of interest for EMI Shielding.

The development of light weight, plastic shielded enclosures is also being driven by the search for alternatives to the heavy metal boxes used to shield electronic components in the automotive industry. The value of electronic components per car is expected to increase from $500 in 1984 to over $1,500 by the early 1990s. This crowding of microprocessor controls, both in the engine and passenger compartments, is already creating cross-talk and interference problems. This interference will be even more important when video screens, mobile communications and even radar applications become standard features in production vehicles.

As mentioned, FCC Regulations cover the range from 30 MHz to 1000 MHz, and they limit the magnitude of the electromagnetic field at a specified distance from the source. Devices are divided into Class A (for equipment used in industrial environments), and Class B (for devices designed for the consumer market). Class B requirements are more stringent, as can be seen in Table I.

TABLE I

RADIATED LIMITS

Frequency (MHz)	Class A at 3m	Class B at 3m
30 - 86	300 μV/m	100 μV/m
86 - 216	500 μV/m	150 μV/m
216 - 1000	700 μV/m	200 μV/m

THEORETICAL BACKGROUND

WAVE IMPEDANCE

Electromagnetic radiation has two components, the electric field, E and the magnetic field, H. These two components are orthogonal, or perpendicular, to each other as shown in Figure 2. The ratio of the electric field to the magnetic field (E_o/H_o) is called "wave impedance" or Z_w and is measured in ohms. A high value for Z_w implies a high electrical component and a low Z_w implies a high magnetic component. The wave impedance will determine the type of radiation that we must shield and will also determine the best procedure to achieve that shielding.

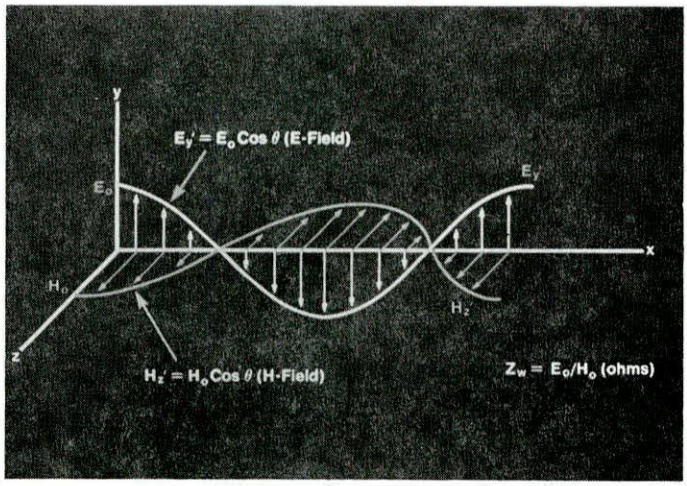

FIGURE 2. Schematic illustration of electrical and magnetic components of an electromagnetic wave.

The wave impedance (Z_W) of the electromagnetic radiation is determined by the physical characteristics of the emitting source. It is also dependent on the distance from the source. At short distances, near field conditions prevail. At long distances, far field conditions are predominant (see Figure 3). Under far field conditions, the wave impedance becomes a constant, determined by the nature of the propagating medium (for air and vacuum the wave impedance is 377 ohms), and the electromagnetic wave is called a plane wave.

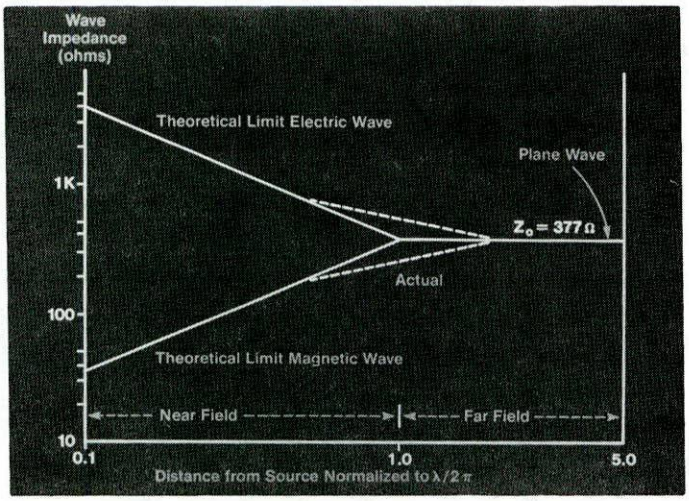

FIGURE 3. Definition of near and far field conditions.

That region between near and far field is called the transition region and it contains the transition point (T.P.), defined as:

$$T.P. = \frac{\lambda}{2\pi}$$

where λ is the wavelength of the radiation. Typical values are given in Table II.

TABLE II

TRANSITION POINT FOR DIFFERENT FREQUENCIES

Frequency (MHz)	Wavelength (m)	T.P. (m)
1	300.0	47.85
30	47.8	1.59
100	3.0	0.48
500	0.60	0.09
1000	0.30	0.05

The transition point varies for different frequency radiations. The transition point can range from more than 1.5 m away from the source at 30 MHz to 5 cm at 1000 MHz. For a particular source and shield, the shield can be under near field conditions for one frequency, and under far field conditions for another.

SHIELDING

There are many ways to limit the amount of electromagnetic radiation which an electronic device emits. One approach is to alter the electronic design. Noise-free design can be attempted by controlling component selection, changing the circuit layout, and by use of filtering and/or grounding techniques. While all these measures will incrementally decrease the amount of radiation emitted, it may not be cost effective to eliminate all noise emission. The advantage of the design approach is that it eliminates emission problems at the source, which is good engineering practice. The limitations of the design approach are that it does not completely eliminate emissions, and that it still leaves the device susceptible to interference from external noise.

Electrical theory teaches that the electrical field inside a solid conductor is always zero, independent of the field outside the conductor (Faraday cage). It can be shown that if there is an electric field inside a grounded conductor the electric field on the outside must be zero. This principle can be applied to shielding of an emitting electronic device. We must remember that the theoretical solid conductor does not allow for connecting cables and vents or openings for CRT displays which are encountered in practice. Should the device be surrounded with a solid metallic conductor, there would be no outside emission.

A solid conductive wall affects incoming electromagnetic radiation in several ways. This is shown in Figure 4. The transmitted radiation should be much smaller than the incident radiation in order to achieve effective shielding.

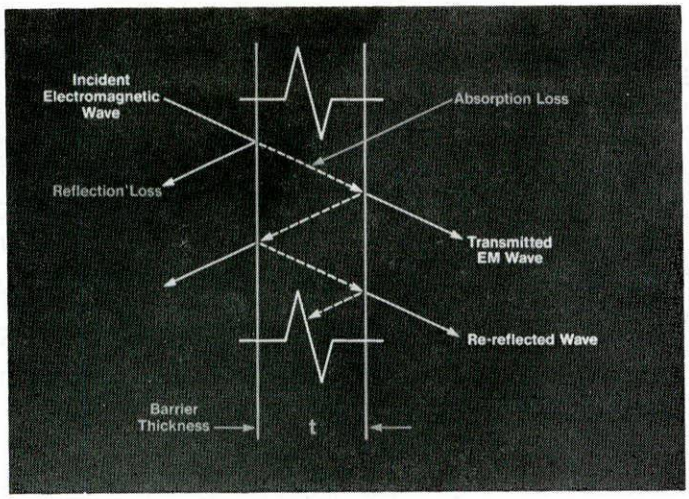

FIGURE 4. Schematic illustration of the interactions of an electromagnetic wave with a solid conductor.

ATTENUATION

A practical approach to compare shields is to determine the shielding effectiveness, which is the attenuation of electromagnetic radiation after it goes through a shield. The shielding effectiveness (SE), or attenuation, is defined as:

$$SE = 20 \log \frac{E_o}{E_t} \quad (dB)$$

or

$$SE = 20 \log \frac{H_o}{H_t} \quad (dB)$$

where E_o and H_o are the incident electric and magnetic fields, and E_t and H_t are the transmitted electric and magnetic fields.

The attenuation unit is the decibel (dB) and according to these definitions, a shield which transmits 1% of the incident radiation has a SE of 20 dB, while a shield with a SE of 40 dB will transmit only 0.01% of the incident radiation. We must remember, however, that a shielding value, per se, will not assure that a unit will comply with FCC regulations. The amount of radiation emitted from the assembled unit depends on the internal noise emissions from the unit and the attenuation value of the shield. Final

compliance must always be determined with a complete unit under open field testing conditions.[5]

The total attenuation of radiation by a shield is expressed as:[6]

$$\text{Attenuation} = \text{Absorbed} + \text{Reflected} + \text{Re-reflected.} \qquad (1)$$

ABSORPTION

The absorption of radiation (A) is independent of near or far field conditions and it will be the same for high or low impedance radiation. It is given by the formula:[5]

$$A = 1.31 \times 10^{-4}\, t \times \sqrt{f \mu_r \sigma_r} \quad \text{(dB)} \qquad (2)$$

$$= 8.7 \frac{t}{\delta} \qquad t = \text{thickness in } \mu m, \quad \delta = \text{skin depth}$$

$$\text{Where } \delta = \frac{6.60 \times 10^4}{\sqrt{f u_r o_r}} \quad (\mu m) \qquad (3)$$

σ_r = relative conductivity
μ_r = relative permeability
f = frequency of radiation

It is shown in equation 3 that A is directly proportional to thickness and inversely proportional to the skin depth(δ) of the shielding material. The skin depth of a material is defined as the thickness of material that will transmit 37% (1/e) of the incident radiation. One skin depth corresponds to an attenuation of 8.7 dB. Therefore, several skin depths are needed in order to achieve significant attenuation by absorption. Table III shows skin depths for several materials at different frequencies.

TABLE III

SKIN DEPTH FOR VARIOUS MATERIALS

Frequency	Copper (μm)	Aluminum (μm)	Steel (μm)
10 MHz	20.88	26.72	2.09
30 MHz	12.04	15.42	1.20
100 MHz	6.58	8.43	0.66
500 MHz	2.95	3.78	0.29
1000 MHz	2.09	2.67	0.21

As can be seen, thick shields will be needed even to attain a modest shielding by absorption alone. For example, about 40 μm of copper would be required to absorb 30 dB of radiation at 30 MHz. Absorption, therefore, will not contribute significantly to the total attenuation for the most practical shielding processes.

REFLECTION

The reflection of radiation (R) differs under near and far field conditions, and also differs for high or low impedance radiation. Reflection is defined as:

Far field

$$R = 168 - 10 \log \left(\frac{\mu_r f}{\sigma_r}\right) \quad \text{dB} \qquad (4)$$

Near field

$$R_{el} = 20 \log \frac{4.5 \times 10^9}{fr|Z_s|} \quad \text{dB} \qquad (5)$$

Where,

$$|Z_s| = 3.68 \times 10^{-7} \frac{\mu_r}{\sigma_r} f \qquad (6)$$

is the shield impedance. In the preceeding equations, f is the frequency of the radiation and r is the distance from the source to the shield in meters.

Similarly, the magnetic component is given by,

$$R_{mag} = 20 \log \frac{1.97 \times 10^{-6} fr}{|Z_s|} \qquad (7)$$

By examining equations 4, 5 and 7, it is evident that in all cases, both near and far field, the reflected radiation will be larger when the shield material has a large electrical conductivity (σ_r) and a low magnetic permeability (μ_r).

Re-reflected radiation is usually negligible, it should be evaluated only for very low frequency magnetic radiation under near field conditions. (It is a negative number, and it will decrease attenuation by at most 15 dB under worst case conditions.)

From our initial equation,

Attenuation = Absorption + Reflection + Re-reflection

we have demonstrated that reflection is the predominant mechanism for attaining effective shielding in a practical manner. Also, the most effective shields must be made from materials with high conductivity and low permeability.

REDUCING THEORY TO PRACTICE

SHIELDING MATERIALS

The relative conductivity and permeability of common materials is shown in Table IV.

TABLE IV

RELATIVE CONDUCTIVITY AND PERMEABILITY OF VARIOUS MATERIALS[6]

	Relative Conductivity	Relative Permeability
Silver	1.05	1
Copper-Annealed	1.00	1
Aluminum	0.61	1
Zinc	0.28	1
Nickel	0.20	100
Steel (SAE 1045)	0.10	1000

It is evident that the shielding material of choice is copper (silver being much more expensive and being only marginally more conductive). Also, under near field conditions, it can be shown that a copper shield provides over 25 dB more attenuation than a similar nickel shield.

We can calculate the attenuation at any frequency for an ideal copper shield by applying the equations and known physical constants for any thickness and distance from the source (see Table V). When the ratio of r/T.P. is smaller than 1, near field conditions apply, and separate calculations must be made for electric and magnetic fields. When the ratio is larger than 1, far field conditions apply and the attenuation for a plane wave is determined. (See Appendix for a sample calculation.)

TABLE V

Theoretical Attenuation of a 1 μm Copper Shield on a Plastic Substrate at 30 cm from the Source

Frequency (MHz)	Attenuation E Vector (dB)	Attenuation H Vector (dB)	Attenuation Far Field (dB)	r/T.P.
10	122	54	-	0.064
30	108	63	-	0.19
100	93	74	-	0.64
500	-	-	84	3.2
1000	-	-	82	6.4

The data can be plotted to show the total attenuation of a thin copper shield (0.75 um) at two different distances from the source as it has been done in Figure 5.[7]

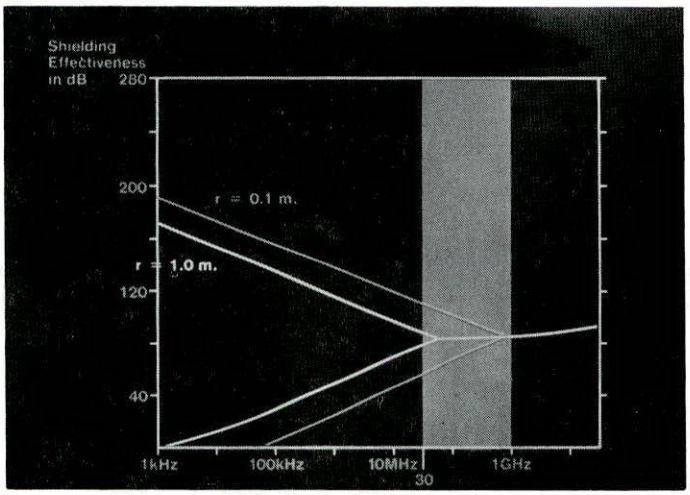

FIGURE 5. Shielding Effectiveness of 0.75 μm of copper.

Considering only the frequency range from 30 MHz to 1000 MHz (the range regulated by FCC), it is observed that at 1 m from the source to the shield, the frequency range falls in the far field region. At a more realistic 10 cm from source to shield, most of the range of interest is in the near field region. Under these circumstances, even for radiation from a pure magnetic wave (the worst case) the attenuation at 30 MHz should be in the proximity of 60 dB. For any other condition (higher E component, higher frequency), the (ideal) attenuation should be above that minimum.

This short analysis of the principles of attenuation theory shows that very thin shields (0.75 μm to 1 μm) of highly conductive materials such as copper can provide substantial attenuation of electromagnetic radiation (on the order of 60 dB) and make very effective shields.

ELECTROLESS DEPOSITION, A PRACTICAL SHIELD

The most efficient production technique for applying a uniform, highly conductive film at the optimum thickness of 0.75-1 μm is especially on complex, three dimensional surfaces and electroless deposition. Modifications of well established electroless chemistry[8] are available which consist of the following processing steps:

PRECONDITIONING uses chemical solvents or mechanical abrasion to smooth and, in some cases, strengthen the plastic surface, and to promote uniform etching and metallic bonding in the next step.

ETCHING renders the plastic hydrophilic, and creates bonding sites for subsequent metallic deposits. Chemicals used in this process are chromic acid and chromic-sulfuric acid mixtures.

NEUTRALIZATION reduces hexavalent chromium left over from etching, and does so through the use of mixtures of mineral acids and reducing agents.

SENSITIZING further prepares the plastic surface for chemical catalysts, and promotes the adhesion qualities of the plastic to the metallic deposits which will follow. Organic amines are frequently used in this step.

ACTIVATION uses mixtures of mineral acids, tin salts, and palladium, which result in the adsorption of catalytic material on the plastic surface.

ACCELERATION exposes active catalytic sites for the deposition of electroless copper and consists of a mixture of mineral acids and tin complexers.

ELECTROLESS COPPER is deposited by catalytic reduction out of a process containing copper salts, chelators (complexers), reducing agents and stabilizers. This coating produces the EMI shielding desired.

ELECTROLESS NICKEL INITIATION promotes the deposition of electroless nickel on the copper shield. This step may be accomplished by deposition of noble metals, created by electric current, or produced by reducing agents.

ELECTROLESS NICKEL improves corrosion resistance, durability, and the appearance of the EMI coating. Nickel salts, chelators (complexers), and reducing agents and stabilizers are also used in this final step in the overall shielding process.

The last step, the electroless nickel deposit, does not contribute to the total shielding effectiveness but helps prevent tarnishing of the copper. Actual attenuation levels determined on panels shielded by electroless deposition are shown in Figure 6.

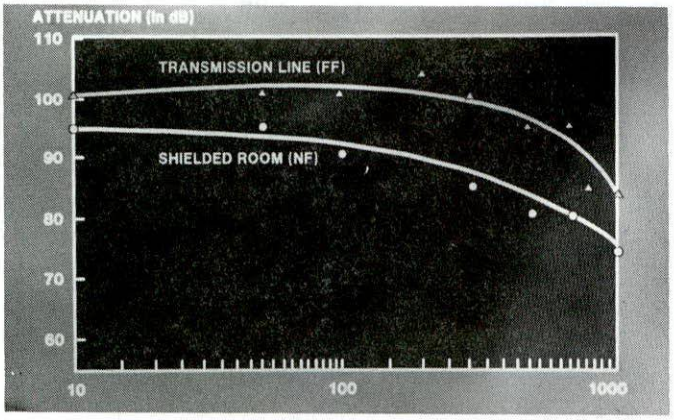

FIGURE 6. Actual attenuation of 1.1 μm electroless copper and 0.1 μm electroless nickel.[9]

It is necessary to have a method to determine that the electroless deposit meets the specifications related to continuity and thickness. Good correlation has been found[10] between thickness and the sheet resistance of the electroless deposit, as shown in Figure 7. Using a sensitive VOM multimeter the sheet resistance can be easily determined nondestructively, and using a calibration plot, the thickness can be found. This method can be used conveniently as a rapid quality control procedure that will ensure a lower percentage of rejected parts due to thin deposits.

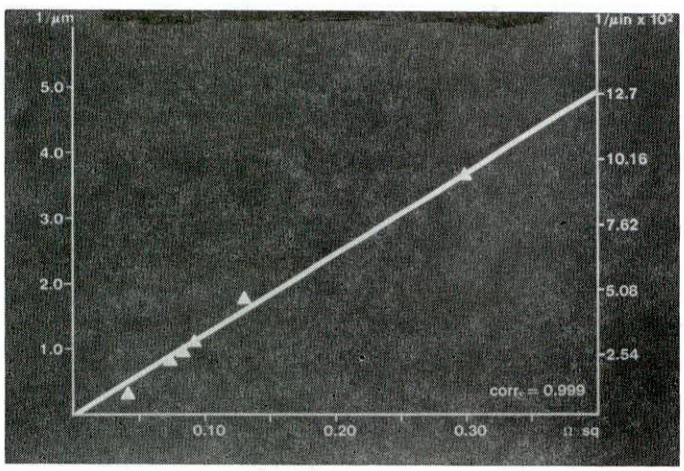

FIGURE 7. Plot of the inverse of thickness of ECu versus sheet resistance of the deposit.

An advantage of electroless plating is that it can deposit uniform thicknesses on very complicated parts, something that is extremely difficult for other shielding processes. An additional benefit of electroless technology is due to the fact that, unlike the line-of-sight coating processes (i.e., painting and vacuum metallization) it provides a coherent coating on both sides of the substrate. Moreover, it can be applied to a wide variety of substrates, extending from smooth injection molded parts to rough foamed mold parts. The difference between these two surfaces is illustrated in Figures 8 and 9.

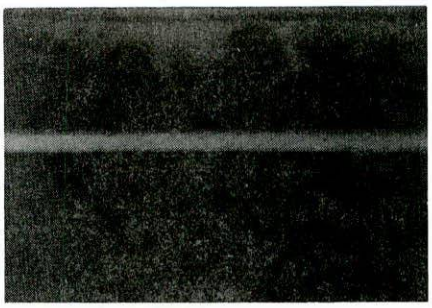

Fig. 8



Fig. 9

FIGURE 8 and 9. Cross-sections of injection molded ABS (Fig. 8) at 500x and foam molded PPO (Fig. 9) at 400x magnification. Note the difference in the resin surface profile.

The requirements of the automotive market are such that extremely stringent properties are required for the plated enclosures.[11] Physical properties of the plastic are then of the utmost importance, as well as the performance of the coating under real life conditions. To meet these needs, new processes have been recently developed capable of achieving superior adhesion of electroless deposits to a variety of high performance engineering resins. These resins include filled nylon, filled polyetherimides, polycarbonates, polysulfones, and several alloys such as ABS/PVC and ABS/polycarbonates. These resins can meet the extreme conditions encountered in the automotive market.

CONCLUSION

The application of some basic theoretical principles shows the attenuation levels that can be achieved using different materials and allows for the selection of the most effective shield. Based on a series of theoretical and practical considerations, the most effective system has been demonstrated to be a thin copper shield in the range of 0.75 to 1 μm in thickness. For best results, a thin topcoat should be used to protect the copper layer and maintain shielding integrity. Electroless deposition provides a uniform metallic layer even in the most intricate enclosures.

Electroless shielding has been successfully applied commercially in a variety of electronic hardware applications. There are units that have been operating in the field for over three years which meet FCC and all manufacturers' requirements. Several new plating lines, both automatic and hoist, have been installed in the last two years which are dedicated exclusively to the EMI/RFI shielding market. The continuing demand for shielding in large housings, as well as for discrete microprocessors is rapidly expanding the market. As designers and OEMs become more aware of the superior performance and cost effectiveness of electroless shielding this approach will continue to gain market share in applications ranging from business machines to automobiles.

Appendix

The calculation for the theoretical attenuation for a 1 μm thick copper shield at 0.30 m from the source will be demonstrated for a frequency of 100 MHz.

First, it should be determined if the shield is under near or far field conditions. Table II shows that T.P. for 100 MHz is 0.48 m, so at 0.30 m from the source the shield is under near field conditions and separate calculations for E field and H field should be made.

Electric Field Calculations

For an electric field, Eq. 1 can be written as:

$$SE_{el} = A + R_{el} \qquad (8)$$

From Eq. 3 and Table III

$$A = 8.7 \frac{t}{\delta} = 8.7 \frac{1\ \mu m}{6.58\ \mu m} = 1.3\ dB$$

From Eqs. 5 and 6 and considering that σ_r and μ_r are 1 for copper:

$$R_{el} = 20 \log \frac{4.5 \times 10^9}{100\ MHz \times 0.30\ m \times 3.68 \times 10^7 \times 100\ MHz}$$

$$= 20 \log (4.076 \times 10^4) = 92\ dB$$

Replacing in Eq. 8

$$SE_{el} = A + R_{el} = (92 + 1.3)\ dB = \underline{93\ dB}$$

Magnetic field calculations

For the magnetic field calculation, Eq. 1 becomes:

$$SE_{mag} = A + R\ mag + Re\text{-}reflected \qquad (9)$$

The absorption term, A is the same as the calculated for the electric field and it is 1.3 dB.

Replacing Eq. 6 in Eq. 7, R mag becomes

$$R_{mag} = 20 \log \frac{1.97 \times 10^{-6} \times 100\ MHz \times 0.30\ m}{3.68 \times 10^{-7} \times 100\ MHz}$$

$$= 20 \log (1.606 \times 10^{4}) = 84\ dB$$

Since the shield is under near field conditions and the radiation is purely magnetic the re-reflected term cannot be ignored. The exact equation for the re-reflected term is

$$Re\text{-}reflected = 20 \log (1 - e^{2t/\delta})\ dB \qquad (10)$$

Replacing the values for t and S in Eq. 10, it becomes

$$Re\text{-}reflected = 20 \log (1 - e^{-2 \times 1\ \mu m/6.58\ \mu m})$$

$$= 20 \log (1 - e^{-0.304}) = 20 \log 0.262$$

$$= -11.6\ dB$$

Replacing these values into eq. 9,

$$SE_{mag} = (1.3 + 84 - 11.6)\ dB = \underline{74\ dB}$$

References

1 F. W. Sears and M. W. Zemansky, "University Physics", Addison-Wesley Publishing Co., Reading, PA, 1962.

2 Federal Communications Commission "Part 15, Radio Frequency Devices". Rules and Regulations, Vol. II U.S. Government Printing Office, Washington, D.C., July 1981.

3 VDE Specification 0871
VDE Specification 0875

4 Business Week, February 11, 1985, p. 114.

5 See FCC document OST - 55.

6 H.W. Ott, "Noise Reduction Technidques in Electronic Systems", John Wiley & Sons, New York, N.Y., 1976, Chapter 6.

7 D. A. White, "A Handbook on Electromagnetic Shielding Materials and Performance", Don White Consultants, Inc., Gainesville, VA, 1980.

8 ATTENUPLATE® Products Technical Bulletin, Udylite/OMI International Corporation, Warren, MI.

9 Data from R&B Enterprises, West Conshohocken, PA, 1984.

10 D. A. Arcilesi and O. E. Roberto, Product Finishing, Vol. 48, March 1984, pp. 54-59.

11 A. D. Conty, Metal Finishing, May 1982, p. 75.

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Electronics
Session O

Subtractive Printed Circuits — The Renaissance of Liquid Negative Working Photoresist for Interconnective Circuit Technology

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SUBTRACTIVE PRINTED CIRCUITS - THE RENAISSANCE OF LIQUID NEGATIVE WORKING PHOTORESIST FOR INTERCONNECTIVE CIRCUIT TECHNOLOGY

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Other existing technologies have reached a practical limit as evidenced by the Institute for Interconnecting and Packaging Electronic Circuits, report IPC-TR-578. The limits of resolution for conventional and leading edge technologies appear to be 4 mil lines/spaces and 15 mil holes and 15 mil holes.

The use of polyvinyl cinnamate negative working photoresist allows a resolution of 1 mil lines/spaces and 15 mil holes. By setting aside some of the more recent developments and returning to a technology shelved approximately a decade ago, the Printed Wiring Board manufacturer may realize a number of significant gains in productivity, reliability, and economics (G.G. Perrin, Jr., A. Price, and S. Simoliunas, "Liquid Photoresist Process for Subtractive and Semiadditive Printed Circuitry," American Electroplaters' Society 67th Annual Technical Conference Proceedings, Milwaukee, Wisconsin, June]980).

Printed circuit manufacturing lithography involves a sequence of copper clad or unclad laminate steps used to pattern a layer of resist - a radiation sensitive polymer - that has been coated on the surface of the laminate. The steps include resist coating, baking, exposure, and development. The completed patterned resist layer serves to mask the underlying surface of the laminate, thus enabling selective etching. The lithography process depends, to a very large extent, on the satisfactory performance of the resist. Resists are typically laminated (dry films) or dipcoated (liquid films) onto substrates, baked and developed on specially designed resist processing systems. Exposure is done with mask-to-substrate aligners or pattern-to-substrate generation systems.

The conventional radiation source for exposing photoresist is ultraviolet (UV) light, energy with a wavelength in the approximate range of 350 to 450 nm, that is flooded through a mask of the desired pattern. Optical mask-to-substrate alignment can be accomplished with three types of systems - contact/proximity, scanning projection, and stepping projection.

It is significant that in lithography neither the exposure system, nor specific resist products are independent from one another, but work as a system. To a great extent the resist processing system is also important in successfully using an exposure-resist system.

Although in semiconductor work today research is centered on DUV, E-beam, x-ray resists capable of submicron resolution, printed circuit industry uses positive and negative working

photoresists.

Positive photoresists are typically three-component systems consisting of an alkaline-soluble novolac resin, a photosensitive dissolution inhibitor and a carrier solvent. The dissolution inhibitor, until it undergoes photochemical decomposition, serves to retard the dissolution rate of the novolac resin in alkaline solutions. With a positive resist, exposing radiation modifies the dissolution inhibitor and renders the polymer soluble in an aqueous developer, thus the exposed regions are developed clear. Generally, positive photoresists exhibit very good resolution, but are subject to degradation in the etching step.

Negative photoresists are typically composed of a synthetic rubber and a photoactive cross-linking agent. Negative resist action occurs as a result of polymeric cross-linking that increases molecular weight and decreases solubility. Negative resists respond in just the opposite manner as positive resists - these resists become less soluble in developers after exposure.

Typically, negative resists are capable of resolution down to 2 μm and are not considered suitable for high resolution work in semiconductor area due to excessive swelling during development and relative poor edge acuity. However, in printed circuit work, where there is a harsh etching step, the negative photoresist is the resist of choice.

In the integrated circuit fabrication liquid photoresists rather than dry films are used. The former have higher resolving power and better spreading/wetting behavior on metal and oxide surfaces.

In the plated through hole printed circuit fabrication the main methods are metal etch resist or dry film tenting. In the first method solder electroplating is an added plating step. Electroplated solder only approaches, but never reaches the true eutectic composition. Dry films do not function well below 4 mil lines/spaces limits.

Polyvinyl cinnamate type liquid negative photoresist process has been developed as an etch resist for plated through hole printed circuitry production. 1 mil lines/spaces on 1 mil thick copper circuitry can be routinely produced by this process. Also this process lends better to serialization than the standard subtractive process, since there is only copper panel plating as opposed to copper and solder pattern plating. With anodic etching, even 0.1 mil lines/spaces on 0.1 mil copper can be routinely produced. Later resist masks can be applied on bare copper circuitry, and the holes may be hot air solder leveled. In this way, galvanic couples between solder and copper are eliminated in the dense circuitry thus minimizing corrosion failures.

Our photoresist is the wet etchable type, having a viscosity of 110-114 centipoise, up to 13% total solids, filtration 0.2 μm, index of refraction 1.550 dry, 1.502 wet, bake temperature 120°c. The useful thickness is 0.1 mil when dry. The shelf life is 3 years.

O-6

Electronics
Session O

Heavy Electrodeposition of Rhodium by Pulse Current

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Heavy Electrodeposition of Rhodium by Pulse Current

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ABSTRACT

Heavy electrodeposition of rhodium is required for various industrial applications. However, cracking of the coating is observed under d.c. Thus, the pulse current method was studied and a crackfree thick deposit was obtained under a wide range of operating parameters. The current efficiency, contact resistance, porosity, microhardness and external morphology of the deposit are investigated and the results will be presented and discussed. Various areas for application of the method will be identified and discussed.

Heavy Electrodeposition of Rhodium by Pulse Current‡

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Introduction

Because of the excellent hardness and the corrosion resistant properties of rhodium, a thick deposit of rhodium is normally employed for engineering use for various applications involving repetitive wearing or under correosive environment at high temperature. e.g. electrical contact for relays. In general, thicker the deposit, better the protection and thus longer will be the life time of the relay. However, it is very difficult to deposit a thick layer of rhodium without experiencing the cracking problem due to the buildup of internal stress

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‡ The work contained in this paper is part of the M.Phil. project taken by Mr. W.S. Miu at the University of Hong Kong.

in the rhodium coating (1 - 4). Various methods had been proposed to solve this problem (5,6), such as using a special composition of electrolyte or by alloying rhodium with magnesium or selenium (6 - 7). However, they all require a high degree of control in the plating process as the usable current range is rather narrow (10 to 20 mA/cm^2) (1,2) and a high concentration of magnesium or selenium is needed to be maintained in the plating bath.

As the pulse current plating method (8,9) is known to reduce the stress buildup in the electrodeposit by allowing the impurities to diffuse away during the off cycle, it is thus investigated in the present study to see whether or not it can produce a crack-free heavy electrodeposit of rhodium with suitable hardness and morphology. Various tests had been performed on both the coatings obtained by D.C. method and by pulse method so as to evaluate the effectiveness of the pulse current method under conditions normally faced in plating process. The results will be presented and discussed in this paper.

EXPERIMENTAL

The current was controlled by the Wenking High

Power Potentiostat , Model HP 72 and the square wave pulse was generated by the Chemical Electronic Waveform Generator, Model 01 and in some of the experiments, by a homemade waveform generator. The experiments were carried out in a very simple bath containing 1-2.5 g/l rhodium and 100 ml/l H_2SO_4. The temperature was maintained at $25^{o}\pm2^{o}C$ with no agitation during the experiment. A simple electrochemical cell was used with encapsulated working electrode and a concentric platinum mesh counter electrode (fig. 1).

The working electrode was either a brass rod of 3 mm diameter or a brass sheet. The electrode areas were maintained constant in different experiments using resist ink or masking rubber so as to maintain a constant area in the region of 0.5 to 1 cm^2. The electrode surface was pretreated by firstly degreased in ultrasonic bath in trichloroethane, followed by cathodic degreasing in alkaline bath, then activated by immersing in 0.1 M H_2SO_4 solution. An undercoat of Ag was deposited on the working electrode using the Ag cyanide bath before the deposition of rhodium.

The current efficiency was determined mainly by the gravimetric method which was periodically checked using the copper coulometer to ensure the reliability of the method. The microhardness of the deposited was determined using the Leitz microhardness tester, Model DM 1000, and

Frant's (10) chemical method was used to test the porosity of the coating (11). The contact resistance (12) was examined using a four terminal system and the external of the coating was observed and recorded using the Olympus Inverted Metallurgical Microscope Model PME, the Olympus Universal Research Microscope, Model VANOX AHM-2-HL and the Cambridge Scanning Electron Microscope, Model S150.

Results and Discussions

As it is advantageous to operate a simple bath with low concentration of rhodium due to its high price, the present investigation is focussing our effort to develop a working procedure for heavy deposition of rhodium from a simple bath with low concentration of rhodium and without the addition of stress reducer or levelling agents. Thus, the bath studied contained only 1 - 2.5 g/l and 100 ml/l H_2SO_4 and was operated under room temperature and nonstirred condition. Thus, our results could provide the basic information to be used by the scaled-up plant, as improvement can be readily made by using stirred solution or at elevated temperature.

Using the pulse current method, a thick and crack-free layer of rhodium was obtained (fig. 2). It shows a great contrast with the results using d.c. method under similar conditions (fig. 2), which gave a powdery solid. Even under low c.d., when both d.c. and pulse method

produced a "coherent" deposit, it was found under SEM that numerous minute cracks appeared at the surface of the deposit using the d.c. method (fig. 3). The range of operating parameters for pulse plating was investigated thoroughly and the results show that a much wider operating range was obtained within which a satisfactory coating can be deposited. The best conditions are obtained using O/F ratio of 1:9 and c.d. range 20 - 80 mA/cm^2. An O/F ratio above 1/5 leads to unstable condition and below 1/27 takes too long a plating time. The range of c.d. to obtain crackfree deposit is wide and ranges from 10 to 160 mA/cm^2.

The coulombic efficiency is found to be affected by the concentration of rhodium and the c.d. In general, because of working in a rather low concentration of Rh (1 - 2.5 g/l), the current efficiency is expected to be low and indeed this has been observed in our study. In all cases, the pulse method is found to have higher efficiency as compared to the d.c. method (fig. 4). However, low concentration of rhodium always leads to lower efficiency for both d.c. and A.C. plating. Nevertheless, for the pulse method, it is much better to use a short plating time (0.1 ms) for the given 1/9 on/off ratio (fig. 4). The c.d. can also affect the current efficiency. Again in this case, the pulse method is shown to be better in all cases as compared to the d.c. method (fig. 5). Higher

c.d. leads to lower efficiency, which is applying to more or less the same extent for both a.c. and d.c. method, though in the pulse method, the short plating time is still giving the best current efficiency.

The following properties of the crackfree deposit were determined and the results were correlated with the operating parameters of the pulse method: contact resistance, porosity and microhardness, as they are important criteria for the application of rhodium as coating material for engineering use. Frant's chemical method was used to indicate the porosity of the coating as determined by the amount of zinc leached out to the solution at given conditions. The results are shown in fig. 6 The pulse method is shown to produce a less porous coating and for an O/F ratio of 1:9, 0.1 ms plating time is found to give the best results, as it is the least porous one the same porosity is obtained at a much wider range of c.d.

The contact resistance (13,14,15) is important in the application for electrical contact point by coating rhodium. Again, the pulse method is found better than the d.c. one and 0.1 ms plating time is the best for an O/F ratio of 1:9 (fig. 7). Similar trend is also observed for the hardness of the coating (fig. 8).

This is especially obvious at high c.d. when the Vicker's hardness number for the d.c. coating drops rapidly.

Besides using silver as the substrate, we had also used molybdenum, stainless steel and titanium as the base material for pulse plating of rhodium. The results obtained are very satisfactory. We had also applied the above method for plating rhodium for electrical contact points in a bonding machine in one of the factory in Hong Kong. The results obtained is overwhelmingly successful as up to now, the life-time of the contact point relay had been more than fifth times their normal lifetime using the d.c. plating method and yet the bonding machine is still running!

References

1. F.H. Reid, Trans. Inst. Metal Finishing, 36. 74(1958-59).
2. F.H. Reid, Metallurgical Reviews, 8(30), 167(1963).
3. L. Serota, Metal Finishing, 64, 84-88 and 82-84(1966).
4. H.M. Smith, Metal Finishing, 81(3), 55(1983); 81(4), 63(1983).
5. A.E. Yaniv, Plating, 54, 721(1967).
6. M.P. Pavanam, V. Raman and B.A. Shenoi, Surf. Technol., 12, 351(1981).
7. C.F. Fung, New Technology for Surface Treatment, Shanghai Science and Technology Publisher, 1981; p. 69-71.
8. N.IBL, Surf. Technol., 10, 81(1980).
9. J. CI. Puippe and N. IBL, J. Appl. Electrochem., 10, 775(1980).
10. F.H. Reid and W. Goldie, Gold Plating Technology, Electrochemical Publication Ltd., 1974; p. 393-403.
11. M.S. Frant, J. Electrom. Soc., 108, 794(1961).
12. ASTM B539-70 (Reapproved 1975), 10 pp.
13. R.I. Gurovich, J. Appl. Chem. (USSR), 41, 1168(1968).
14. R. Olson, Product Finishing, 4, 68(1976); Plat. and Surf. Fin., 68(2), 38(1981).
15. V.I. Belokon, B.B. Chernov and N. Ya Kovaskii, Elektrokimiya, 11(11), 1655(1975).

Fig. 1 Illustration of the Electrochemical Cell

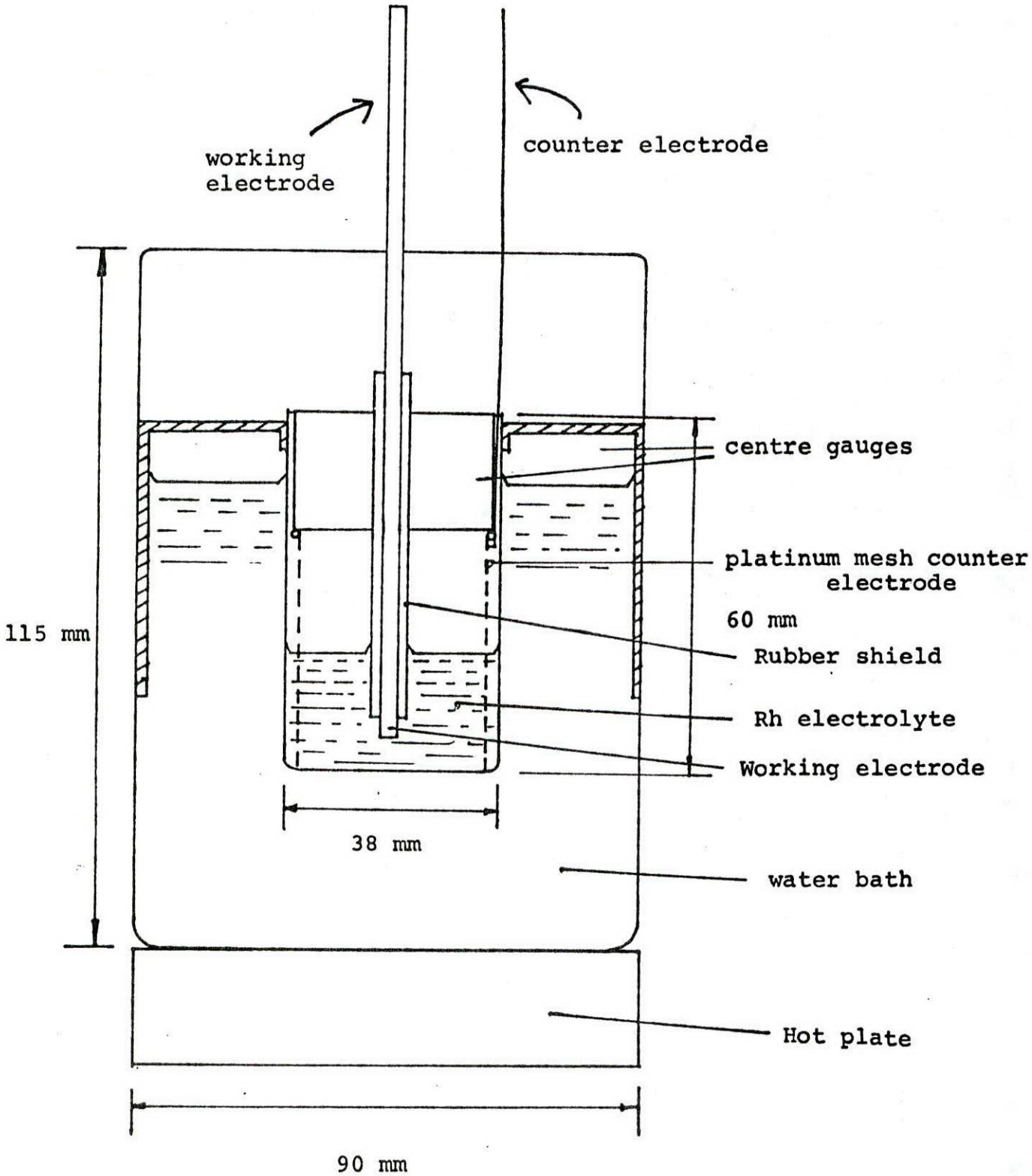
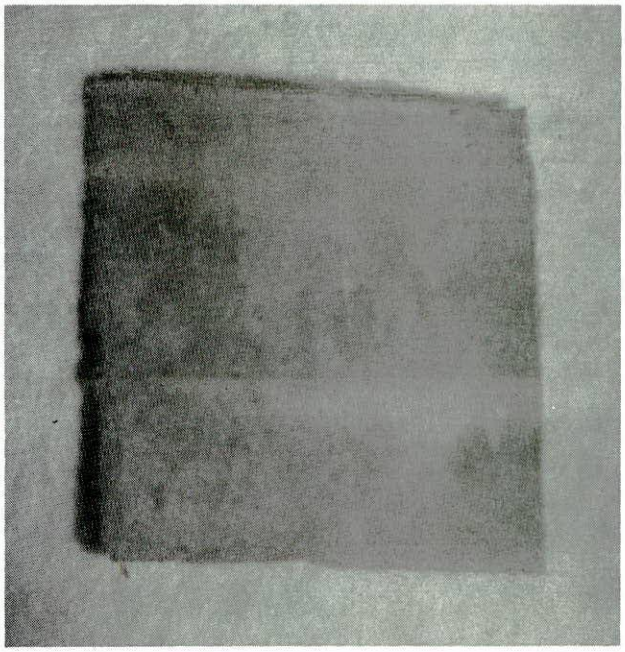


FIG. 2 External morphology of the rhodium deposit using pulse and d.c. method

A) Pulse method



c.d. = 40 mA/cm^2
O/F ratio = 1/9
on time = 0.1 ms

B) D.C. method
c.d. = 40 mA/cm^2

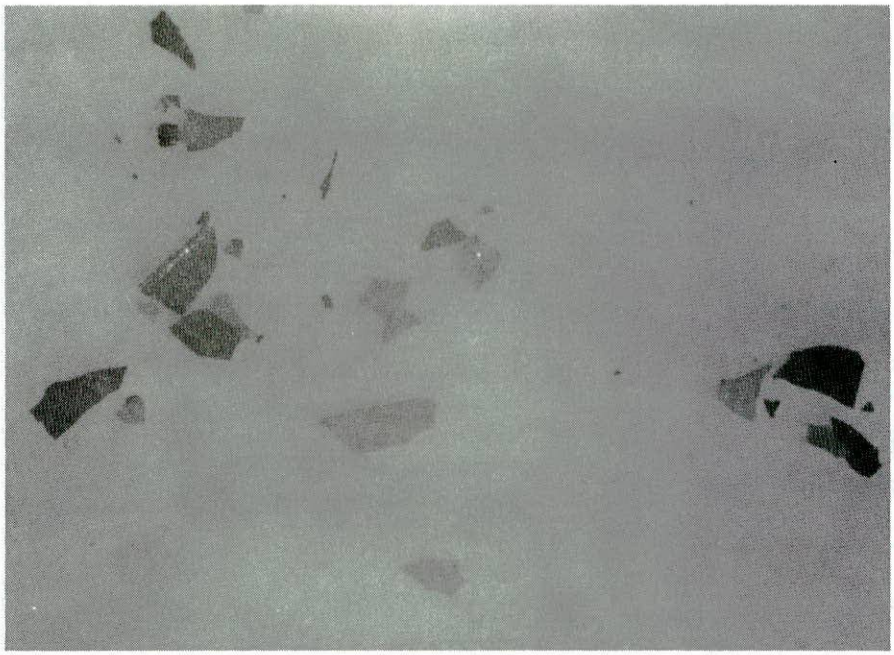
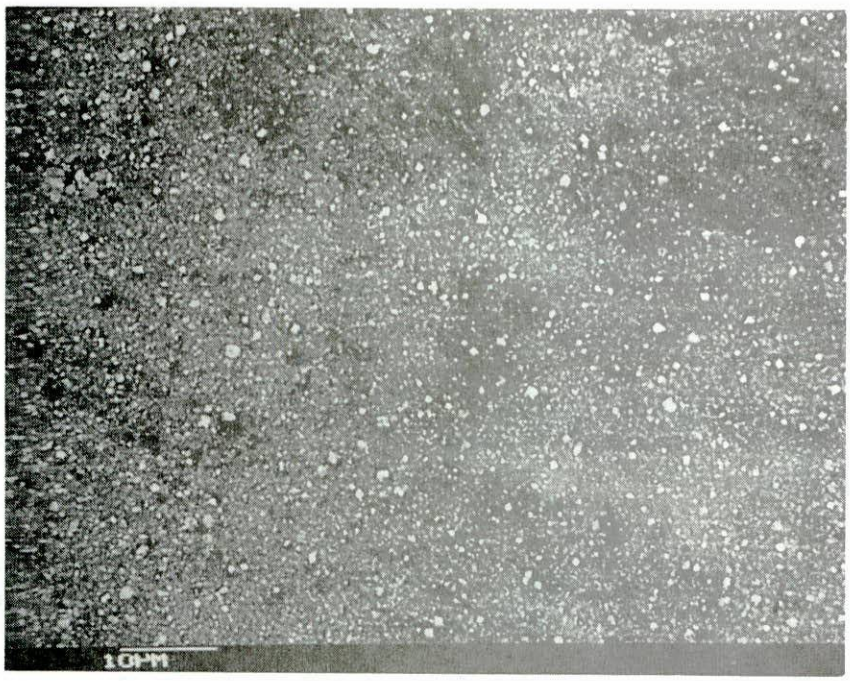


FIG. 3. External features of the rhodium electrodeposit surface as reviewed by the SEM

A) Pulse Method

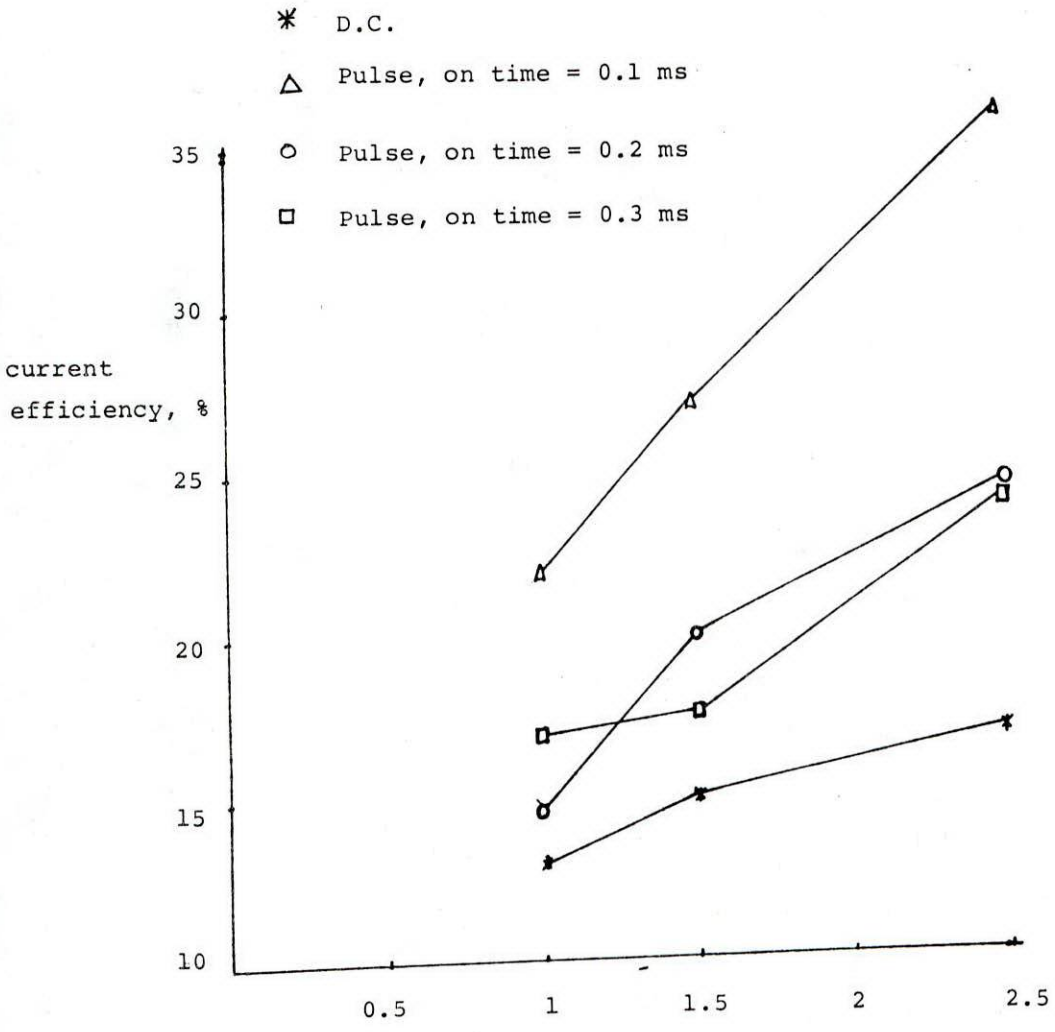


c.d. = 40 mA/cm^2
O/F ratio = 1/9
on time = 0.1 ms
plating time = 2 hrs

B) D.C. method
c.d = 40 mA/cm^2
plating time = 2 hrs



FIG. 4 The effect of rhodium concentration on the current efficiency



N.B. 1) Temperature of bath = 18 - 20°C
2) H_2SO_4 concentration = 100 ml/l
3) c.d. for both D.C. and Pulse method = 40 mA/cm^2
4) For Pulse method, O/F ratio = 1/9

FIG. 5 The effect of current density on the current efficiency

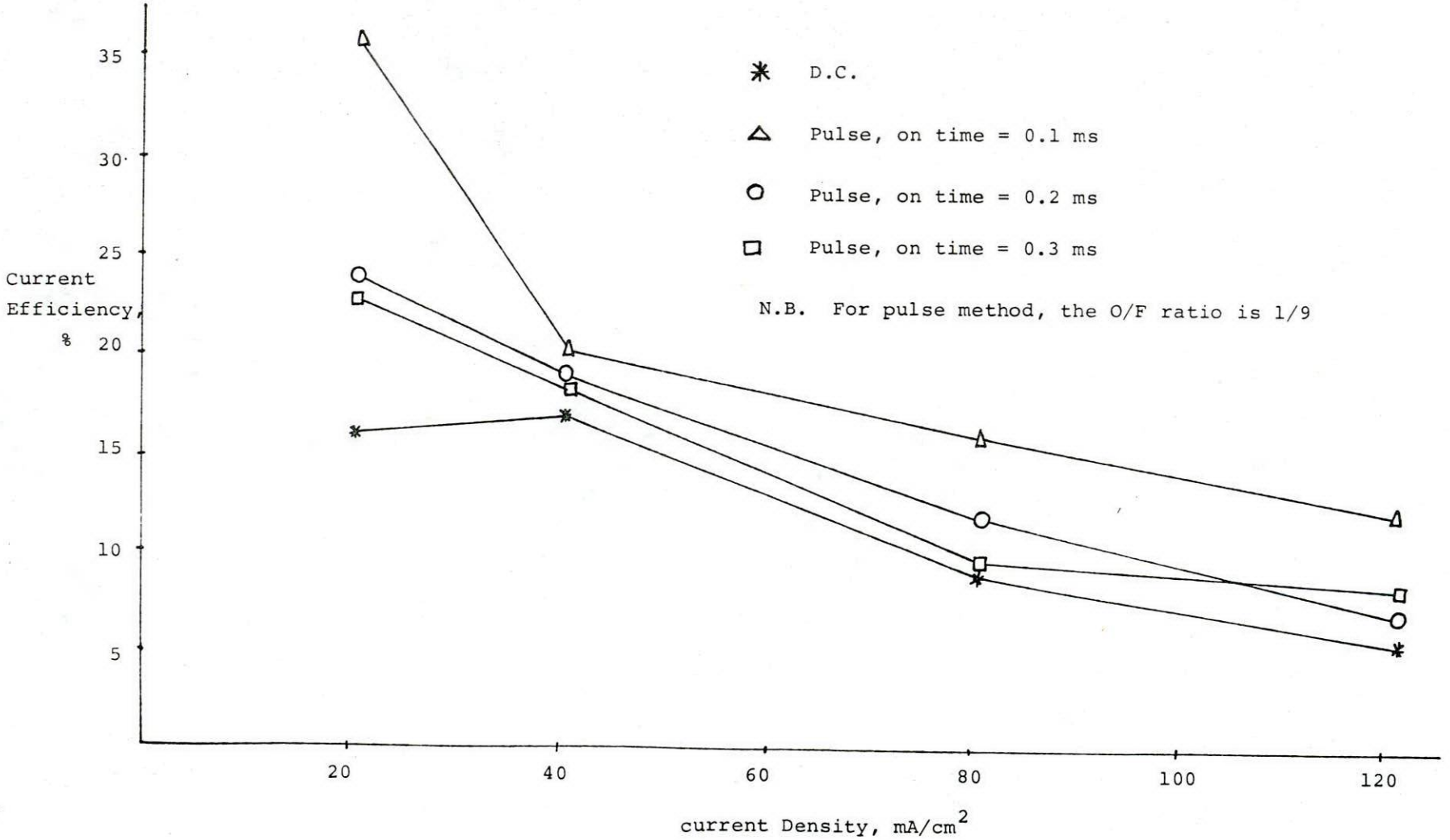


FIG. 6 The porosity of the rhodium coating

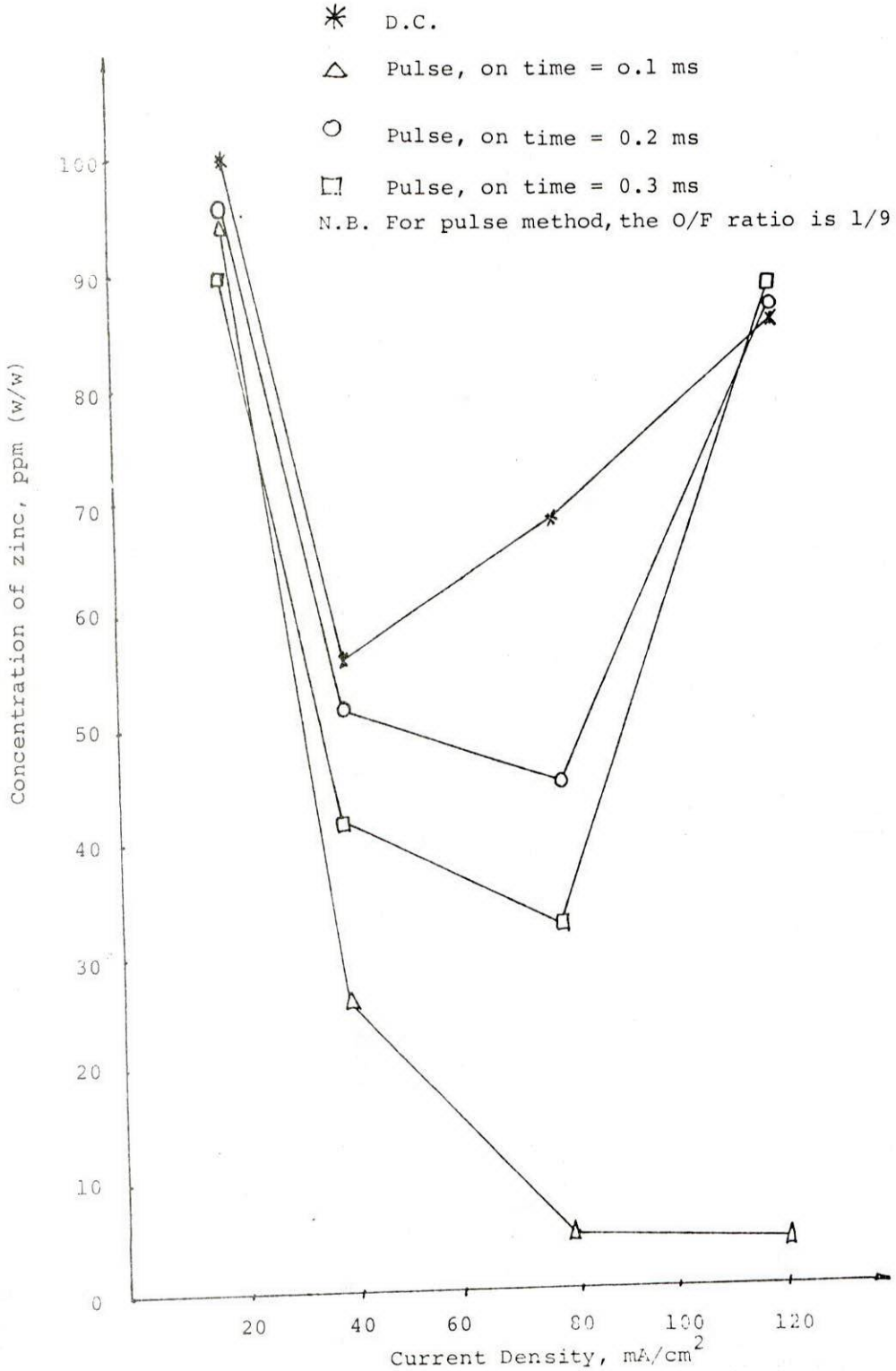


FIG. 7 The contact resistance of the rhodium coating

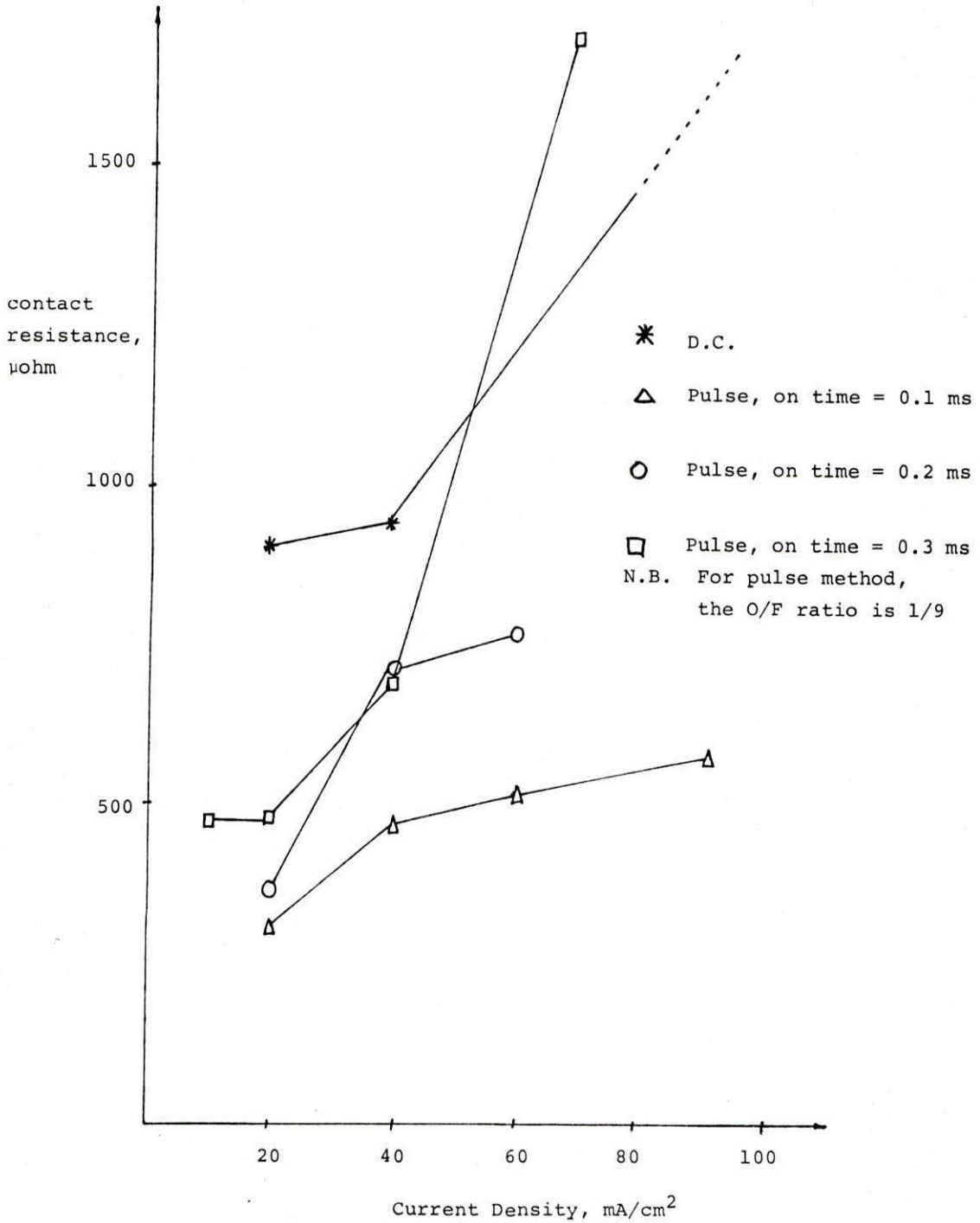
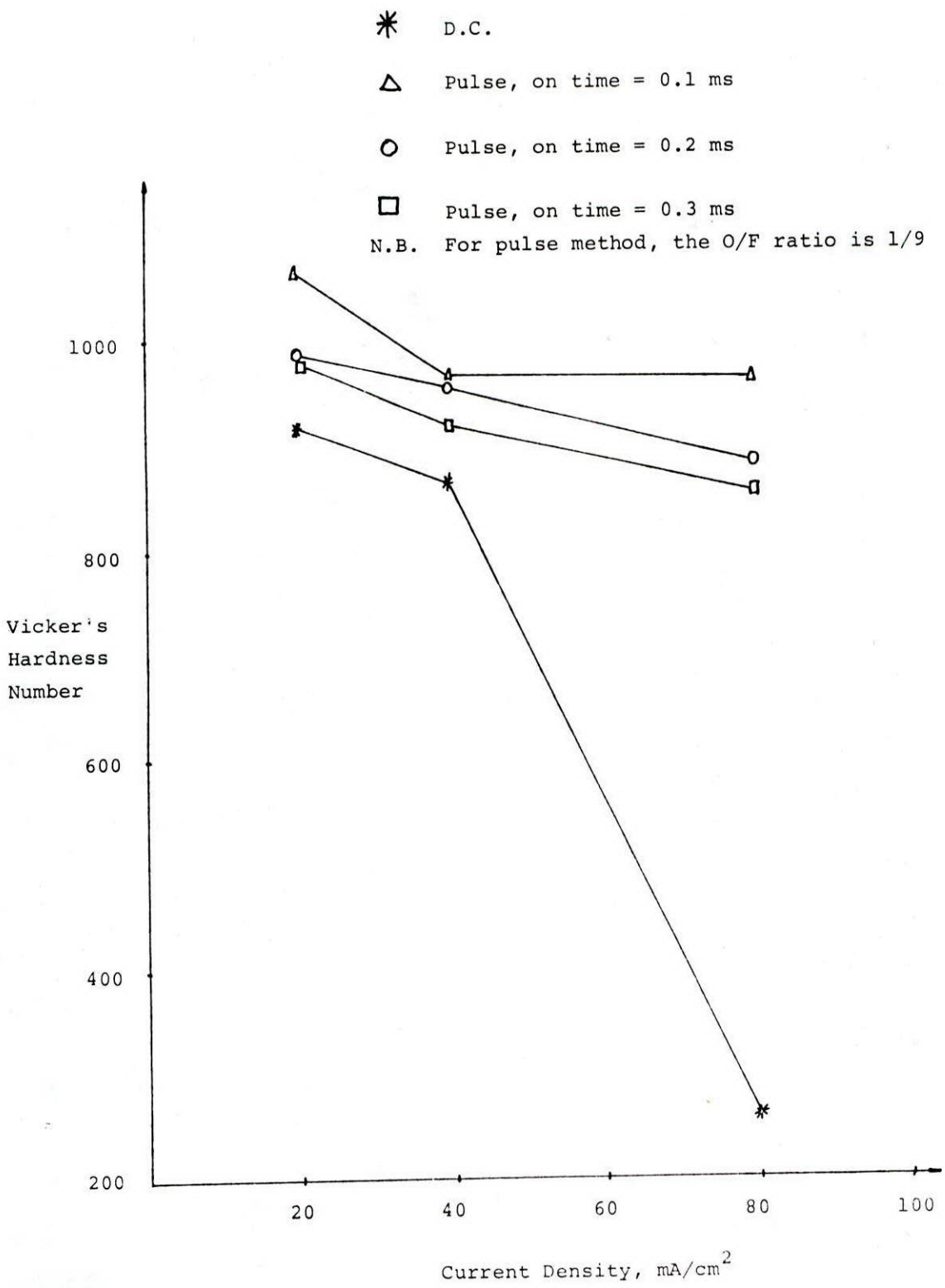


FIG. 8 The microhardness of the rhodium coating



Alloy Plating
Session P

AES Research Project 58
Electrodeposition Of Nickel-Chromium Alloys

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ABSTRACT

A process to electrodeposit alloys of nickel and chromium is described, along with a description of the electrochemistry. Some of the properties of this new kind of alloy are given, including corrosion and hardness. The alloy was shown by transmission electron microscopy to consist of a solid solution of chromium in nickel. The grain size can be controlled by varying either DC current density or by manipulating pulse parameters.

INTRODUCTION

It is recognized that coatings can often provide surface properties equivalent or superior to bulk materials of the same nominal composition. It has been estimated, that by using coatings with the properties of stainless steel that up to a 30 wt% savings in imported chromium could be achieved (1). Chromium seems to be important in establishing passivity in many environments. It was reported by Kruger and McBee (2) that for materials with chromium contents greater than 20 wt%, the surface would be covered with an amorphous film more resistant to corrosion than its crystalline counterpart. They found that materials whose chromium content was less than this amount were covered with a crystalline film.

Throughout this project both direct current and pulsed galvanostatic deposition were used to deposit nickel-chromium alloys. Pulsing the current provides two additional parameters that affect the deposition process in important ways. These parameters are duty cycle and cycle time. Pulsing can also provide another parameter not examined here--the current during the "off" time. These parameters are illustrated in Fig. 1. In this study the "off" current was set to zero. Among the advantages that pulsing can provide are: (1) relief from hydrogen embrittlement; (2) control over mass transport; and (3) small grain size because at very high current densities (high overpotential) grain size is reduced due to rapid nucleation and grain growth.

The potential applications for the electrodeposition of stainless steel type coatings [Fe, Ni, Co-Cr] has resulted in a great deal of work done on development of a suitable process to deposit these alloys. This subject was reviewed by Chisom (3) who at the time concluded that there was no commercial process available to electrodeposit a useful Fe-Ni-Cr alloy. Typical problems encountered were: (1) inability to deposit coatings thicker than 25μm;

(2) inability to deposit alloy containing more than a few percent chromium; and (3) highly stressed or dendritic coatings. Recent papers of Hayashi (4,5) and the patent of Stromatt (6) seem to describe more successful processes. Hayashi's study was of an iron-nickel-chromium process which made use of electrolytes containing chromium (III) and various complexing agents. Hayashi found that by pulsing the current, coatings could be produced with crystal structures very much different than those observed by direct current deposition techniques. This final report summarizes our investigation of a process to deposit a simple binary alloy of nickel with varying amounts of chromium along with an evaluation of the corrosion performance, wear performance, and a discussion of how these properties are affected by microstructure.

Polarographic Study of Electrolyte Components

The functions of the various components of the plating electrolyte, shown in Table I, were investigated in a series of polarographic experiments. Graphical analysis of polarograms, obtained from the reduction of 7.0 mM Cr(III) or 5.0 mM Ni(II) in various supporting electrolytes, yielded values of the half-wave potentials ($E_{1/2}$) for the reduction of these metals. Each $E_{1/2}$ value corresponds to the reduction potential for the corresponding element in the given supporting electrolyte. Potentials are reported in millivolts (mV) vs. the saturated calomel electrode (SCE).

Table I. Electrolyte Composition

Constituents	Amounts
$NiCl_2 \cdot 6H_2O$	30 - 40 g/L
$CrCl_3 \cdot 6H_2O$	100 g/L
Formic Acid (95%)	35 - 40 ml/L
NaBr	15 g/L
NH_4Cl	50 g/L
Boric Acid	30 - 40 g/L
Sodium Citrate Dihydride	80 g/L
non-ionic, non-sulfur containing surfactant	according to type
pH	3.8
T	30 - 40°C

Experimental $E_{1/2}$ values for the different supporting electrolytes used are summarized in Table II. The compositions and pH values of the supporting electrolytes were chosen to determine the effect of citrate ion (Cit^{3-}) on the reduction potentials for Cr and Ni. Preliminary investigations indicated that precipitation of $Cr(OH)_3$, and $Ni(OH)_2$ in solutions of pH greater than 5.5 was suppressed in the presence of citrate, but not in the presence of the formate ion or boric acid (not listed in Table). These results point to the citrate ion as the species most likely responsible for the suspected shifts in the reduction potentials for Cr(III) and Ni(II).

TABLE II. HALF WAVE POTENTIALS FOR NICKEL(II) AND CR(III) IN VARIOUS SUPPORTING ELECTROLYTES.

		$E_{1/2}$ - values (mV vs SCE)[a]		
Supporting Electrolyte	pH	Cr 1st wave	Cr 2nd wave	Ni
Standard reduction potentials		-654	-989	-496
0.1M KNO_3	3-4	-940 (aged)[b]	-1410	-1075
0.1MNa_3Cit+HCl	3-4	-925	-1480	-1085[c]
0.1M Na_3Cit	7	-1190[c]	-1720	no wave
0.1M KNO_3	3-4	-850[d]	-1410[d]	-1080[d]
0.M KNO_3 + 0.1M Na_3 Cit	7	-1140[d]	-1710[d]	no wave not
0.075M KNO_3 + 0.1M H_3BO_3	3-4	-905	-1450	-1065

Notes: [a]Separate solution used for Ni(II) and Cr(III) determinations except as noted.

[b]-570 mV in freshly prepared solution.

[c]Wave height is reduced

[d]$E_{1/2}$ values from solution containing both 7.0 mM Cr(III) and 5.0mM Ni(II).

The polarograms for Cr(III) consisted of two waves. The first wave corresponds to the reduction of Cr (III) to Cr(II), and the second corresponds to the reduction of Cr(III) to Cr metal (8). Cr(III) solutions freshly prepared from $CrCl_3 \cdot 6H_2O$ were green in color and gave an $E_{1/2}$ value of -570 mV for the Cr(III) - Cr(II) reduction; solutions prepared from $CrCl_3 \cdot 6H_2O$ stock solution after heating and aging for 12 hr. were purple in color and gave an $E_{1/2}$ - value of -940 mV. This shift reflects the greater reversibility of the green $Cr(H_2O)_4\ Cl_2^+$ species as compared to the purple $Cr(H_2O)_6^{3+}$ species (9). The $E_{1/2}$ values remained unchanged for the reduction of Cr(111) to Cr metal from both solutions.

The data from Table II indicate that citrate ion at neutral pH complexes Ni(II). Reduction of the Ni(II) -citrate complex does not take place prior to the onset of solvent breakdown, i.e. -1900mV in 0.1 M citrate at pH 7. Any current resulting from the reduction of the Ni-citrate complex is obscured by the much larger cathodic current resulting from the production of H_2. At pH 3-4, the $E_{1/2}$ value for Ni(II) is unchanged, but the wave height is reduced by 40-50 percent. This indicates that approximately half of the Ni(II) is complexed by citrate ion at this pH, forming the non-electroactive Ni-citrate complex. The remaining, uncomplexed Ni(II) is still reduced at the same potential observed in the absence of citrate. The pH dependence of this decrease in the fraction of Ni(II), present as uncomplexed Ni^{2+}, is consistent with the conditional formation constant for the Ni(II)-citrate complex (10), which has a value of 1.6 at pH 2 and 2.5×10^{-4} at pH 7.

The data for Cr indicate that a Cr(III)-citrate complex is also formed at pH 7 as shown by the 250-300 mV shifts in the potentials of the Cr(III) reduction waves. In contrast to the behavior of the Ni-citrate complex, the Cr-citrate

complex is electroactive and is reduced at the mercury electrode. At pH 3-4, the $E_{1/2}$ values for the reduction of Cr(III) are similar to those observed in the absence of citrate, indicating that Cr(III) is not appreciably complexed by citrate ion (citric acid) at this pH.

Data from the literature indicate values for the stability constant of 2.9×10^8 for the Cr(III)-citrate complex (11,12) and 1.7×10^5 for the Ni(II)-citrate complex(11,13). Based on these stability constants and classical polarographic theory (14), the negative shift in the $E_{1/2}$ value caused by citrate ion would be greater for Cr(III) than for Ni(II). However, the reductions of both Cr(III) and Ni(II) are highly irreversible, as shown in Table II by the large differences between the standard reduction potentials and the experimental $E_{1/2}$ values in KNO_3 solution. Because of this irreversibility, the reduction potentials for Cr(III) and Ni(II) are both governed by kinetic factors, and the shifts in the reduction potential are not predictable from classical polarographic theory. The experimental results indicate that the Ni(II)-citrate complex is not electroactive at potentials more positive than -1900mV, but that the Cr(III)citrate complex can still be reduced at the mercury electrode. These results suggest that the electroinactivity of the Ni(II)-citrate complex is the prime factor in the effect of citrate ion on the composition of Ni-Cr alloys.

The $E_{1/2}$ values for the simultaneous reduction of Cr(III) and Ni(II) show no substantial differences from the corresponding values obtained in solutions containing only one metal, both in the presence and absence of citrate ion. This indicates that the mechanisms for the reduction of Cr(III) and Ni(II) remain unchanged in solutions containing both metal ions.

The data for the reduction potentials obtained in 0.075 M KNO_3 + 0.1M H_3BO_3 show no significant differences from values obtained in the absence of H_3BO_3. This indicates that H_3BO_3 does not influence the mechanism of reduction of

Cr(III) or Ni(II). The pH of the plating bath, 3.5, is also too low to result in significant buffering action by H_3BO_3. H_3BO_3 has a first acid dissociation constant of 5.8×10^{-10} and therefore has negligible buffering capacity in solutions below pH 9. This pH value is significantly greater than that expected within the depletion layer as a result of reaction of H^+ ions to form H_2. Inspection of the dissociation constant for formic, citric, and boric acids indicates that a pH of 9 is not reached prior to quantitative dissociation of formic and citric acids to form formate and citrate (Cit^{3-}) ions.

These considerations also indicate that formic acid, present in the plating solution at a concentration of 0.9 mol/L, functions primarily as a buffering agent. Formic acid has a dissociation constant of 1.8×10^{-4}, and the formic acid/formate ion system has maximum buffering capacity at a pH of 3.75, close to that of the plating electrolyte.

Effect of Citrate Concentration and Current Density on Composition and Current Efficiency for Ni-Cr Electrodeposition

The elemental composition of Ni-Cr electrodeposits and the overall current efficiency for galvanostatic deposition were studied as functions of the concentration of citrate ion in the plating bath and the current density. The electrodeposits were produced on interchangeable, sheet brass cathodes of 1.00 cm^2 area in stirred solutions under galvanostatic conditions. The cell current, time of deposition, pH, and concentration of sodium citrate in the electrolyte were recorded for each run.

These deposits were analyzed by atomic absorption spectrometry (AAS). Each brass cathode (with its deposit) was dissolved in 20 mL aqua regia (1 HNO_3:3 HCl), and the resulting solutions were diluted to 100.0 mL with distilled water. A 1:5 dilution of each solution was then prepared, containing sufficient

added HCl to bring the concentration of H^+ to 2.6 mol/L. The concentration of Cr and Ni in each of these solutions were obtained by comparison with calibration curves (absorbance-concentration) obtained using standard solutions (5-25 ppm) of Cr(III) and Ni(II) in 2.6M HCl. Absorbance measurements were performed at wavelengths of 232 nm for Ni and 357.8 nm for Cr using an acetylene-air flame. For each sample, that solution was used which had an absorbance within the range of the corresponding calibration curve.

Weight percentages of Cr in the deposit were calculated directly from the concentrations (ppm) of Cr and Ni in the sample solutions, assuming each deposit to consist solely of Cr and Ni. Current efficiencies were calculated from the total weights of Cr and Ni in each deposit, the deposition current, I_{dep}, and the deposition time, t_{dep}, assuming deposition from Cr(III) and Ni(II).

The results of these experiments are presented in Table III. The weight percentage of Cr in the deposit reaches a maximum at sodium citrate concentration of 50-100 g/L and decreases at larger concentrations. The current efficiency for the electrodeposition generally decreases with increasing concentrations of sodium citrate. This behavior is consistent with the following model, which is based on the results of the polarographic experiments, as well as on known properties of Cr(III), Ni(II), and citric acid.

Table III. Composition of Ni/Cr Deposits as Determined by AAS

$[Na_3Cit]$ (g^{L-1})	pH	I_{dep} (mA)	t_{dep} (min)	Wt% Cr	current efficiency (%)
0	2.6	100	60	5.46	8.32
0	1.7	150	62	6.95	11.8
50	3.0	100	90	16.5	13.2
50	3.6	150	80	10.8	7.93
100	4.2	100	75	15.1	3.23
100	4.0	150	85	7.04	3.32
150	4.4	100	65	7.87	3.52
150	4.4	150	65	5.51	1.11
150	3.7	100	69	8.31	2.34
180	--	100	145	6.08	1.13
230	4.5	100	90	4.27	0.700
230	3.6	100	125	10.5	0.808
230	--	150	100	6.20	0.897

In the absence of sodium citrate, the percentage of Cr in the deposit is low as shown in Table III. This reflects the more negative reduction potential of Cr(III) to Cr metal, as compared to the Ni(II) reduction, in the absence of complexation. At the pH of the plating solution, 3.5, citrate ion from the added sodium citrate is predominantly present as citric acid and consequently only partially complexes Cr(III) or Ni(II). However, the reaction of H^+ at the cathode to form H_2 increases the pH of the solution in the depletion layer, directly adjacent to the cathode surface, by as much as several pH units(15). The increase in pH in this layer is sufficient to cause significant dissociation of citric acid to citrate ions, which are then available for complexation of Cr(III) and Ni(II). Because the kinetics of formation of the Cr(III)-citrate complex from $Cr(H_2O)_6^{3+}$ are very slow ($k=1.5\times10^{-3}$ sec^{-1} at 25° and pH=5.4(16), the Cr(III)-citrate complex does not have time to form

during the period of residence (typically << 1 sec) of the $Cr(H_2O)_6^{3+}$ ions in the depletion layer. In contrast, $Ni(H_2O)_6^{2+}$ ions react rapidly with citrate ion to form the Ni(II)-citrate complex, typical rate constants for liquid-exchange reactions of $Ni(H_2O)_6^{2+}$ being on the order of 10^4 sec^{-1} (17). Hence, the solution in the depletion layer contains Ni(II) predominantly in the form of nonelectroactive Ni(II)-citrate complex, and the effective concentration of electroactive, uncomplexed $Ni(H_2O)_6^{2+}$ is reduced. This results in an increase in the percentage of Cr in the Ni-Cr deposit. The magnitude of this enhancement [of the percentage of Cr in the deposit] reaches a maximum at a sodium citrate concentration of about 75 g/L.

Further increases in citrate concentration, beyond 100 g/L, cause significant decreases in the percentage of Cr in the deposit. This effect likely arises from the partial complexation of Cr(III) in the bulk solution (outside the depletion layer), which is thermodynamically favorable at this pH but kinetically slow (16). Because the citrate at pH 3.5 is predominantly present as citric acid, significant concentrations of sodium citrate must be added to cause sufficient complexation of the $Cr(H_2O)_6^{3+}$ present, and the effect is not apparent until the added concentration of sodium citrate exceeds the concentration of Cr(III) present. This complexation in the bulk solution is not subject to the kinetic limitations which govern the transient complexation of Ni(II) within the depletion layer. The majority of complexation of Cr(III) most likely occurs in the preparatic of the plating solution.

Complexation of the Cr(III) at high concentrations of added sodium citrate reduces the percentage of Cr in the deposit. This is because the reduction potential of the Cr(III)-citrate complex, as demonstrated in the polarographic experiment, is more negative than that of the free $Cr(H_2O)_6^{3+}$ ion.

Increases in the concentration of sodium citrate uniformly result in decreases in the overall current efficiency for the galvanostatic electrodeposition. This

effect is readily understood by considering the partial currents at the cathode. At constant pH, negative shifts in the electrode potential increase the partial current for the reduction of H^+ to H_2. Hence, the fraction of the total electrode current which effects reduction of Cr(III) or Ni(II) is reduced, and the current efficiency decreases. At low concentrations of sodium citrate, negative shifts in the cathode potential result from the complexation of Ni(II) by citrate in the depletion layer. At high concentrations of added sodium citrate, the negative shift in the cathode potential results from the negative shift in the reduction potential for Cr(III) produced by its complexation with citrate ion.

The above effects rely on the pH of the electrolyte as the major controlling factor for the complexation of Cr(III) and Ni(II). Large decreases in the bulk pH of the solution make it impossible to reach a sufficiently high pH in the depletion layer to cause complexation of Ni^{2+}; also, the complexation of Cr(III) in the bulk solution is hindered at low pH. Increases in the bulk pH result in complexation of Ni^{2+} by citrate in the bulk solution, as well as in precipitation of $Cr(OH)_3$ in the depletion layer.

Parameter Study

It has been reported by Brenner (18) that in order to form an alloy it is desirable that the deposition potentials of the different species be as close together as possible--generally within two tenths of a volt. If the potentials are further apart than this, the more noble of the two metals will usually tend to deposit at its limiting current.

The chromium deposition potential in the absence of complexes is in the neighborhood of -0.744 V vs. SHE and nickel about -0.250 V vs. SHE. The difference is about -500 mV.* In the electrolyte given in Table I, the deposition potential for nickel is about -1.1 V SCE at a pH of 3 and for chromium -1.37. The difference now is about 270 mV, which is close to Brenner's criteria for

*These are thermodynamic values. The actual potentials are influenced by the kinetics of the reaction as shown in Table II.

alloy formation. This does not take into account kinetic effects resulting from pH changes within the diffusion layer.

The amount of chromium in the electrolyte was optimized fixing the concentration of nickel chloride hexahydrate at 30 g/L and varying the chromium chloride hexahydrate from 0 to 130 g/L. Measurements of chromium content of the coating were made by X-ray fluorescence using the procedure described by Rasberry and Heinrich (19). It was found that the chromium content of the deposit exhibited a peak at a solution content of 100 g/L of chromium hexahydride as is shown in Fig. 2.

The amount of chromium in the electrolyte was then fixed at 100 g/L and the nickel content varied. The chromium content in the coatings was found to peak at 30 g/L nickel, as also shown in Fig. 2. This value was then fixed for future experiments. The maximum chromium current efficiency for the deposition of chromium was found to be around 14.4 percent by weight. This value compares with the current efficiency of typical hexavalent chromium plating solutions which is usually around 13 wt%.

The dependence of the current efficiency for chromium deposition on the current density is shown in Fig. 3. At about 20 A/dm^2 direct current deposition yields coatings of about 18 wt% chromium.

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

Pulsed Current Deposition

Pulsed current deposition was undertaken in order to determine the effect on coating morphology and composition. Duty cycle in the following discussion is defined as:

$$(1)\ \text{Duty Cycle} \equiv \frac{t_{on}}{t_{on} + t_{off}}$$

Current density is the value during the On-Time. The effects of pulsing the current in the above manner were discussed by Ibl (20,21) and Cheh (22, 23) and a number of investigators have found important effects on both morphology and composition (21, 22). During the On time, the concentration of both nickel and chromium ions is reduced within a certain diffusion distance. This diffusion layer pulsates with the same frequency as the applied current as described by Ibl (21). Its magnitude is also related to the peak density but reaches a limiting value governed by the diffusion coefficient. During the off-time the concentration of the reactants builds up again and, if enough time is passed, will reach the equilibrium concentration of the bulk electrolyte. Typically, for frequencies of several hundred cycles per second, this diffusion distance is rather less than the corresponding diffusion distance for direct current deposition; therefore, it can be expected that the resulting morphologies of coatings under direct current deposition will be more dendritic or nodular than coatings formed under pulsed conditions. This is only a general description and a rigorous treatment of the problem would have to take into account the diffusion parameters of each ion separately as well as other mass transport conditions. If this diffusion distance is comparable to the dimension of the surface roughness, then the asperities of the surface which protrude into the diffusion layer will be exposed to a concentration of reactants which is higher than at the average

surface and therefore will experience a higher deposition rate. During pulsing, however, the average diffusion distance can be made small compared to the surface roughness so that the surface sees a uniform concentration of ions even at its rough places. Then the deposition rate is everywhere about the same and a smoother deposit results.

The effects of pulsed galvanostatic deposition on chromium content were determined as a function of current density and period as shown in Fig. 5, for a fixed off time of 2 ms. Generally as the current density increases, so does the chromium content for all duty cycles from 20 to 90%. However the higher the duty cycle the higher the chromium content. There is a significant difference in the surface morphology of deposits produced by different waveforms as might be expected from Ibl's explanation of the deposition process. In Figs. 6a and 6b a comparison is made of surface morphology, using scanning electron microscopy, between a typical direct current deposit and a coating produced by pulsed current deposition. The surface of the direct deposit is clearly much rougher.

The effects of increasing duty cycle and increasing current density are shown in Figs. 7 a, b, and c. The diffraction patterns indicate a single phase solid solution of chromium in nickel. As the current increases, the grain size decreases. The duty cycle seems to effect the grain size in the opposite way as Fig. 7 c illustrates.

Cross sections of a typical coating show that the deposit grows in a layered structure with the layers exhibiting marked chromium concentration gradients. The scanning elecron micrograph shown in Fig. 8 is of a coating produced at a 33% duty cycle at 50 A/dm^2 and an On-Time of 0.2 ms. It was deposited on copper and etched in aqua regia.

PROPERTIES

Hardness

Microhardness measurements have been made on several coatings as a function of duty cycles and are shown in Fig. 9, for current densities of 25 A/dm2 and

50 a/dm^2. Both current density values result in a minimum microhardness at around 50% duty cycle. The chromium content generally increases with the duty cycle so that higher hardness alloys are also high in chromium content.

Wear Performance

The wear performance was characterized by dry sliding using the ring on block geometry (22). These results are shown in Table IV and indicate that for the sample tested, the wear rate is between that of hardened tool steel and that of nickel. For comparison, nickel-phosphorus wear rates are included in the table.

TABLE IV. A COMPARISON BETWEEN WEAR RATES OF NICKEL, NICKEL CHROMIUM, NICKEL PHOSPHORUS AND HARDENED O-2 TOOL STEEL.

DRY SLIDING WEAR RESULTS (10 N load, argon, 20 m/s)

ALLOY	FRICTION COEFFICIENT	WEAR RATE (10^{-4} mm^3/m)
Nickel (from a sulfamate electrolyte)	0.97	3.4
Nickel-Chromium 20 wt.%)	0.98	2.3
O-2 tool steel (hardened 670 KNH)	0.71	1.1
NiP (12 wt%P) homogeneous	0.8	1.3 $\pm$ 0.2
Ni-P (12 wt% P) Composition modulated or layered	0.78	0.99 $\pm$ 0.16

Corrosion

Brass discs were coated by pulse-plating at conditions which led to nickel-chromium alloys with 5, 10 and 15% Cr. The thickness of the deposits was 50µm. The discs were mounted on a standard cell holder to expose an area of 3.5 cm^2. For comparison, commercial "Nichrome" (20%Cr) discs were similarly exposed. The specimens were polarized in a 3.5% solution of NaCl in distilled water. The solution was deaerated for several hours by bubbling high purity

argon, prior to the experiment. The specimens were first cathodically reduced at -650 mV(SCE) for 5 minutes and then potentiodynamically scanned at a rate of 0.1mV/sec to 0.150 mV(SCE). The experiments were then repeated for each alloy after soaking in aerated solutions at open circuit for 1 hour. Cathodic and anodic plots were recorded and corrosion rates were assessed by extrapolation of Tafel slopes to the mixed potential. The anodic polarization was extended into the passive range and then reversed in order to check the tendency for pitting. A polarization resistance measurement was also carried out at a span of 50mV around the open circuit potential.

The mixed potential after exposure at open circuit in an aerated solution was -0.210V(SCE) i.e. in the initial part of the limiting current range. Polarization resistance measurement around this potential was 2.964×10^{-5} corresponding to a corrosion rate of 0.8μm/hr. Anodic and cathodic curves around the "Mixed potential" showed Tafel slopes (computed by the system) to be 0.082 and 0.087 respectively which corresponded by extrapolation to corrosion rates of between 0.6(b_a) and 0.8μm/yr(b_c).

Reversing the scan in the passive range showed no evidence for passivity breakdown ("Pitting tendency") at 0.092V(SCE).

Similar measurements were also taken for 5 and 15% Cr deposited films and some for the commercial "NICHROME" alloy with 20% Cr. The results are summarized in Table V.

Table V. Corrosion behavior in 3% NaCl of Electrodeposited Ni-Cr alloys

%Cr	nature of Polarization curve	Width of Passivity	corrosion rate (μm/yr) By b_a	by b_c	by pol. res.
5	Primary and secondary passivity	150mV (Prim.)	3.6	1.04	0.63
10	Primary indication and secondary passivity	20mV(Seco,)	0.6	0.8	0.8
15	wide passive range	400	1.3	4.7	4.1
20 "Ni-chrome"	wide passive range	1600			

It follows from the above results that all three coatings exhibited a very good corrosion resistance at a relatively corrosive solution with a chloride concentration similar to that in sea-water. It should also be mentioned that with passivatable metals true "Tafel" slopes are not measured and the corrosion rates as assessed by extrapolation of tangents to the polarization curves are higher than would be found in reality.

The chromium content did not seem to decrease the corrosion rate in the test solution but it considerably stabilized the passive range. Alloys with higher chromium content should therefore be more immune to changes in the oxidizing conditions in the system. A 50μm thick coating can be expected to last for at least several years in conditions like sea-water, based on the assessment of corrosion rates.

CONCLUSIONS

1. A process has been developed that is capable of producing thick coatings of nickel-chromium alloy whose chromium content can be controlled through the deposition parameters in a range from about 0.1 wt% chromium up to about 20 wt% chromium.

2. The resultant coatings exhibit unusual corrosion resistance in chloride environments. This behavior may be a result of their layered structure.

3. Microhardness and the wear performance of these coatings seem to be intermediate between chromium and nickel.

4. Distinct differences in surface morphology and in the types of crystal phases present has been observed between coatings produced by direct current deposition and by pulsed current deposition. The differences in surface morphology or roughness can be accounted for by Ibl's theory describing the pulsating diffusion layer.

FUTURE WORK

A proposal has been submitted to the Research Board of AES to continue this study for both nickel-chromium and for ternarynickel-chromium-molybdenum alloys. This work would entail scaling the process up toa 75L capacity, barrel plating and a study of the electrochemistry and properties of nickel-chromium-molybdenum systems.

ACKNOWLEDGEMENTS

The author gratefully acknowledges the financial support of the American Electroplaters Society and Center for Materials Science of the National Bureau of Standards. The following students have worked on this project: Carlos Beauchamp, Ann Perry, and JoAnne Weinroth. Their assistance has contributed a great deal to the success of the project as has the considerable efforts of Dr. Ilan Weisshaus, a guest worker in our group at NBS, and Dr. Ken Pratt of the NBS Analytical Chemistry Group.

REFERENCES

1. H. J. Grey, ASM News, vol. 10, No. 12 Dec. 1979, p. 1.
2. C. L. McBee and J. Kruger, Electrochem. Acta. 17, 1337 (1972).
3. C. U. Chissom and R. J. G. Carnegie, Plating and Surface Finishing, 59, 12 (1972) 28.
4. T. Hayashi and A. Ishihama; Plating, 66 (1979) 36.
5. A. Ishihama and T. Hayashi. Bull. Univ. Osaka Prefecture, A29 (1), 33 (1980)
6. M. A. Shluger and V. A. Kazakov. J. Phys. USSR 33 (1969) 101 and 33 (1960) 649.
7. M. Gilshinski and J. Yaholom, J. Electrochem. Soc. 129, 11 (1982) 2433.
8. Kolthoff, I. M.; Lingane, J. J. "Polarography; Interscience Pub.: New York, NY, 1965; Vol. 2, pp. 453-5.
9. Sidgwick, N. V. "The Chemical Elements and Their Compounds"; Clarendon Press, Oxford, 1951; Vol. 2, p. 1012.
10. Ringbom, A. In "Chemical Analysis," Elving, P. J.; Kolthoff, I. M., Eds.; Interscience Pub.: New York, NY, 1963; Vol. 16, pp. 352-9.
11. Sillen, L. G. "Stability Constants of Metal-Ion Complexes"; The Chemical Society: London, 1971; Supplement no. 1, pp. 411-5.
12. Tripathy, K. K.; Patnaik, R. K. J Indian Chem Soc. 1966, 43, 772.
13. Patnaik, R. K.; Pani, S. J Indian Chem Soc 1957, 34, 19.
14. Kolthoff, I. M.; Lingane, J. J. "Polarography"; Interscience Pub.: New York, NY, 1965; Vol. 1, Chap. XII.
15. Based on 70% current efficiency for H_2 deposition.
16. Hamm, R. E.; Johnson, R. L.; Perkins, R. H.; Davis, R. E. J Am. Chem Soc 1958, 80, 4469.
17. Cotton, C. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; Interscience Pub.: New York, NY, 1972; pp. 657-8.
18. A. Brenner in Electrodeposition of Alloys, Principles and Practice, Vol. 1 Academic Press, NY 1963. pp 49.
19. S. D. Rasberry and F. J. Heinrich, Analytical Chemistry 46, 1 (1974) 81.
20. N. Ibl. J. Cl. Puippe and A. Angerer, Surface Technology 6(1978) 287.
21. N. Ibl., Surface Technology 10 (1980) 81.
22. K. Viswanathan, M. A. F. Epstein and H. Y. Cheh. J. Electrochem Soc. 125, 10 (1978) 24. Proceedings, 1979 International Pulse Plating Symposium. Am. Electroplaters Soc., Winter Park, FL.

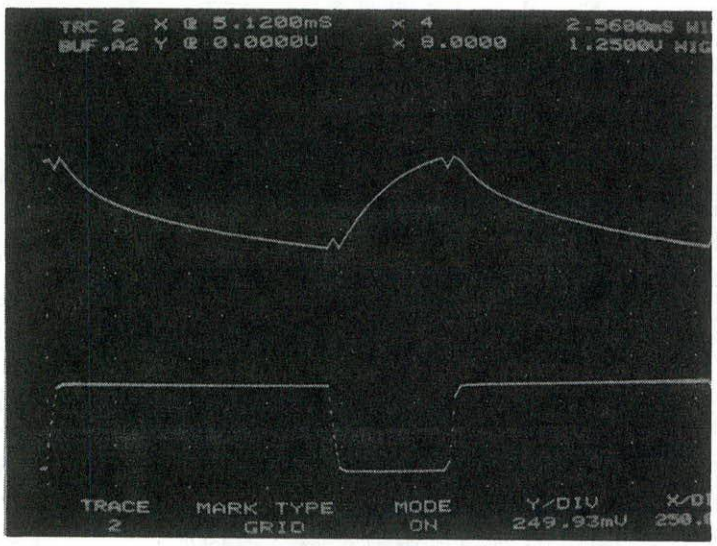

Fig. 1. Typical potential and current waveforms for pulsed galvanostatic deposition of nickel-chromium.

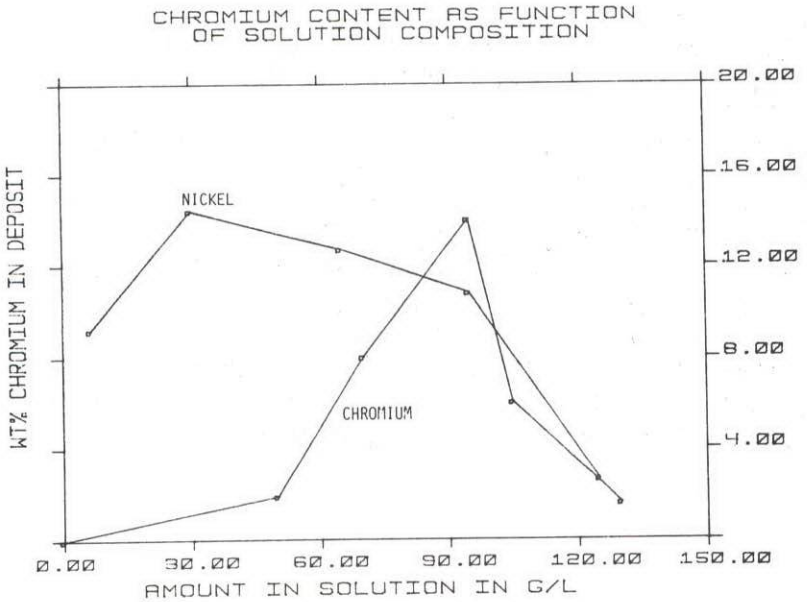

Fig. 2. The dependence of the amount of chromium in the deposit on the amount of nickel and chromium hexahydrate in solution. For nickel, $CrCl_3 \cdot 6H_2O$ = 100 g/L; For chromium, $NiCl_2 \cdot 6H_2O$ = 30 g/L.

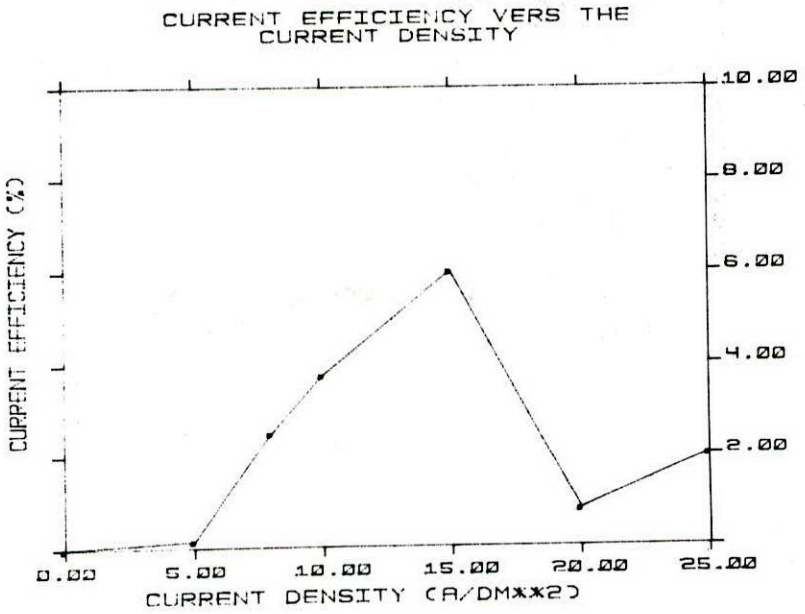

Fig. 3. The chromium efficiency as a function of overall current.

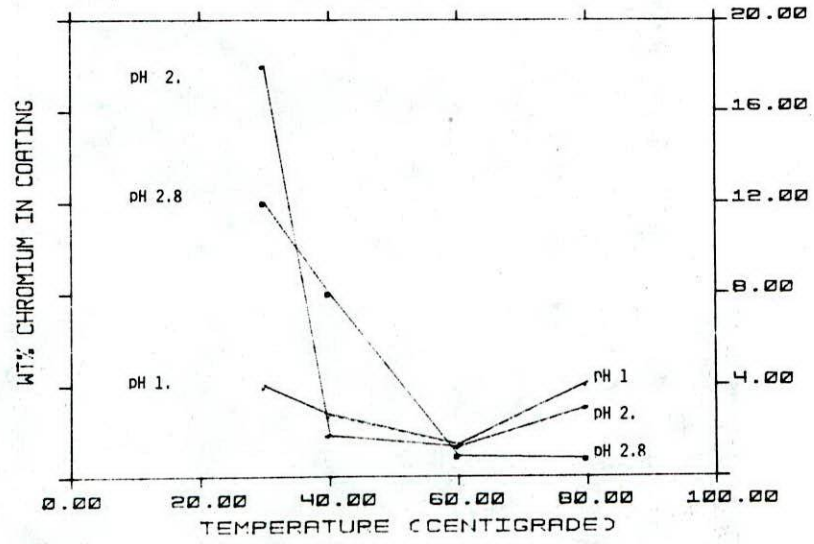

Fig. 4. The dependence on the amount of chromium in the deposit on temperature and pH.

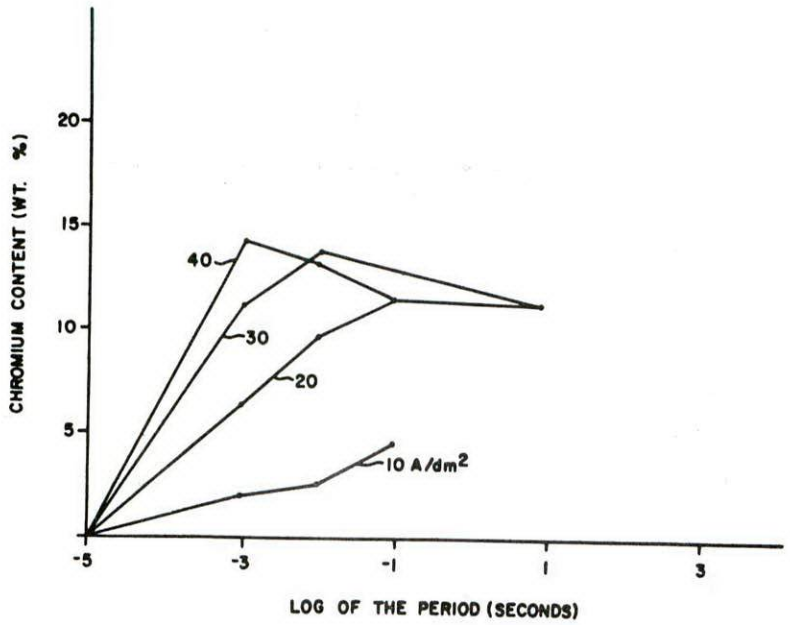

Fig. 5. The dependence of the amount of chromium in the deposit on the period and the peak current density.

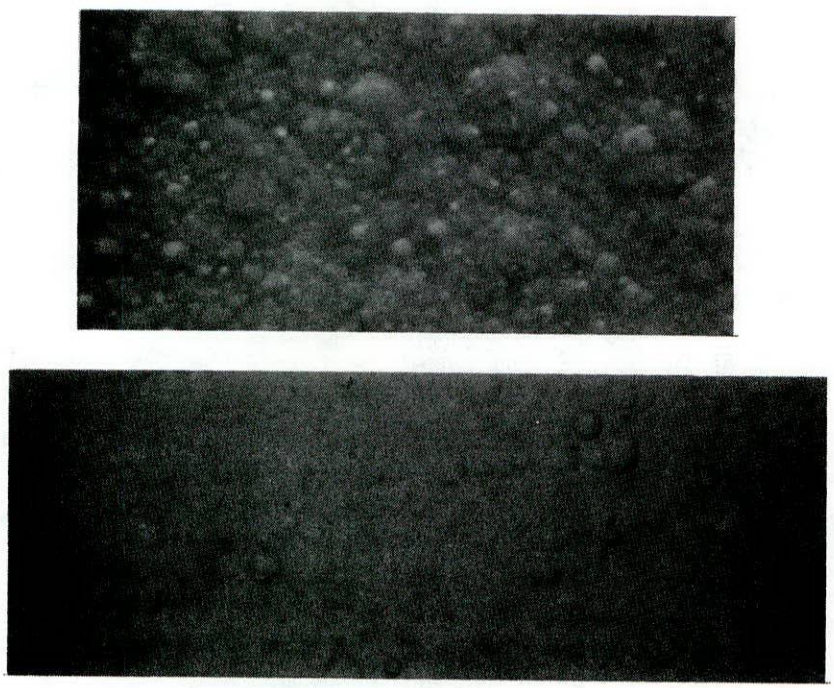

Fig. 6. A comparison of surface morphology of (a) DC: 1 A/dm^2 and (b) pulsed: 1.25 A/dm^2 50% duty cycle, t_{on} = 2.5 ms.

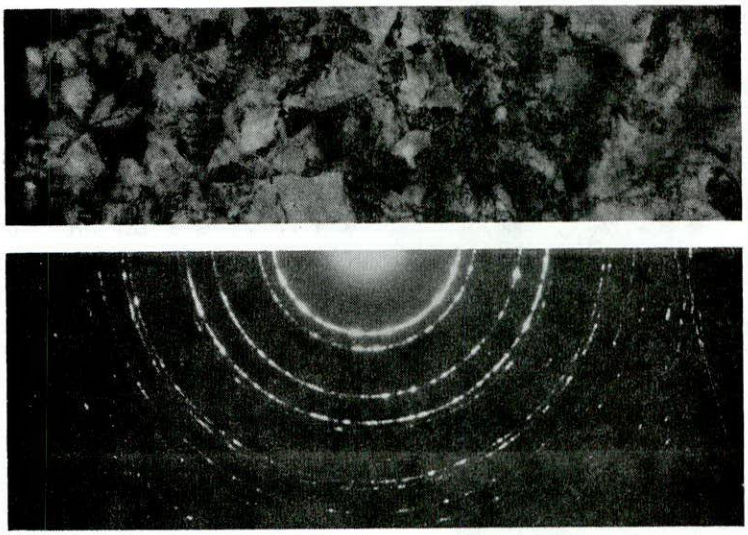

Fig. 7a. A TEM micrograph of a Ni - 3% Cr alloy that was produced by pulse plating. (25% duty cycle, 1875μs on 50 mA/cm^2).

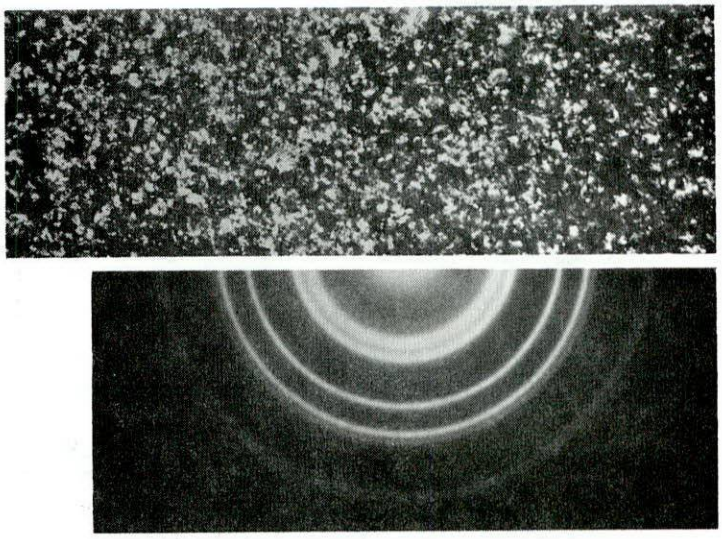

Fig. 7b. A TEM micrograph of a Ni 12% Cr alloy that was produced by pulse plating (50% duty cycle, 1250μs on, 125 mA/cm^2).

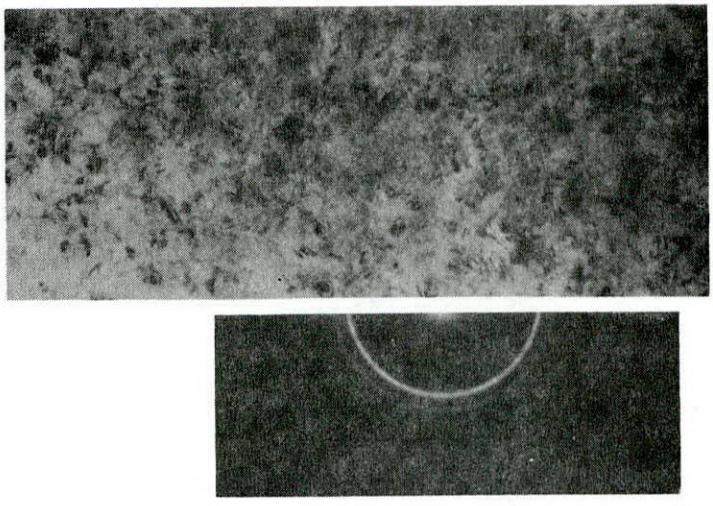

Fig. 7c. A TEM micrograph of a Ni-28% Cr alloy that was produced by pulse plating (75% duty, 625μs on, 250 mA/cm^2).

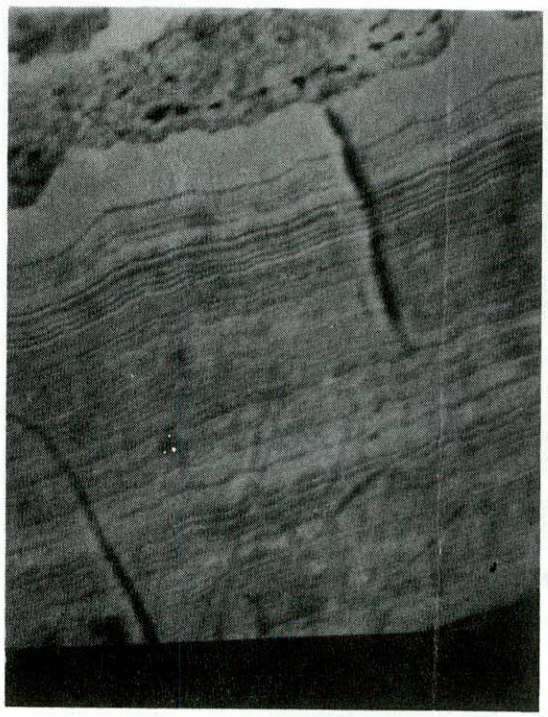

Fig. 8. A SEM micrograph of an etched cross section of Ni-Cr electrodeposit. The superimposed x-ray line scan on CrKα shows tha the layered structure results fro concentration variations.

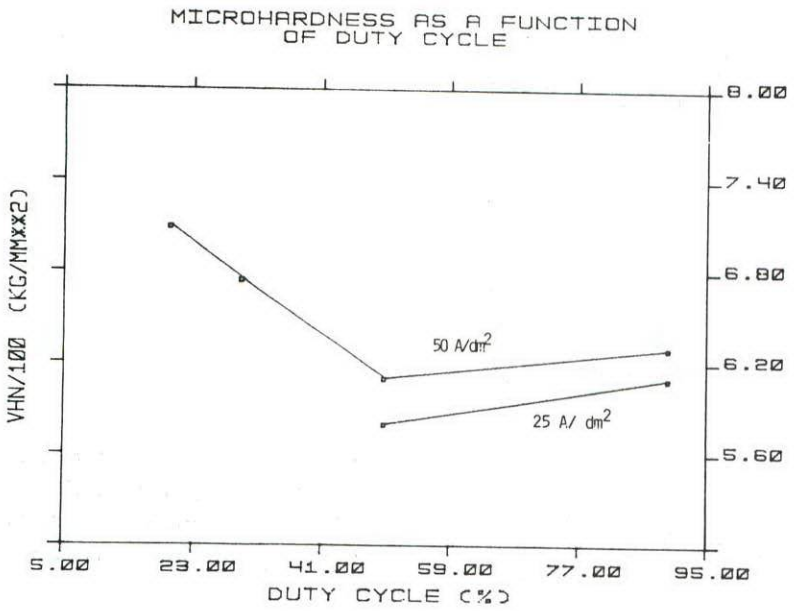

Fig. 9. The variation of micr hardness with duty cycle for t different current densities. The hardness varies with depos tion parameters and can vary from 450 to 875 VHN (Kg/mm_2).

P-2

Alloy Plating
Session P

Electroplated Compound Semiconductors For Photovoltaic Applications

V.K. Kapur
B.M. Basol
E.S. Tseng
International Solar Electric Technology
Inglewood, CA

Paper not received in time for printing

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P-3

Alloy Plating
Session P

Conditions Which Control The Alloy Of Electroless Nickel

Phillip D. Stapleton

CONDITIONS WHICH CONTROL THE ALLOY OF ELECTROLESS NICKEL

by Phillip D. Stapleton

Electroless Nickel Deposits are being produced throughout the world to meet a significant challenge of wear and corrosion. By altering the chemistry and operating conditions the alloy produced will range in phosphorus content from 2% to 13%, providing a wide range of performance in specific applications.

This paper examines some of the factors controlling the phosphorus content and how the equilibrium between the solution and deposit influence the alloy produced. This study takes into effect the polorization and how it relates to the phosphorus content.

Over the years, electroless nickel solutions have been studied with keen interest in controlling of the alloy produced. This interest has been sparked by noticeable difference in wear and corrosion performance of different deposits. These differences are produced by variation in bath chemistry and process conditions.

For the purpose of this discussion, we will only be discussing two solutions. Solution A produces a mid phosphorus deposit while solution B produces a high phosphorus deposit.

The control of the electroless nickel alloy is dependent on several factors. The primary ones are:

Process Conditions
- pH
- Hypophosphite
- Sulfide
- Temperature

Solution Chemistry
- Carboxcylic Acids
- Stabilizers

Of the Process condition, pH has the greatest effect. Other factors like H_2PO_2 and hydrogen sulfide concentration will also effect the phosphorus content of the alloy.

The understanding of these relationships have been difficult in the past. This is because wet methods have provided erroneous and confusing results until the recent use of the Induction Coupled Plasma (ICP). This tool provides for quick and accurate analysis of all the elements within the deposit which provides the researcher with instant confirmation of the experiment.

To understand the effect of process conditions we first must describe the process in electrochemical terms. The electroless nickel reaction can be divided into several oxidation and reduction reactions. These reactions take place simultaneously on the surface while the deposit is being produced. The basic reactions are as follows:

Reduction

$$Ni^{++} + 2e^- \text{ --- } Ni$$
$$2H^+ + 2e^- \text{ --- } H_2$$

Oxidation

$$H_2PO_2^- + H_2O \text{ --- } H_2PO_3^- + 2H+ + 2e^-$$
$$H_2PO_2^- + 2(H_2O) \text{ --- } H_2PO_4^- + 4H+ + 4e^-$$

Deposition Reaction

$$Ni^{++} + H_2PO_2^- + H_2O \text{ --- } Ni+H_2PO_3^- + 2H^+$$

If these reactions and others for phosphorus and nickel are expressed in electrochemical terms near the conditions of solution operation, an equilibrium diagram can be generated. These potential-pH equilibrium diagrams can provide an understanding of the conditions where the oxidation and reduction will take place in the process.

SELECTED EQUILIBRIA for OXIDATION of HYPOPHOSPHITE

$$H_2PO_2^- + H_2O \text{ --- } H_2PO_3^- + 2H^+ 2e^-$$

1) $$E_0 = -0.504 - 0.0591pH + 0.0295 \log \frac{(H_2PO_3^-)}{(H_2PO_2^-)}$$

$$H_2PO_2^- + H_2O \text{ --- } HPO_3^{--} + 3H^+ + 2e^-$$

2) $$E_0 = -0.323 - 0.0886pH + 0.0295 \log \frac{(HPO_3^{--})}{(H_2PO_2^-)}$$

When these values are used to produce a potential-pH equilibrium diagram, the relationship between the oxidation of hypophosphite and reduction of nickel can be seen. In the diagram of a mixed system of nickel and hypophosphite the region we are interested in is bounded by a pH of 4 to 7 and -1.2 to 0.2 volts. This is the active region where most processes for both mid and high phosphorus operate. (see figure 1.)

The areas on the graph represent the chemical species and the edges, the points where the equilibrium exists. It is these conditions which determine when nickel and phosphorus oxidation and reduction in the solution and ultimatly the alloy in the deposit.

These equilibria are calculated from the reaction with water and approximate the conditions in the plating solution. Experimantal results provide different values and provide us a limited understanding of the complex workings of the solution chemistry.

Over the last several years we have developed many formulas in our laboratory which operate efficently in production. In the interest of time and clarity we will identify the mid phosphorus process as Bath A and the high phosphorus process as Bath B. Both of these solutions operate in the acid pH range of 4.1 to 4.9 and both are commerical baths.

The differences between these two solutions is identified in the

following table:

Electroless Nickel Plating Bath Chemistry Features

Feature	BATH A	BATH B
Nickel Metal	6.8 gm/l	6.8 gm/l
Hypophosphite (sodium)	28 gm/l	35 gm/l
Carboxcylic acids	46 gm/l	49 gm/l
Temperature	90 (C)	90 (C)
RCA Nitric Acid Test	fail	pass
ASTM B117 Test (1 mil)	400+ hrs	10000+ hrs
3.5% NaCl corrosion rate	0.4 MPY	0.12 MPY
Hardness	520 VHN	480 VHN
Elongation	0.5 %	1.5 %
Internal Stress on steel	200 lbs	-4000 lbs

It was our interest to characterize the differences between these two process by studying their polarization. These studies were produced by first plating a thin deposit onto an ASTM G5 plug in an operating solution. Simultanously, the electrochemical cell was loaded with a solution missing the hypophosphite and purged with nitrogen. After 10 minutes of plating and purging the plug was transferred and allowed to equilibrate for 30 seconds and then a cathodic scan was started.

As the potential was decreased the deposition of nickel slowed and then began to strip. It was our intent to discover the Cathodic Tafel constants for the solutions and analyze them against the equilibria information and the alloy produced.

The study was carried out using three pH points for each bath. Successive scans were made on fresh 4130 steel ASTM G5 plugs at a scan rate of 2 mv/sec. Coupons were produced in the initiation solution simultanously for alloy analysis by the ICP.

The results of these test were collected on a PAR 350 Corrosion cell and analyzed with a computer. The values reported here were developed from averages of several test on different days. Figure 2 provides a copy of the a single test run.

The test results are reported in cathodic and anodic Tafel constants and Ecorr and Icorr. The Tafel constant is the slope of the curve produced from a scan. A Tafel constant of 0.123 would mean that for every decade of current density change a 0.123 change in voltage would be produced. The terms Ecorr and Icorr are the theoritical values where the anodic and cathodic scans would meet on the curve. By using these values and formulas developed from Faraday's Law the corrosion and deposition of metals can be characterized.

A similiar set of experiments are being completed on solutions missing the nickel. In these analysis the reduction of phosphorus will be characterized.

From the results of the experiments carried out to date, some general conclusions can be made:

The effect of the pH condition of the process with high ionic concentration solutions is not significant (see figure 3). In production it is recommended that the pH not vary greater 0.2 pH points. This will insure a 0.4% range for the phosphorus in the alloy. In low concentrations solutions based on lactic or acetic acids the pH can have a significant effect on the phosphorus in the deposit.

The effect of specific carboxcylic acids on the cathodic Tafel constant is significant (see figure 4). In this plot the effect of pH can be seen to have little effect while the solution chemistry appears to control the Tafel slope.

Another interesting result is the tight Ecorr and Icorr values for each bath (see figure 5). In this plot, the intersect for cathodic and anodic Tafel constants are displayed. As more specific work is accomplished the relationship to bath aging and specific carboxcylic acids will be developed.

As we continue to expand our understanding of the relationships between the process conditions and deposit performance, the opportunities for new applications and higher levels of performance will be provided. It is our hope that this information will contribute to this understanding and help expand the application of electroless nickel.

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figure 1.

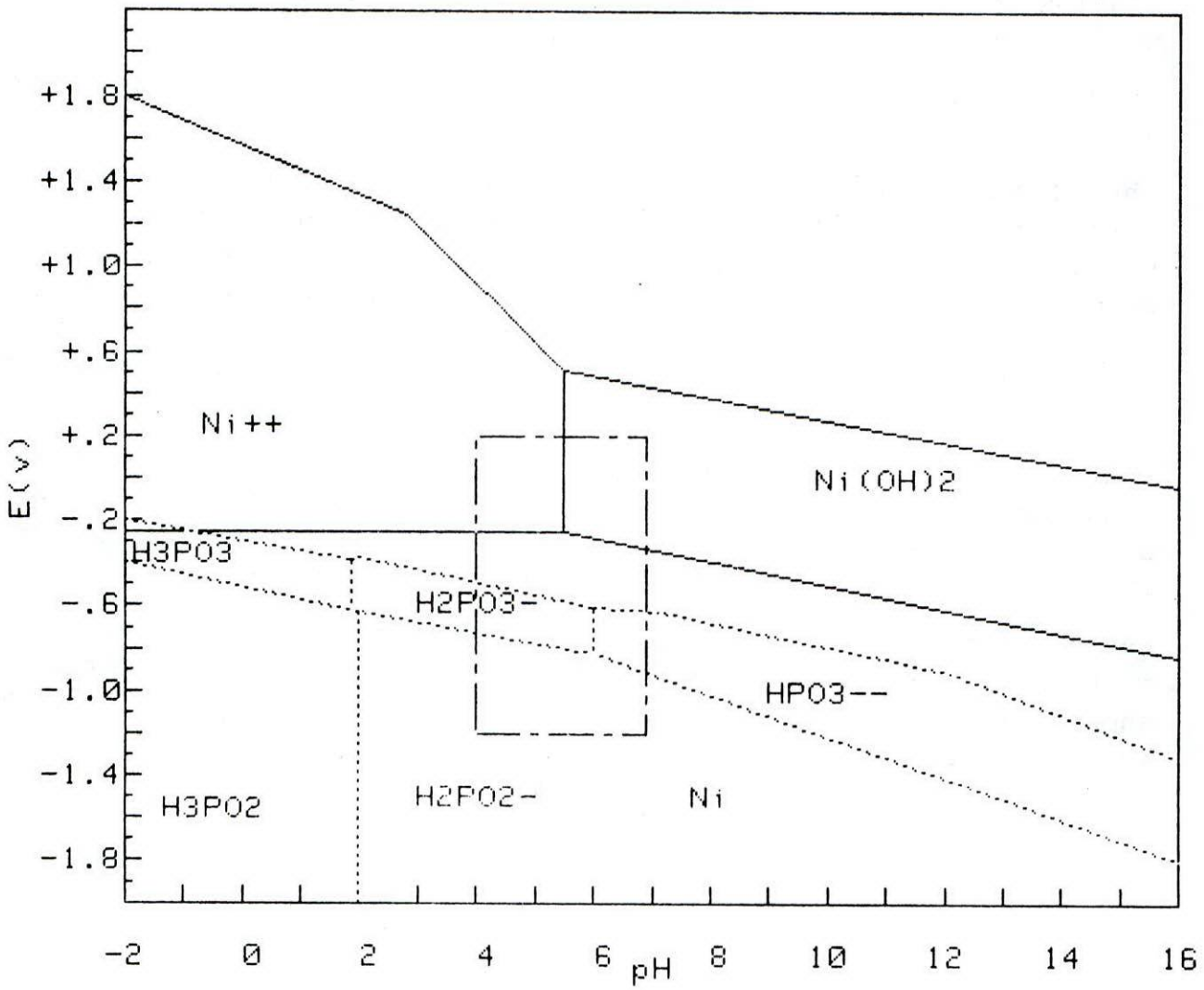
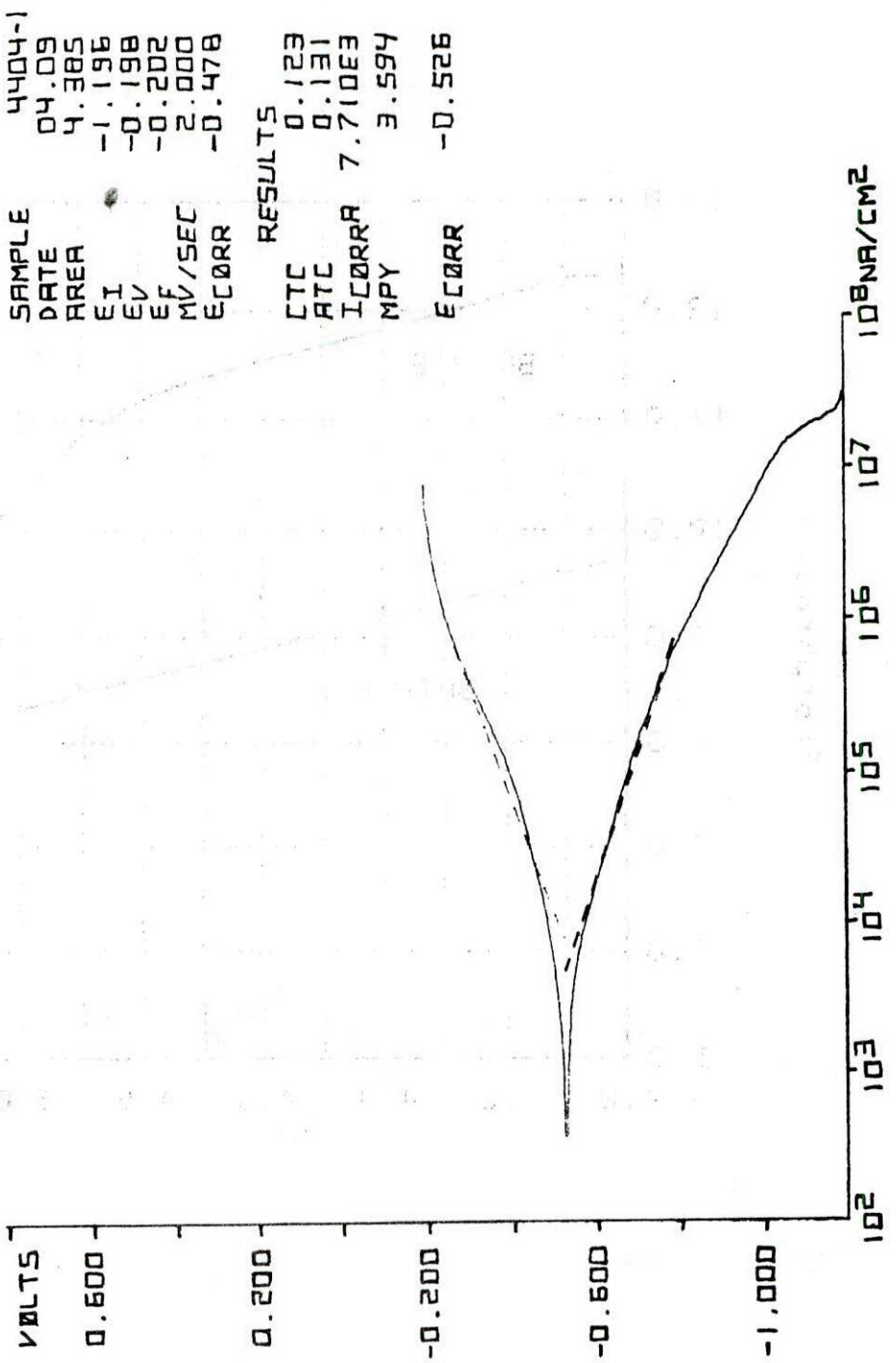


figure 2.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AREA 4.385
EI -1.196
EV -0.198
EF -0.202
MV/SEC 2.000
ECORR -0.478
RESULTS
CTC 0.123
ATC 0.131
ICORRA 7.710E3
MPY 3.594
ECORR -0.526
VOLTS
0.600
0.200
-0.200
-0.600
-1.000
10^2
10^3
10^4
10^5
10^6
10^7
10^8 NA/CM^2

figure 3.

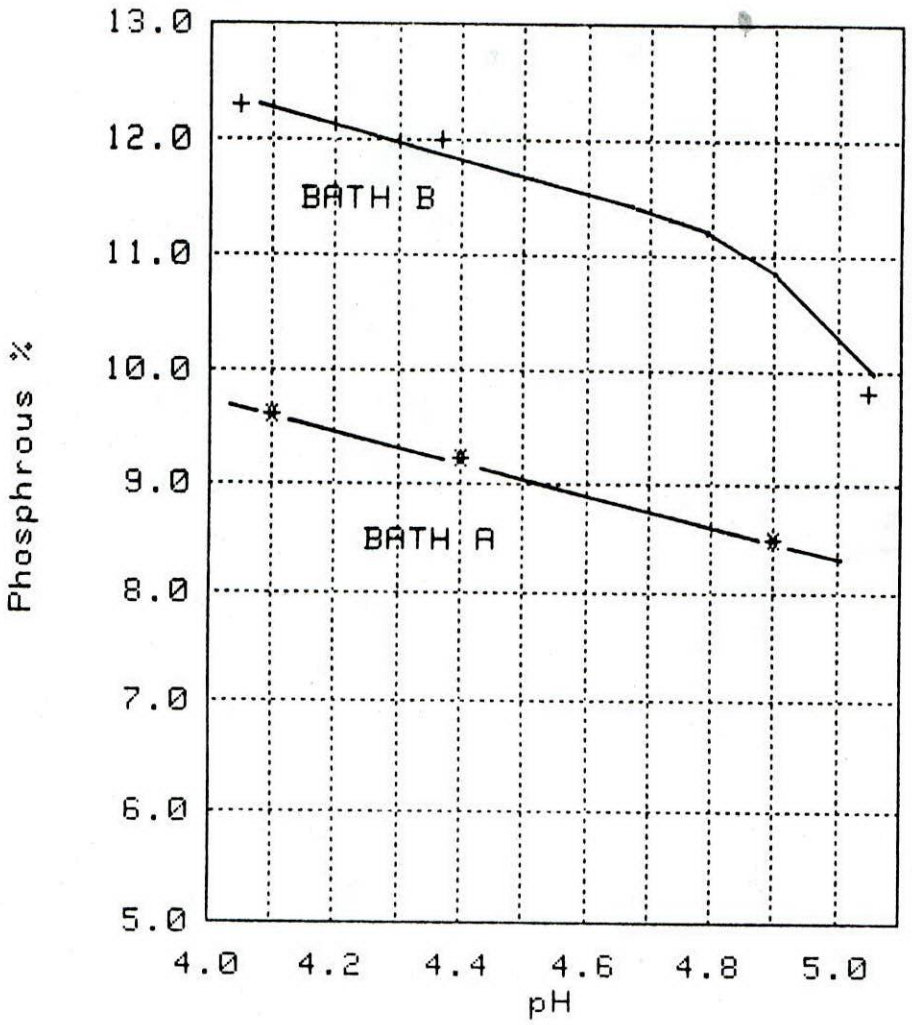
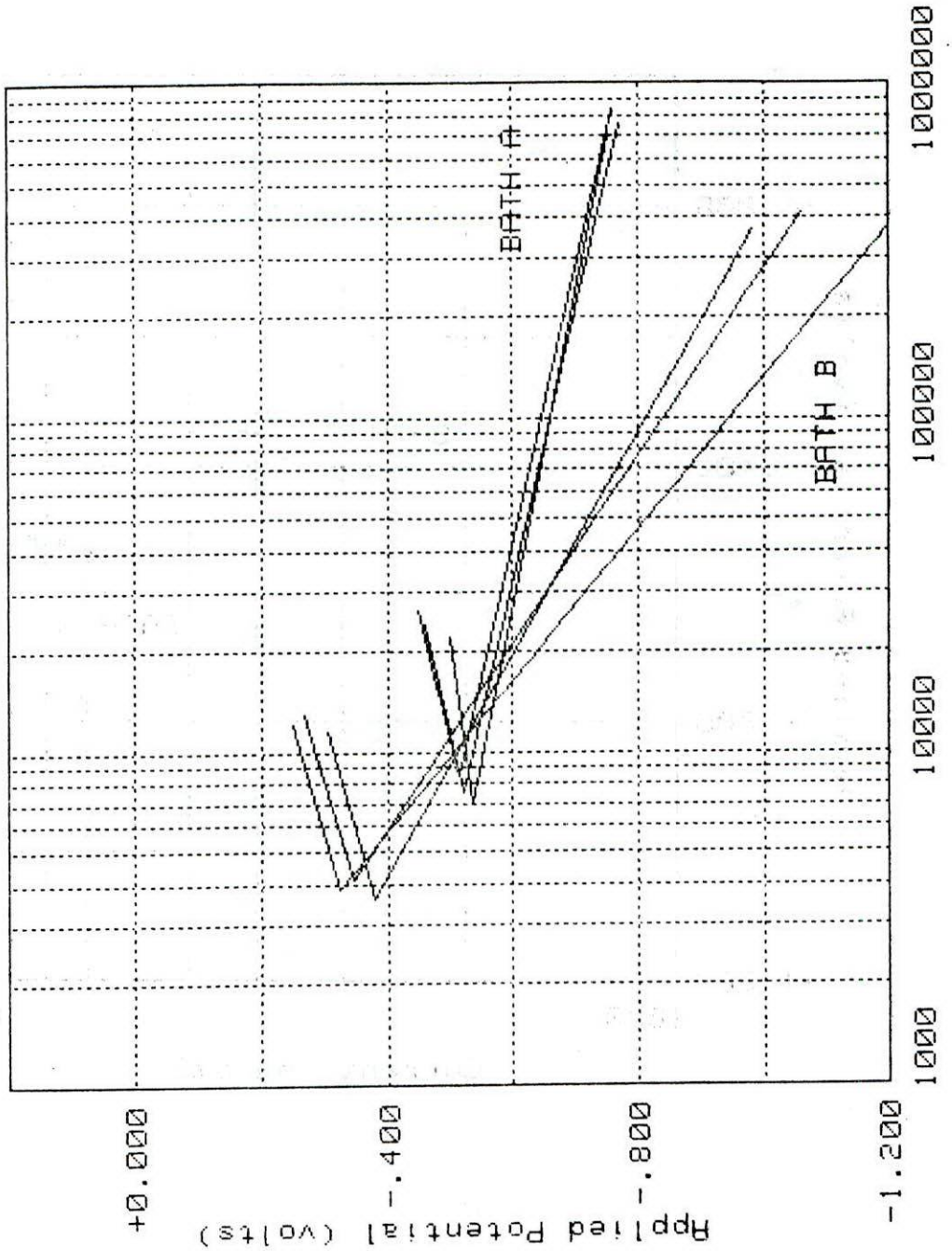

13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
Phosphrous %
BATH B
BATH A
4.0
4.2
4.4
4.6
4.8
5.0
pH

figure 4.


BATH A
BATH B
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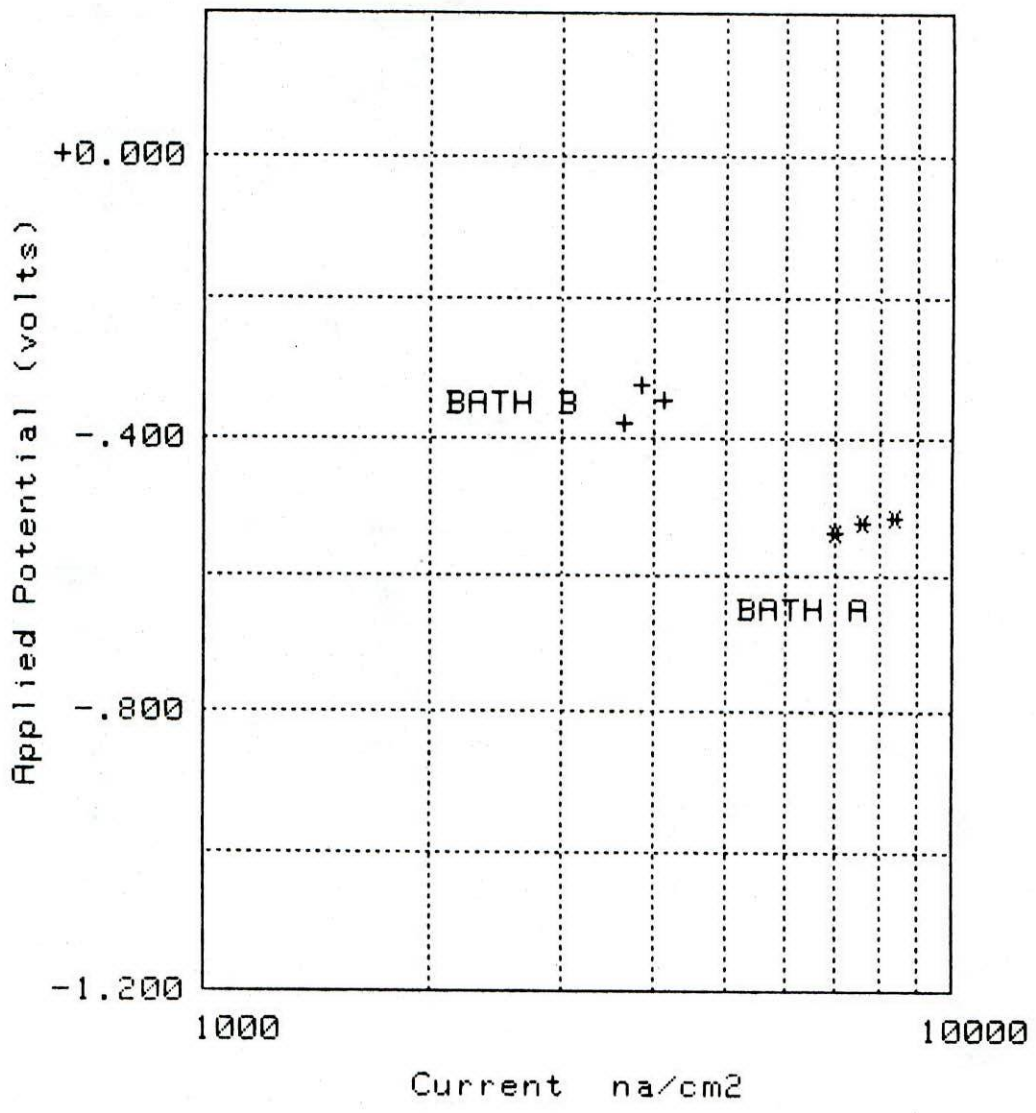
100000
10000
1000
Current na/cm2
+0.000
-.400
-.800
-1.200
Applied Potential (volts)

figure 5.


+0.000
-.400
-.800
-1.200
Applied Potential (volts)
BATH B
BATH A
1000
10000
Current na/cm2

P-4

Alloy Plating
Session P

Effects of Chromium Electroplating Solution Composition on Properties of the Deposits

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EFFECTS OF CHROMIUM ELECTROPLATING SOLUTION COMPOSITION ON PROPERTIES OF THE DEPOSITS

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and

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SUNY, Albany, NY 12222

ABSTRACT

Deposits from a conventional chromium electroplating bath are compared with those from baths containing additives (e.g., methanol, Cl^-, Fe^{2+}), which increase current efficiency.

Surface morphology, microstructure, crystal structure, microhardness, iron and hydrogen content are compared. Baths containing iron produce ferromagnetic deposits with non-uniform distributions of iron.

INTRODUCTION

The properties of chromium deposits from conventional plating baths have been studied extensively (1-9). The exceptional hardness of chromium deposits has been attributed to small grain size (2, 3) and to the effect of dispersed oxygen in the deposit (2, 10). The hardness of the deposits from baths containing CrO_3 and H_2SO_4 with 1:100 ratio is said to depend on deposition temperature (5, 6) and on the catalyst type ($SO_4^{=}$ or F^-) (2). It is known that the hardness of Cr deposits is related to deposit appearance. The bright deposits have the highest hardness (1). The hardness of the bright Cr deposits is 900-1100 Vickers hardness number (11).

Thick deposits from conventional baths always crack, and even the "crack-free" type has some cracks (1, 3). These cracks, Snavely believes, are produced by decomposition of hexagonal close packed (hcp) or face centered cubic (fcc) chromium hydrides to body centered cubic (bcc) Cr. These decompositions are accompanied by 15% shrinkage of volume which results in cracking of the deposit (12). The grain size of the deposit is said to be on the order of 10^{-9} m (2) and 10^{-7} m (3) and thus grains are not visible under the light microscope. A banded (striated or laminated) structure has been observed for Cr from a conventional bath (3), for Cr-Fe alloy deposit (13) and for Cr-Ni alloy deposit (14). Columnnar growth has also been observed (3).

The crystalline structure of Cr deposits were studied by Hume-Rothery and Wyllie (6) and Snavely (3), using X-rays, and later by Cleghorn et. al. (9) and Szirmae and Fisher (15), using electron diffraction methods, Fomichev et. al. (16) also studied the structure of Cr deposits from a conventional bath with or without gallic acid or methylene blue. All

observed the occurrence of bcc structure in Cr deposits. Hume-Rothery and Wyllie obtained [111] preferred orientation for bright deposits. Snavely suggested that Cr can be deposited as a metal with bcc structure and as hydrides with hcp and fcc structure.

The hydrogen content of the deposits has also been studied (2, 12). The methods of these measurements did not allow for the study of the distribution of hydrogen.

EXPERIMENTAL RESULTS

To measure hardness and hydrogen concentration and to study the morphology and crystal structure, deposits were made from the following solutions:

A) 250 g/l CrO_3, 2 ml/l H_2SO_4

B) A + 4 ml/l methanol

C) A + 64 g/l $CrCl_3.6H_2O$, 76 g/l $FeCl_2.4H_2O$, and 20 ml/l methanol

D) A + 128 g/l $CrCl_3.6H_2O$ and 20 ml/l methanol

E) A + 144 g/l $FeCl_2.4H_2O$ and 20 ml/l methanol

F) 250 g/l CrO_3, 90 g/l $FeSO_4.7H_2O$, and 30 ml/l methanol

G) 250 g/l CrO_3, 90 g/l $FeSO_4.7\ H_2O$, 120 g/l $Cr_2(SO_4)_3.nH_2O$, 100 g/l NaOH, and 160 g/l $BaCO_3$ at 1.57 pH.

The plating apparatus and reasons for using these solutions have been discussed elsewhere (17-21). The temperature was 40° C and J, current density, was 25 A/dm^2. Between 4 and 6 experiments, each with 5 min. deposition time, were performed with each solution, A-G, and then an experiment with one hour deposition time was performed. Thin deposits, 5

min. deposition time, were used mainly for .pa hydrogen measurements. The thick deposits were used for X-ray, and hardness measurements.

Hardness

The Knoop Hardness Number (KHN) of the samples were measured on polished cross-sections (cut from the centers of the deposits) before etching. The long axis of the diamond indentation was parallel to the surface of the deposit. The thickness of each deposit was several times larger than the width of the indentations. The hardnesses were measured only where there was compact deposit with no crack, before or after the indentation. The load was 50 g. The results are in Table 1.

Table 1 The average hardness of the deposit cross-sections (from centers of samples) from the above solutions, and the standard deviation SD are given as KHN$\pm$SD. The deposition conditions are: deposition 60 min., 25 A/dm^2, 40° C and Pb anode, except for G which had Pt anode. The load was 50 g. The hardness is the average of 10 measurements.

Solution	Average Hardness Number KHN	CE %
A	820$\pm$100	21
B	800$\pm$120	22
C	750$\pm$190	56
D	860$\pm$90	37
E	860$\pm$70	49
F	730$\pm$110	36
G	710$\pm$80	56

Surface Morphology

The surface morphology of both 5 min. and 60 min. deposits from the above solutions were studied with a scanning electron microscope (SEM). Deposits from solutions A and B were cracked. The 5 min. deposits were smoother than 60 min. deposits. The edges were rough, and this became more pronounced with 60 min. deposition time than 5 min. deposition time.

The deposits from solution C, with 5 min. deposition time, were probably crack free. With 60 min. deposition time the deposit was cracked. Fig. 1 a and b show that, as time of deposition increased, the hemisphere size on the surface increased, but the regions surrounding the hemispheres became smoother. The center was smoother than the edges. The edges of these deposits were dull, and the centers were shiny.

The surface morphology of deposits from solution D was basically the same as above, but the centers did not have large hemispheres. The edges of the 5 min. deposits were gray.

The deposits from solution E were crack-free when deposition time was 5 min. and cracked when deposition time was 60 min. Fig. 1 shows the surface morphology of these deposits. The surface hills are no longer hemispheres for 5 min. deposits. The matrix of the 60 min. deposit is not as smooth as the corresponding one from solution C (compare Fig. 1 b and d).

No cracks were seen on deposits from solution F with 5 min. or 60 min. deposition time. Fig. 2 a and b show the surface morphology of the center of these deposits. The center of both deposits are relatively smooth with no large hemispherical hills. But the edges had hemispherical hills. Compare Fig. 2 a and b with Fig. 1.

The deposits from solution G seemed to be crack-free (Fig. 2 c and d). The 60 min. deposit is gray and uniform. Fig. 2 d is a micrograph of

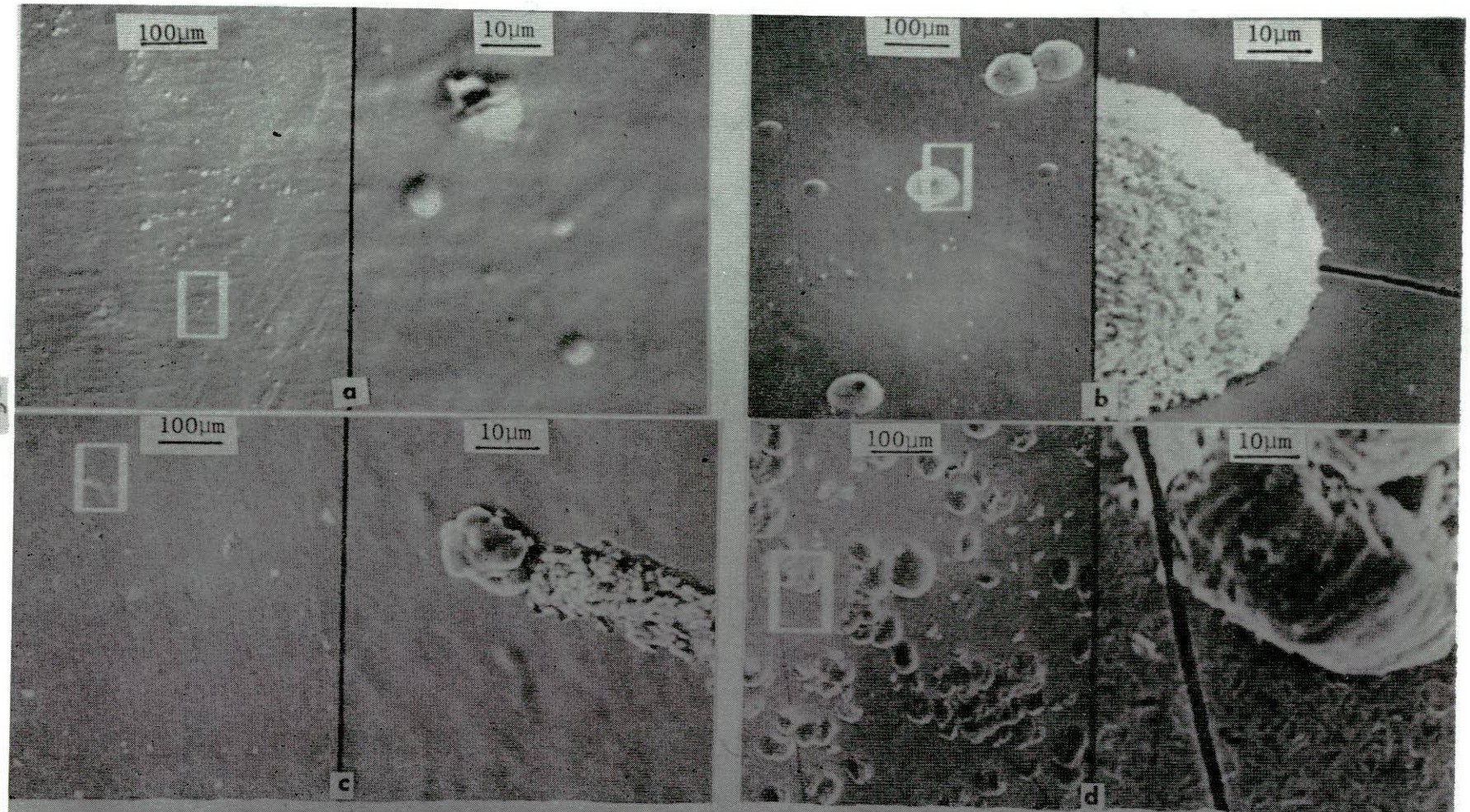

Figure 1 The surface morphology of the center of deposits obtained from solutions C and E at 40° C and 25 A/dm^2, with Pb anode. The deposition time and solutions were as follows: a) 5 min., C; b) 60 min., C; c) 5 min., E; and d) 60 min., E.

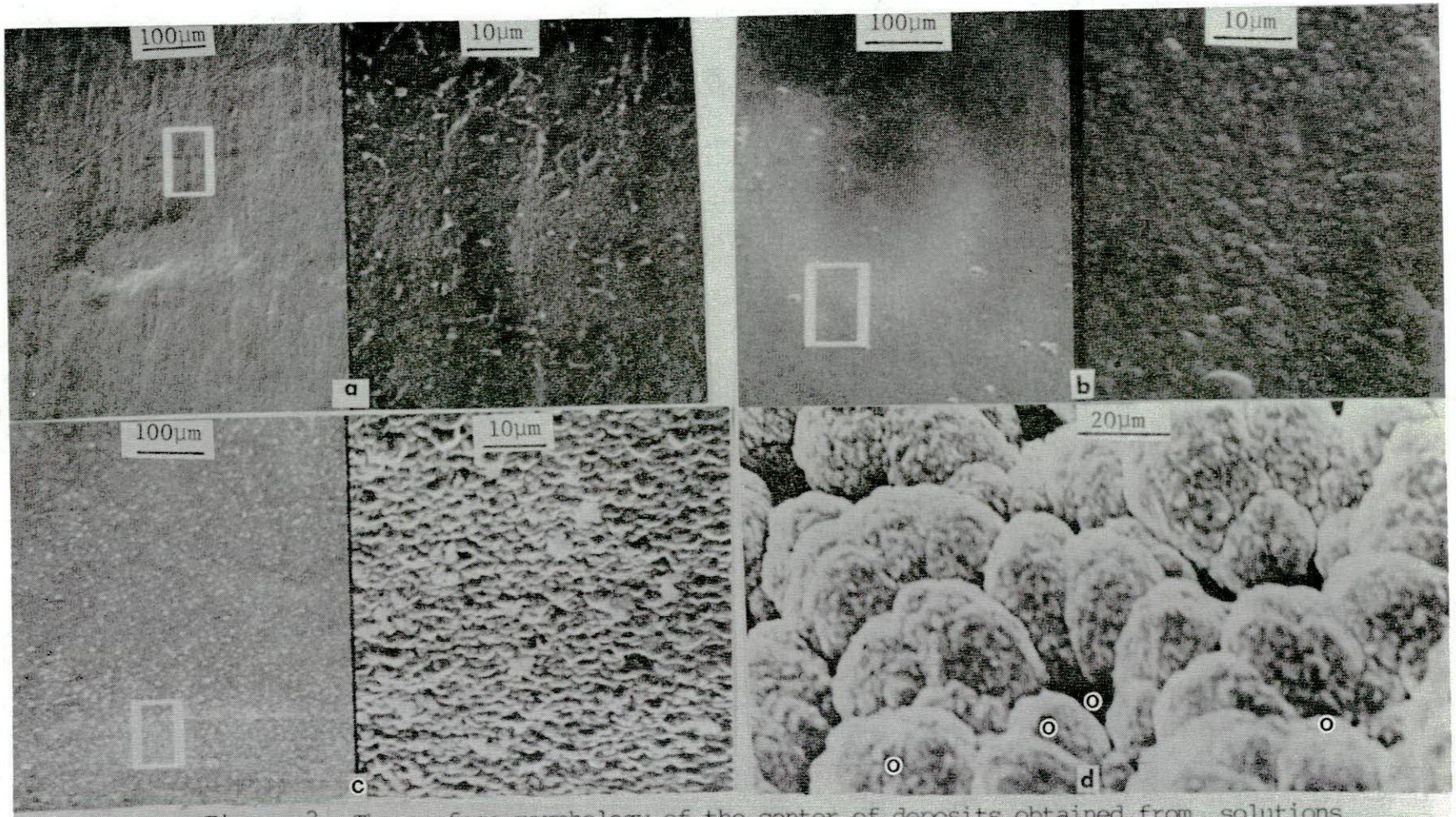

Figure 2 The surface morphology of the center of deposits obtained from solutions F and G at 40° C, and 25 A/dm^2. The anode was Pb for solution F and Pt for solution G. The deposition time and solutions were as follows: a) 5 min., F; b) 60 min, F; c) 5 min., G; and d) 60 min., G.

the center of the deposit surface. The four points on the micrograph are the spots where Cr and Fe were measured with an energy dispersive spectrometer (EDS), the results of which will follow. The EDS results showed that the alloys did not contain any of the substrate elements, i.e., the incident electron beams did not penetrate completely through the deposits.

Cross-Sectional Structure of the Deposits

The cross-sectional structure of deposits obtained from solutions C and F are shown in Fig. 3. These deposits are layered. This type of microstructure was also observed for most of the other deposits.

The Crystalline Structure of the Deposits

The surfaces of the deposits from all of the above solutions were examined with an X-ray diffractometer. The results are summarized in Fig. 4. The plating time was 60 min., temperature was 40° C, J was 25 A/dm^2, and the anode was Pb for solutions A-F and Pt for solution G.

Fig. 4 shows that possibly all deposits have bcc Cr, simple cubic (SC) Cr, Cr_3O_8, Cr_2O_3 and CrOOH with different proportions i.e., deposits from G and E probably have large amounts of bcc Cr because of the strong line at 2.04Å.

Elemental iron cannot be detected by our X-ray diffractometer because bcc iron has a lattice parameter so close to Cr that it cannot be distinguished from Cr with the resolution obtained in this work (about .02Å).

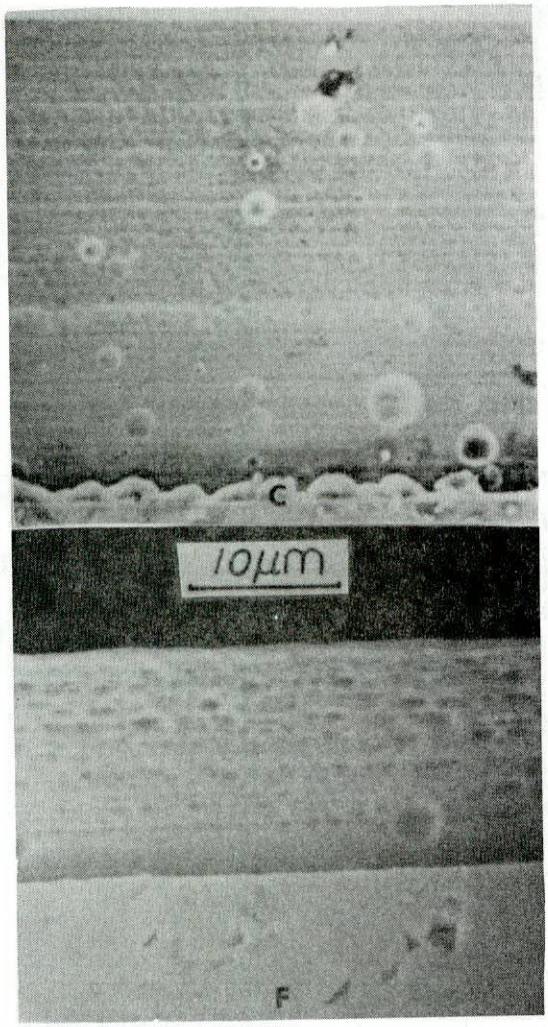

Figure 3 The cross-sectional structures of two deposits are shown above. The letters on the pictures are the designated solutions. Plating temperature, time and J were 40° C, 60 min., and 25 A/dm^2.

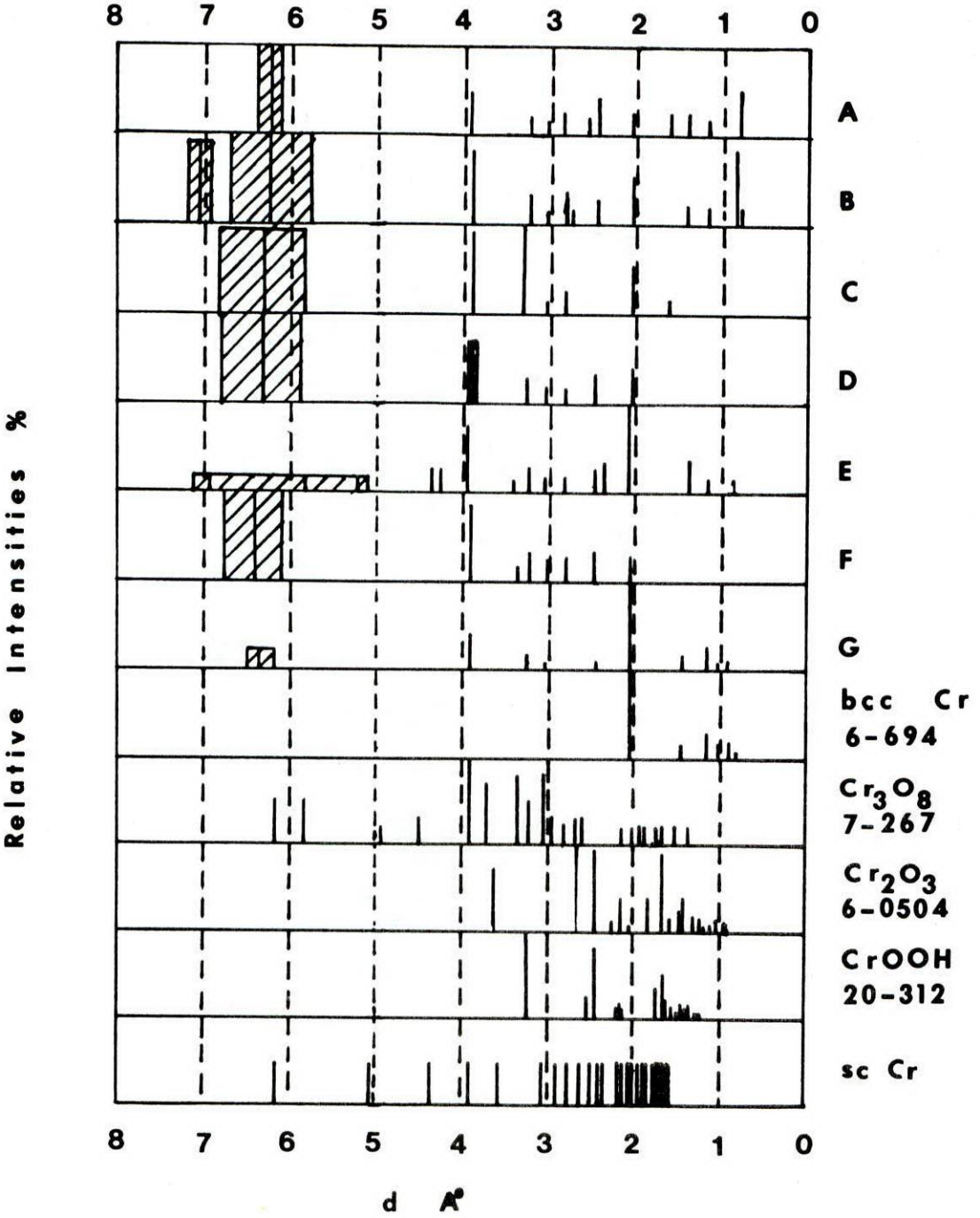

Figure 4 The X-ray diffraction patterns of the deposits obtained from solutions A-G which are identified on the right hand side, and the standard diffraction patterns of Cr and Cr compounds as identified above. The number under the name of the compound is the powder diffraction card number (58). For SC Cr d spacing is calculated from the lattice parameter, a = 8.735A°. The width of the maximum is shown by cross-hatched rectangles when necessary.

If iron exists as an alloy, it also cannot be detected by X-ray diffraction because at room temperature it does not make a known, different phase (22).

The information about simple cubic Cr (it may be a hydride) is calculated from the value of the lattice parameter (23). Thus, intensities for SC Cr are not known. For other structures powder data existed in the file which gave intensity as well as d (plane spacings) (24).

Electron diffraction patterns from thin (17 nm) deposits obtained from solution A confirm the existence of bcc structure. The diffraction patterns, obtained from circular areas of 2 μm diameter, were multicrystalline, indicating crystal diameters much less than 2 μm. Electron diffraction patterns (obtained by using a 1500 KeV electron microscope) of a thicker deposit ($\sim$4μm) from solution F showed that this deposit contains simple cubic crystals with a lattice parameter of 5.2 ± 0.1 A^{o}. The latter diffraction patterns were obtained from the insides of cracks. The crystals were about 0.2μm diameter.

Hydrogen Content of the Deposits

Two deposits from each solution (A-G) were studied. The method of measuring hydrogen content has been described by Lanford et. al. (25-27). This method can be simply described as follows: A resonant reaction between nitrogen -15 and hydrogen produces an α particle and a 4.43 MeV γray. If the sample is bombarded with ^{15}N, the above reaction occurs and the number of characteristic γ rays is proportional to H concentration. If the ^{15}N beam has an energy of 6.385 MeV (in the lab frame of reference) then the number of characteristic γ rays is proportional to hydrogen on the surface of the sample. To measure the hydrogen deeper in the sample, the energy of the ^{15}N beam is raised. The ^{15}N loses energy as it penetrates

into the sample. At some depth the energy is just that needed for the reaction to occur, and now the number of γ-rays produced is proportional to the hydrogen at that depth. Hence, by measuring yield of γ-ray vs. ^{15}N energy the hydrogen concentration versus depth can be measured.

The experimental results are given in Fig. 5, which shows the atomic percent of hydrogen versus depth for samples plated in solutions A-G. The hydrogen concentration at the surface was measured both at the beginning and at the end of each bombardment to see if the sample was stable under bombardment. Except for some change in the amount of hydrogen in the large surface peak present in some samples, e.g. E and F (see Figure 5), these samples seem completely stable during analysis.

Deposits from solutions A and B had the same amount of hydrogen at all depths measured. Their average hydrogen concentrations were $4.4\pm.6\%$ for deposits from solution A and $4.4\pm.7\%$ for deposits from solution B, i.e., the two sets of deposits have the same amounts of hydrogen.

The other samples, generally have higher hydrogen concentration at the surface than at greater depths. The only exception is one of the deposits from solution C. In all cases the concentration of hydrogen levels off at a depth of about 100 nm and in many cases, D, E, and G, at less than 50 nm depth.

All deposits from solutions containing Cl^- had more than 10% hydrogen. The average hydrogen concentrations (neglecting the surface plates) were $13\pm.7$, 11.5 ± 1.2, and $13.7\pm1.0\%$ for deposits from solution C, D, and E, respectively (see Figure 5). These results imply that to within the reproductibility of these samples, the three solutions produced deposits with the same amount of hydrogen.

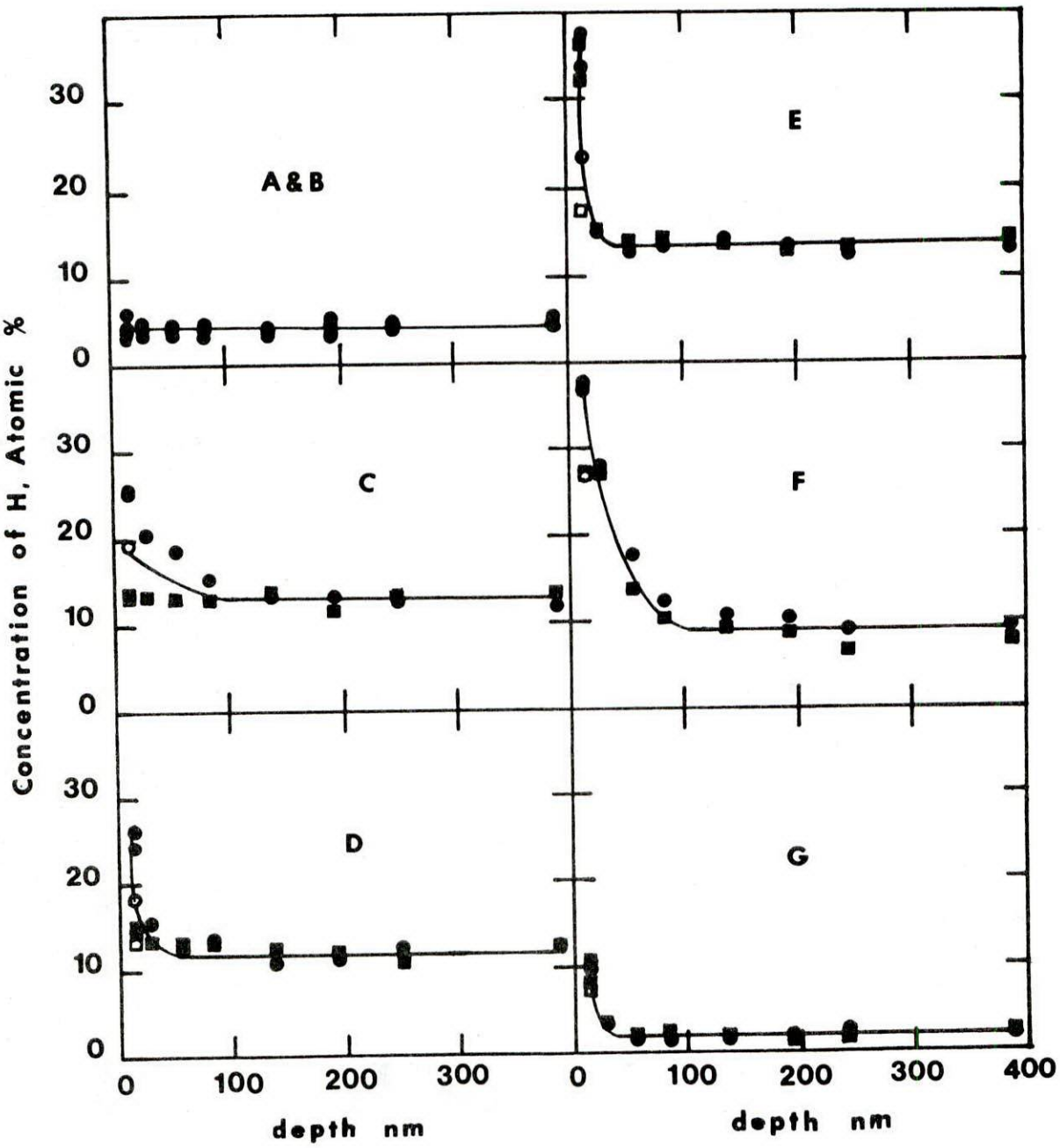

Figure 5 The atomic percentage of hydrogen versus depth is shown. The letters on the graph are the designated solutions. Two deposits from each solution were used, and their results are shown with circles and squares. Empty symbols are the last measurement to affirm stability. Solution A and B gave the same H concentrations at all depths, thus one figure is used for the two of them. Temperature of plating was 40° C, J was 25 A/cm^2, plating time 5 min., and anode Pb except G had Pt anode.

Neglecting the surface peaks, the deposits from the solution containing no methanol or Cl^-, had the lowest concentration of hydrogen, $1.8\pm.4\%$. Solution F yielded deposits which had hydrogen concentration between deposits from Cl^- containing solutions and A, B, and G solutions, $9.0\pm1.4\%$.

In general it can be said that deposits from solutions containing Cl^- and 20 ml/l methanol have the highest hydrogen concentrations. Deposits from the solution containing no Cl^- and 0 to about 4 ml/l methanol give the lowest hydrogen concentration. Deposits from solution F containing no Cl^-, but relatively large amounts of methanol, 30 ml/l, had intermediate hydrogen concentrations.

Iron in the Deposit

Using EDS method (28) the iron in the deposits from iron- containing solutions (Table 1) was estimated and corrected for the fluorescence effect by a known method (29).

Table 1 The intensity of K_α X-rays of Cr and Fe, the relative concentration of Fe and the concentration of Fe after correction. Number of counts at K_α of pure Cr and Fe were 30297 and 26903 respectively, which were used as standards. The counts are averages of at least 2 (C and G) and at most 6 (E) measurements. The total number of counts in each experiment was 200,000.

Solution	Counts K_α Cr	Counts K_α Fe	Atomic %FE (uncorrected)	Atomic %Fe (corrected)
C	21646	569	2.9	6.3
E	24652	1866	7.9	18.8
F	19672	682	3.8	7.5
G	23572	71	0.34	0.82

The iron in the deposits is in the form of a separate phase which is either pure Fe or a high Fe- containing alloy. The reason is as follows: a deposit from a conventional bath, a deposit from bath E and another deposit from bath G were chosen. The deposit from one side was removed and then they were separately put in concentrated, hot HNO_3. Copper and nickel were dissolved and only the deposit remained. The deposits were put in a magnetic field. The first deposit was not attracted to the field, but the other two were. Since the deposits overall have less than 20% (atomic) iron and Fe-Cr alloys with less than about 30% (atomic) iron do not have ferromagnetic properties (30), therefore, the iron is either pure or in a phase where its concentration is less than 30% (atomic).

SUMMARY

1) The deposits have essentially the same hardness.
2) The deposit from solution F has the smoothest surface, and the deposit from solution G has the roughest surface.
3) Most of the deposits have layered microstructures.
4) The X-ray results show that all deposits are probably mixtures of bcc Cr, SC Cr, Cr_2O_3, Cr_3O_8, and CrOOH.
5) Deposits from solution G had lowest hydrogen content and deposits from solutions C, D, and E had highest hydrogen content.
6) The deposits contain between 0.82 and 18.8% Fe. The Fe is not distributed uniformly because the deposits showed ferromagnetic properties.

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REFERENCES

1. G. Dubpernell, Modern Electroplating, (John Wiley and Sons, Inc., NY) (1974).

2. A. Brenner, P. Burkhead and C. Jennings, J. Research National Bureau of Standards, 40, 31 (1948).

3. C.A. Snavelly and C.L. Faust, J. Electrochem. Soc. 97(3), 99 (1950).

4. A.H. Sully and E.A. Brandes, Chromium 2nd ed. (Butterworths London), p. 211-257 (1967).

5. A.T. Vagramian and Yu. S. Petrova, The Mechanical Properties of Electorlytic Deposits, (Consultants Bureau Enterprises, Inc. NY) (1962).

6. W. Hume-Rothery and M.R.J. Wyllie, Proc. of Royal Soc. of London, 181A, 331 (July 1943).

7. G.N. Flint, J. Electrochem. Soc. India, 16(2) (49)(1967).

8. B. Rivolta, M. Lazzari and L.P. Bicelli, J. Phys D: Appl, Phys., 9, 2215 (1976).

9. W.H. Cleghorn, D.H. Warrington and J.M. West, Electrochemica Acta, 13, 331 (1968).

10. J.J. Dale, Discussion of Snavely's paper J. Electrochem. Soc. 97(12), 466 (1950).

11. H. Chessin and E.H. Fernald, Metals Handbook Vol. 5, 170, (1982).

12. C.A. Snavely, Trans. Electrochem. Soc. 92,537 (1947).

13. L.D. McGraw, J.A. Gurklis, C.L. Faucet and J.E. Bride, J. Electrochem. Soc., 106(4), 302 (1959).

13. D.S. Lashmore, Proc. AES, 1, Paper A-2 (1983).

14. A. Szirmae and R.M. Fisher, Proc. of 41st Electron Microscopy of Am. (1983).

16. V.T. Fomichev, A.G. Malyakina, A.F. Bol'shakov and A.M. Ozerov, Protection of Metals, 14, 42 (Jan. 1978).

17. A.M. Kasaaian and J. Dash, Proc. AES, 69, U-4 (1982).

18. A.M. Kasaaian and J. Dash, Proc. AES, 71, E-3 (1984).

19. A.M. Kasaaian and J. Dash, Plating and Surface Finishing 71(11), 66 (1984).

20. A.M. Kasaaian and J. Dash, U.S. Patent 4,447,299.

21. A.M. Kasaaian, Portland State University Dissertation (1985).

22. ASM, Metals Handbook, 8, 291, Cr-Fe phase diagram (1973).

23. J. Donnay and H.M. Ondik Christal Data 3rd. ed., 2, C232, (NSRDS and JCPDS (1973) Department of Commerce).

24. Powder Diffraction File, (Joint Committee on Powder Diffraction Standards, Philadelphia) (1967).

25. W.A. Lanford, H.P. Trautvetter, J.F. Ziegler and J. Keller, Applied Physics Letters, 28(9), 566 (1976).

26. W.A. Lanford, R.S. Alwitt and C.K. Dyer, J. Electrochem. Soc. 127(2), 405 (1980).

27. W.A. Lanford and M.J. Rand, J. Applied Phys., 49(4), 2473 (1978).

28. J.C. Ross, Elemental X-ray Analysis of Materials EXAM Methods, (EDAX International, Inc., Raleigh, NC) (1972).

29. S.D. Rasberry and K.F.J. Heinrich, Analy. Chem., 46(1), 81 (1974).

30. R.P. Elliot, Constitution of Binary Alloys, First Supplement, (McGraw-Hill Book Co.), p.347 (1958).